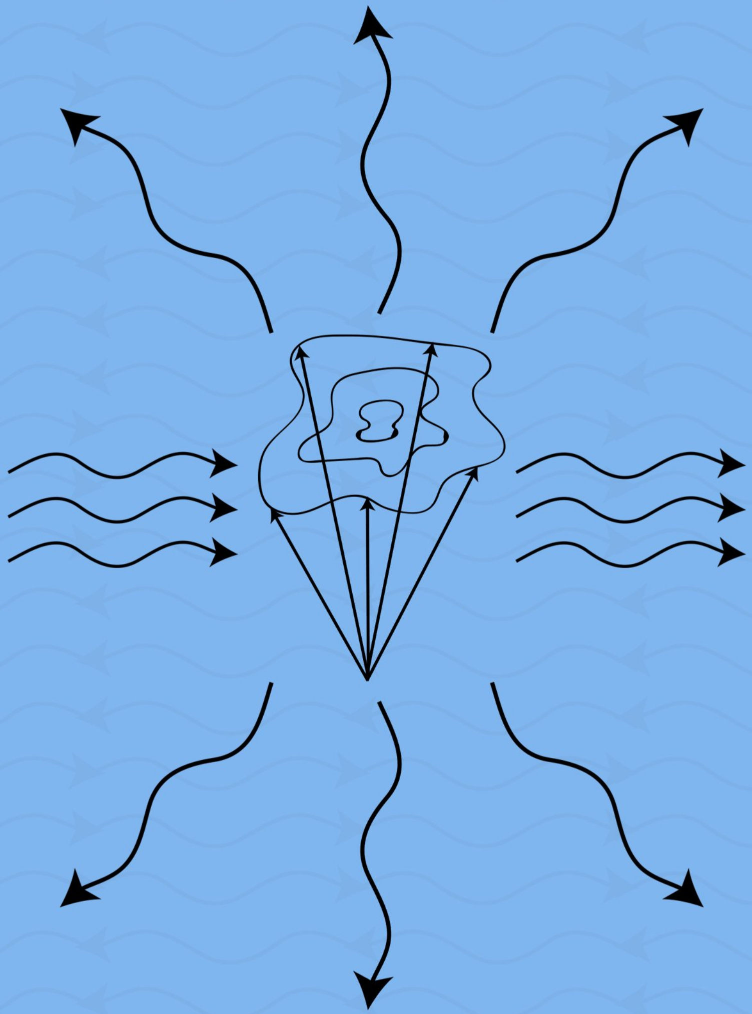

Magnetic and Electric Resonance

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Cambridge
Scholars
Publishing

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This book first published 2018

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-5275-0598-7
ISBN (13): 978-1-5275-0598-8

Contents

1 Preface

A less known aspect of the quasi-classical approximation to quantum-mechanical motion is presented in this book.

As it is well known, the quasi-classical approximation exists whenever the relevant amount of mechanical action is large in comparison with the quantum of action $\hbar$ (Planck's constant). This happens at high values of energy, associated with large quantum numbers, where the wavefunction exhibits many oscillations in time and space. Under these circumstances, Bohr's correspondence principle holds and the quantum-mechanical motion is approaching the classical limit. According to Dirac, the quantum-mechanical commutators become the classical Poisson brackets in this case. Similarly, in the limit $\hbar \to 0$, the quantum waves may exhibit a trajectory, like the wave rays in the approximation of the geometrical optics, and the Bohr-Sommerfeld quantization conditions of the Old Quantum Mechanics (related to the adiabatic invariants) are valid; this is known as the Jeffreys-Wentzel-Kramers-Brillouin (JWKB) approximation. Moreover, in the same conditions, a superposition of waves yields wavepackets localized in space, with sharp values in energy (extended in time), which mimic classical particles; moving with the group velocity and obeying the classical equations of motion, according to Ehrenfest.

All these aspects refer mainly to stationary states. The investigations presented in this book refer especially to the quasi-classical aspect of the quantum-mechanical transitions (quantum jumps).

The starting point of the matters discussed here is the equation of motion

$$\dot{O}(t) = \frac{i}{\hbar}[H, O(t)] \tag{1.1}$$

for Heisenberg's representation $O(t) = e^{\frac{i}{\hbar}Ht} O e^{-\frac{i}{\hbar}Ht}$ for operators O, where H is the time-independent hamiltonian; in the energy representation, equation (1.1) reads

$$\dot{O}_{nm} = \frac{i}{\hbar}(E_n - E_m)O_{nm} \ , \tag{1.2}$$

where E_n, E_m are the energies of the states n, m, or

$$\dot{O}_{nm} = i(\omega_n - \omega_m)O_{nm} \ , \tag{1.3}$$

where $\omega_{n,m} = E_{n,m}/\hbar$. For large n, m (E_n,E_m), where small deviations $s = m - n$ are relevant, we may write approximately $\omega_m = \omega_{n+s} = \omega_n + s(\partial\omega_n/\partial n)$ and, denoting $\omega_s = s(\partial\omega_n/\partial n)$ for fixed n, we get

$$\dot{O}_{n,n+s} = -i\omega_s O_{n,n+s} \ . \tag{1.4}$$

On the other hand, the matrix elements $O_{n,n+s}$ of the dynamical variables vanish rapidly with increasing s and depend slightly on n so we may approximate $O_{n,n+s}$ by $O_{n,n+s} \simeq O_s$.[1] Therefore, we have

$$\dot{O}_s = -i\omega_s O_s \ . \tag{1.5}$$

With $O_s = O_s^{(1)} + iO_s^{(2)}$ we get $\dot{O}_s^{(1)} = \omega_s O_s^{(2)}$, $\dot{O}_s^{(2)} = -\omega_s O_s^{(1)}$ and

$$\ddot{O}_s^{(1)} = -\omega_s^2 O_s^{(1)} \ , \ \ddot{O}_s^{(2)} = -\omega_s^2 O_s^{(2)} \ . \tag{1.6}$$

This is the classical equaton of motion of a free harmonic oscillator with the eigenfrequency ω_s. The classical quantity corresponds either to $O_s^{(1)}$ or $O_s^{(2)}$. This observation opens the possibility to approximate the quantum-mechanical operators by classical harmonic oscillators in the quasi-classical conditions. The effective hamiltonian which governs the motion of $O_s^{(1,2)}$ is

$$H_{eff} = \frac{1}{2m}P_s^{(1,2)2} + \frac{1}{2}m\omega_s^2 O_s^{(1,2)2} \ , \tag{1.7}$$

where $P_s^{(1,2)}$ is the momentum associated to the dynamical variable $O_s^{(1,2)}$. We may drop out the suffix s and the upper indices 1, 2 and write equations (1.6) as

$$\ddot{O} + \omega_0^2 O = 0 \ , \tag{1.8}$$

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[1] Angular coordinates like φ or θ of the rotation motion are an exception; rather their trigonometric functions like $\cos\varphi$, $\cos\theta$ are representative for the assertion made in the text.

where we introduced the notation $\omega_0 = \omega_s$. Equation (1.8) has a twofold nature: classical and quantum-mechanical. On one hand, it is the classical equation of a harmonic oscillator; on the other hand, it contains the oscillator eigenvalue ω_0 which is the difference $\omega_0 = \omega_s = (E_m - E_n)/\hbar$ of two quantum-mechanical frequencies (two energy levels), which may be involved in a quantum transition. For this reason, and taking into account the conditions used in deriving it, we call this equation a quasi-classical equation of motion.

In the presence of an external interaction H_{int} equation (1.5) acquires an additional term $\dot{O}_s^{cl}$,

$$\dot{O}_s = -i\omega_s O_s + \dot{O}_s^{cl} \ , \tag{1.9}$$

which denotes the part in the time derivative of the classical quantity O that arises from the external interaction; the harmonic-oscillator quasi-classical equation of motion becomes

$$\ddot{O} + \omega_0^2 O = \left(\frac{\partial}{\partial t}\dot{O}^{cl}\right)_{int} \ ; \tag{1.10}$$

the *rhs* of this equation is a generalized force, the suffix *int* indicating explicitly that this force is generated exclusively by the external interaction. The calculation of the generalized force is performed by means of the Poisson brackets:

$$\left(\frac{\partial}{\partial t}\dot{O}^{cl}\right)_{int} = \{\{O, H_{eff}\}, H_{int}\} + +\{\{O, H_{int}\}, H_{eff}\} \ , \tag{1.11}$$

where we retain only the first-order contribution of the interaction hamiltonian. Indeed, we are interested in the particular solution of equation (1.10), which, under these circumstances, has the character of a small perturbation; consequently, it is convenient to use the symbol δO in equation (1.10),

$$\delta\ddot{O} + \omega_0^2 \delta O = \left(\frac{\partial}{\partial t}\dot{O}^{cl}\right)_{int} \ , \tag{1.12}$$

indicating the variation of the quantity O for small changes in the quantum numbers ($s \ll m$). If δO appears in the generalized force, it should be neglected for consistency. If, for some special forms of

H_{int}, the variable O or/and its conjugate momentum P appear in the generalized force, then approximate schemes should be used, which depend on the specific problem. For other special prblems there may not exist a classical hamiltonian of interaction, but only equations of motion (for instance, for magnetic moments); in that cases, the generalized force is computed according to the basic meaning of the time derivative.

One of the most simple forms for the interaction hamiltonian is

$$H_{int} = fO\cos\omega t \ , \tag{1.13}$$

which corresponds to the interaction of a harmonic oscillator with an external field of strength f and frequency ω. The quasi-classical equation of motion reads

$$\delta\ddot{O} + \omega_0^2\delta O + 2\alpha\delta\dot{O} = -\frac{f}{m}\cos\omega t \tag{1.14}$$

($\dot{O} = P/m$, $\dot{P} = -\omega_0^2 O - f\cos\omega t$), where the friction (damping) term $2\alpha\delta\dot{O}$ is introduced. The particular solution of this equation is

$$\begin{gathered} \delta O = a\cos\omega t + b\sin\omega t \ , \\ a = \tfrac{f}{2m\omega_0}\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha^2} \ , \ b = -\tfrac{f}{2m\omega_0}\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ , \end{gathered} \tag{1.15}$$

for ω near ω_0. This is a typical resonance solution. From equation (1.14) we get

$$\frac{d}{dt}\left(\frac{1}{2}m\delta\dot{O}^2 + \frac{1}{2}m\omega_0^2\delta O^2\right) + 2\alpha m\delta\dot{O}^2 = -f\delta\dot{O}\cos\omega t \ , \tag{1.16}$$

which shows that

$$\delta P_{osc} = -\overline{f\delta\dot{O}\cos\omega t} = -\frac{1}{2}fb\omega \tag{1.17}$$

is the mean rate of energy absorption (dissipated power) of the oscillator. Making use of equation (1.15) we get

$$\begin{gathered} \delta P_{osc} = -\tfrac{1}{2}fb\omega \simeq \tfrac{f^2}{4m}\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \rightarrow \\ \rightarrow \tfrac{\pi f^2}{4m}\delta(\omega_0 - \omega) \ , \ \alpha \rightarrow 0^+ \ . \end{gathered} \tag{1.18}$$

The power given by equation (1.18) should be compared with the mean power absorbed by the oscillator in quantum transitions. For the interaction hamiltonian $H_{int} = h\cos\omega t$ the amplitude of transition $n \rightarrow k$ is given by

$$c_{kn} = -\frac{h_{kn}}{2\hbar}\frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha} \; ; \tag{1.19}$$

the rate of transition is

$$\begin{gathered} \tfrac{\partial|c_{kn}|^2}{\partial t} = \tfrac{|h_{kn}|^2}{2\hbar^2}\tfrac{\alpha}{(\omega_{kn}-\omega)^2+\alpha^2} \rightarrow \\ \rightarrow \tfrac{\pi|h_{kn}|^2}{2\hbar^2}\delta(\omega_{kn}-\omega) \; , \; \alpha \rightarrow 0^+ \end{gathered} \tag{1.20}$$

and the absorbed power is

$$P = \frac{\pi\left|h_{kn}\right|^2}{2\hbar}\omega_{kn}\delta(\omega_{kn}-\omega) \; . \tag{1.21}$$

For $h = fO$, the matrix elements $O_{n+1,n} = \sqrt{\hbar(n+1)/2m\omega_0}$ of the harmonic oscillator and $\omega_{kn} = \omega_{n+1} - \omega_n = \omega_0$ we get

$$P = \frac{\pi f^2}{4m}(n+1)\delta(\omega_0-\omega) \; ; \tag{1.22}$$

we can see that $\delta P = \delta P_{osc}$ given by equation (1.18) for large n.

For other, simple quantum-mechanical motions the difference between the two powers is only a numerical factor; the planar rotator and the spatial rotator (spherical top) analyzed in this book illustrate this point. The difference indicates the deviation of the quantum-mechanical motion from the motion of the harmonic oscillator; it originates in the approximations made in deriving the quasi-classical equation of motion given by equation (1.12).

The extension of the quasi-classical equation of motion to condensed matter exhibits a few particularities. Because of the residual interactions the quantum-mechanical motion in condensed matter has certain limitations; the energy levels are not well defined, the wavefunctions are wavepackets superpositions and the elementary quasi-particle and collective excitations (with their finite lifetime) are relevant for the quantum-mechanical motion. In addition, in condensed matter we measure quantum-mechanical expectation values and statistical averages, a situation which bring us close to a quasi-classical approximation. Moreover, the rapid oscillations in space and time of the wave functions and the fields in condensed matter are locally averaged in a coarse-graining average, which enables a quasi-classical description. Let O_i be a dynamical variable of the i-th atomic constituent in a set of N such constituents placed around any point in a sample of condensed matter, and let $O = N^{-1}\sum_{i=1}^{N} O_i$ be the coarse-graining average. The motion of any O_i may imply a small amount of mechanical action, of the order of $\hbar$, but only large amounts of mechanical action are relevant, corresponding to the average O. Consequently, we may apply a quasi-classical approximation in these conditions. Moerover, we can see that even for small quantum numbers corresponding to the motion of any O_i this approximation is now valid. Such a quasi-classical approximation is described in this book for magnetic resonance and nuclear quadrupole resonance. In addition, by means of this method of quasi-classical description, a new feature, called parametric resonance, is revealed in the rotation spectra exhibited by molecules endowed with an electric dipole moment or a magnetic moment and placed in a static electric field or a static magnetic field, respectively.

In conclusion, we may say that a new method of quasi-classical approximation is presented in this book, for treating the interaction of quantum-mechanical motion with an external time-dependent interaction; the method, which is derived from Heisenberg's equation of motion, belongs to the class of quasi-classical approximations in Quantum Mechanics (correspondence principle, the JWKB approximation, $\hbar \to 0$ limit), and it may prove useful in various spectroscopies in condensed matter.

2 Introduction

The Maxwell equations in vacuum read

$$\begin{gathered} div\mathbf{E} = 4\pi\rho \ , \ div\mathbf{H} = 0 \ , \\ curl\mathbf{E} = -\tfrac{1}{c}\tfrac{\partial\mathbf{H}}{\partial t} \ , \ curl\mathbf{H} = \tfrac{1}{c}\tfrac{\partial\mathbf{E}}{\partial t} + \tfrac{4\pi}{c}\mathbf{j} \ , \end{gathered} \tag{2.1}$$

where $\mathbf{E}$ and $\mathbf{H}$ are the (real) electric and magnetic field, respectively, ρ and $\mathbf{j}$ are the charge and current densities, respectively, and c is the speed of light in vacuum ($c = 3 \times 10^{10} cm/s$); the charge and the current are related by the continuity equation

$$\frac{\partial\rho}{\partial t} + div\mathbf{j} = 0 \tag{2.2}$$

(charge conservation); they originate in the elementary charges and currents associated with the atomic structure of matter. For a point charge q placed at $\mathbf{r}_0$ the density is $\rho = q\delta(\mathbf{r} - \mathbf{r}_0)$ and the current density is $\mathbf{j} = q\dot{\mathbf{r}}_0\delta(\mathbf{r} - \mathbf{r}_0)$ (convection current).

Equations (2.1) tell that ρ and $\mathbf{j}$ generate electromagnetic fields. Indeed, we introduce the scalar potential Φ and the vector potential $\mathbf{A}$ through $\mathbf{E} = -(1/c)\partial\mathbf{A}/\partial t - grad\Phi$ and $\mathbf{H} = curl\mathbf{A}$ and see immediately that two Maxwell equations are satisfied identically ($div\mathbf{H} = 0$ and $curl\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}$), while the remaining two equations lead to the wave equations

$$\tfrac{1}{c^2}\tfrac{\partial^2\Phi}{\partial t^2} - \Delta\Phi = 4\pi\rho \ , \ \tfrac{1}{c^2}\tfrac{\partial^2\mathbf{A}}{\partial t^2} - \Delta\mathbf{A} = \tfrac{4\pi}{c}\mathbf{j} \ , \tag{2.3}$$

providing the Lorenz gauge $div\mathbf{A} + (1/c)\partial\Phi/\partial t = 0$ is satisfied; under the gauge transformations $\mathbf{A} \rightarrow \mathbf{A} + grad\chi$, $\Phi \rightarrow \Phi - (1/c)\partial\chi/\partial t$ which preserve the fields, the Lorenz condition amounts to $(1/c^2)(\partial^2\chi/\partial t^2) - \Delta\chi = 0$. Particular solutions of the wave equations are given by

Kirchhoff's retarded potentials

$$\begin{aligned} \Phi(\mathbf{r},t) &= \int d\mathbf{r}' \tfrac{\rho(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|} \ , \\ \mathbf{A}(\mathbf{r},t) &= \tfrac{1}{c}\int d\mathbf{r}' \tfrac{\mathbf{j}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|} \ . \end{aligned} \tag{2.4}$$

The general solution is obtained by adding the free fields which satisfy the homogeneous (source-free) equations (2.3). It is worth noting that the fields given by equations (2.4) propagate (and are extended), while the charge and current distributions are localized. The Lorenz gauge in equations (2.4) is ensured by the charge conservation (continuity equation).

Free fields are generated conventionally by charges and currents placed at infinity; in the regions of interest they satisfy the free Maxwell equations; they act with the Lorentz force

$$\mathbf{f} = \rho\mathbf{E} + \frac{1}{c}\mathbf{j}\times\mathbf{H} \tag{2.5}$$

upon charges and currents placed in the regions of interest; these fields are external fields for these charges and currents. Under the action of the Lorentz force the state of motion of the charges and currents is changed.

The field generated by a charge and a current localized at some point in space acts upon the charges and currents localized at other points in space; this amounts also to saying that the fields generated by a charge and current distribution act upon the distribution that created them; this can be called an internal field. Therefore, there is an interaction between charges and currents on one side and their corresponding fields on the other, incorporated in the Maxwell equations. Indeed, we get easily from equations (2.1)

$$\frac{1}{8\pi}\frac{\partial}{\partial t}\left(E^2+H^2\right) + \mathbf{jE} + \frac{c}{4\pi}div(\mathbf{E}\times\mathbf{H}) = 0 \ , \tag{2.6}$$

which tells that the electromagnetic energy $(E^2+H^2)/8\pi$ plus the mechanical work $\mathbf{jE}$ done by the field upon charges per unit time plus the energy radiated through the surface by the Poynting vector $\mathbf{S} = \frac{c}{4\pi}(\mathbf{E}\times\mathbf{H})$ is zero: the total energy of the electromagnetic field and charges and currents is conserved. It is easy to see that a convection current is $\mathbf{j} = \rho\mathbf{v}$, which justifies the interpretation of the term $\mathbf{jE}$ as the work done by the Lorentz force $\mathbf{f}$ given by equation (2.5) per unit time (and per unit volume). Such an equation of conservation of the energy can be written either for the fields produced by the distributions ρ and $\mathbf{j}$ (particular solutions of the Maxwell equations, internal fields), or for external fields, or for the total fields which are the sum of internal and external fields. We can see that energy conservation implies quadratic quantities in fields, while the fields obey the superposition principle (Maxwell equations are linear in fields); the energy of two superposed fields is not the sum of the energies of the two fields, which amounts to say that the fields interact. Similarly, we get from Maxwell equations (2.1)

$$\begin{gathered}\rho\mathbf{E} + \tfrac{1}{c}\mathbf{j}\times\mathbf{H} + \tfrac{1}{4\pi c}\tfrac{\partial}{\partial t}(\mathbf{E}\times\mathbf{H}) + \\ + \tfrac{1}{4\pi}(\mathbf{E}\times curl\mathbf{E} + \mathbf{H}\times curl\mathbf{H} - \mathbf{E}div\mathbf{E} - \mathbf{H}div\mathbf{H}) = 0 \ ,\end{gathered} \tag{2.7}$$

which tells that the Lorentz force plus the reaction of the field (field momentum $(\mathbf{E}\times\mathbf{H})/4\pi c$) plus the stress force of the field is zero; the total momentum of the charges, currents and field is conserved, as for a closed system. The components of the last term in equation (2.7) can be written as $\partial_j\sigma_{ij}$, where

$$\sigma_{ij} = \frac{1}{8\pi}\delta_{ij}(E^2 + H^2) - \frac{1}{4\pi}(E_iE_j + H_iH_j) \tag{2.8}$$

is a stress tensor. It is worth noting that energy conservation given by equation (2.6) shows that the electromagnetic field, apart from acting upon charges and currents, has and carries energy. Similarly, the momentum conservation given by equation (2.8) suggests the existence of a medium, similar with an elastic medium, which sustains an electromagnetic field which carries momentum and produces a stress; this medium is suggestive of a luminiferous aether.

In matter, there appear internal electromagnetic fields, produced by the charges and currents of the atomic constituents. Some of these charges and currents are permanent, some other are induced by external fields. By analogy with Gauss's law $div\mathbf{E} = 4\pi\rho$, we admit the existence of an electric field $\mathbf{P}$, called polarization, which generates a "material" charge density $\rho_m = -div\mathbf{P}$, such that we write Gauss's law in matter as

$$div\mathbf{E} = 4\pi\rho - 4\pi div\mathbf{P}\ ,\ div(\mathbf{E} + 4\pi\mathbf{P}) = 4\pi\rho\ ; \tag{2.9}$$

since matter is usually electrically neutral, it is easy to see that the polarization $\mathbf{P}$ is in fact a density of dipoles moments. A current density $\mathbf{j}_p = \partial\mathbf{P}/\partial t$ corresponds to the charge density $\rho_p = -div\mathbf{P}$, such that the continuity equation is satisfied; therefore, the Maxwell-Ampere equation $curl\mathbf{H} = \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t} + \frac{\mathbf{4\pi}}{\mathbf{c}}\mathbf{j}$ will include the term $\frac{4\pi}{c}\frac{\partial\mathbf{P}}{\partial t}$; in addition, this equation suggests also the existence of another current density given by a magnetic field $\mathbf{M}$, called magnetization, through $curl\mathbf{M} = \frac{1}{c}\mathbf{j}_m^{'}$; the continuity equation admits such a current density, since $div \cdot curl = 0$. It follows that the Maxwell-Ampere equation in matter can be written as

$$curl\mathbf{H} = \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t} + \frac{\mathbf{4\pi}}{\mathbf{c}}\mathbf{j} + \frac{4\pi}{c}\frac{\partial\mathbf{P}}{\partial t} + 4\pi curl\mathbf{M}\ ; \tag{2.10}$$

in matter, instead of $\mathbf{H}$, we denote this magnetic field by $\mathbf{B}$, and call it magnetic induction; the magnetic field is $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$. Introducing also the electric displacement $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ we get the Maxwell equations in matter

$$\begin{gathered} div\mathbf{D} = 4\pi\rho\ ,\ div\mathbf{B} = 0\ , \\ curl\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}\ ,\ curl\mathbf{H} = \frac{1}{c}\frac{\partial\mathbf{D}}{\partial t} + \frac{4\pi}{c}\mathbf{j}\ , \end{gathered} \tag{2.11}$$

where ρ and $\mathbf{j}$ are external charge and current densities, respectively. We have here two independent equations and four unknowns. Additional knowledge is necessary in order to solve these equations. It is easy to see that magnetization is the density of magnetic moments, similar with the polarization, which is the density of dipole moments. Indeed, the density of magnetic moments is $\frac{1}{2c}\mathbf{r} \times \mathbf{j}_m$ and the total magnetic moment is

$$\frac{1}{2c}\int d\mathbf{r} \cdot \mathbf{r} \times \mathbf{j}_m = \frac{1}{2}\int d\mathbf{r} \cdot \mathbf{r} \times curl\mathbf{M} = \int d\mathbf{r}\mathbf{M}\ . \tag{2.12}$$

In this respect, the "magnetic" current density is reminiscent of Ampere's molecular currents (or "electric vortices"). From equations

(2.11) we get the energy conservation

$$\frac{1}{4\pi}\left(\mathbf{E}\frac{\partial \mathbf{D}}{\partial t}+\mathbf{H}\frac{\partial \mathbf{B}}{\partial t}\right)+\mathbf{jE}+\frac{c}{4\pi}div(\mathbf{E}\times\mathbf{H})=0 \tag{2.13}$$

and the momentum conservation

$$\begin{gathered}\rho\mathbf{E}+\tfrac{1}{c}\mathbf{j}\times\mathbf{B}+\tfrac{1}{4\pi c}\tfrac{\partial}{\partial t}(\mathbf{D}\times\mathbf{B})+\\ +\tfrac{1}{4\pi}(\mathbf{D}\times curl\mathbf{E}+\mathbf{B}\times curl\mathbf{H}-\mathbf{E}div\mathbf{D}-\mathbf{H}div\mathbf{B})=0\ .\end{gathered} \tag{2.14}$$

3 Electric and Magnetic Moments

3.1 Electric dipole and quadrupole moments

With usual notations the scalar electromagnetic potential is given by Kirchhoff's solution

$$\Phi(\mathbf{r},t)=\int d\mathbf{r}'\,\frac{\rho(\mathbf{r}',t-|\mathbf{r}-\mathbf{r}'|/c)}{|\mathbf{r}-\mathbf{r}'|}\ \ , \tag{3.1}$$

where ρ is the charge density (and c denotes the speed of light); it is a particular solution of the wave equation

$$\frac{1}{c^2}\frac{\partial^2\Phi}{\partial t^2}-\Delta\Phi=4\pi\rho\ . \tag{3.2}$$

In matter charges perform a finite motion, so we can average equation (3.2) over this motion and get the static equation

$$\Delta\Phi=-4\pi\rho \tag{3.3}$$

and the Coulomb potential

$$\Phi(\mathbf{r})=\int d\mathbf{r}'\,\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ ; \tag{3.4}$$

in this limit the electric field is given by

$$\mathbf{E}=-grad\Phi=\int d\mathbf{r}'\,\frac{\rho(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\ . \tag{3.5}$$

Similar results are obtained in the quasi-static limit, where the wavelengths are much larger than the relevant distances. For charges distributed over distances much smaller than the distance of observation r we may limit ourselves to $\rho(\mathbf{r}', t - r/c)/\left|\mathbf{r} - \mathbf{r}'\right|$ in equation (3.1); this quantity can be expanded in powers of $\mathbf{r}'$. For a classical charge q localized at $\mathbf{r}_0$ the charge density is $\rho(\mathbf{r}) = q\delta(\mathbf{r} - \mathbf{r}_0)$, and we have to expand the function $q/\left|\mathbf{r} - \mathbf{r}_0\right|$ in powers of $\mathbf{r}_0$. A quantum charge density is $\rho = q\left|\psi(\mathbf{r}, t)\right|^2$, where ψ is the wavefunction, and we need to expand the function $q\left|\psi(\mathbf{r}', t - r/c)\right|^2/\left|\mathbf{r} - \mathbf{r}'\right|$ in powers of $\mathbf{r}'$; similarly, for several charges the charge density is given in terms of the multi-particle wavefunction (or the field operator for identical particles). Usually, the particle density $\left|\psi(\mathbf{r}, t)\right|^2$ is localized over a limited space region of some extension r_0, which amounts to an integration over this region of the expansion of the function $\left|\psi(\mathbf{r}', t - r/c)\right|^2/\left|\mathbf{r} - \mathbf{r}'\right|$ in powers of $\mathbf{r}'$. We can see that the expansion in multipoles of the electromagnetic field is an expansion with generic coefficients (the multipoles), which are determined by the particular structure of the charge distribution. In this context it is worth recalling the quantum nature of the field equations like equation (3.2).

Let us consider a classical point charge q placed at $\mathbf{r}_0$; the potential becomes

$$\Phi = \frac{q}{\left|\mathbf{r} - \mathbf{r}_0\right|} = \frac{q}{r} + \frac{q\mathbf{r}_0\mathbf{r}}{r^3} + \frac{1}{2}qx_{0i}x_{0j}\frac{3x_ix_j - r^2\delta_{ij}}{r^5} + \dots \ , \tag{3.6}$$

where we have expanded in powers of x_{0i} ($r \gg r_0$) (and summation over repeated indices is included). We may also sum over several charges. The first term $\Phi_0 = q/r$ is the Coulomb law, the second term

$$\Phi_1 = \frac{q\mathbf{r}_0\mathbf{r}}{r^3} = \frac{\mathbf{d}\mathbf{r}}{r^3} \ , \ \mathbf{d} = q\mathbf{r}_0 \tag{3.7}$$

is the dipole contribution, the third term

$$\Phi_2 = \frac{1}{2}qx_{0i}x_{0j}\frac{3x_ix_j - r^2\delta_{ij}}{r^5} \tag{3.8}$$

is the quadrupole contribution; $\mathbf{d} = q\mathbf{r}_0$ is the dipole moment, its electric field is

$$\mathbf{E}_1 = -grad\frac{\mathbf{dr}}{r^3} = \frac{3(\mathbf{dr})\mathbf{r} - r^2\mathbf{d}}{r^5} \ . \tag{3.9}$$

Since

$$\Delta\frac{1}{r} = \delta_{ij}\frac{3x_ix_j - r^2\delta_{ij}}{r^5} = 0 \ , \tag{3.10}$$

we can write the quadrupole contribution as

$$\begin{aligned} \Phi_2 &= \tfrac{1}{6}q(3x_{0i}x_{0j} - r_0^2\delta_{ij})\tfrac{3x_ix_j - r^2\delta_{ij}}{r^5} = \\ &= \tfrac{1}{2}q(3x_{0i}x_{0j} - r_0^2\delta_{ij})\tfrac{x_ix_j}{r^5} = \tfrac{1}{2}D_{ij}\tfrac{x_ix_j}{r^5} \ , \end{aligned} \tag{3.11}$$

where

$$D_{ij} = q(3x_{0i}x_{0j} - r_0^2\delta_{ij}) \tag{3.12}$$

is the quadrupole moment; it is a traceless tensor with five components. The quadrupole electric field is given by

$$E_{2i} = \frac{3}{2}D_{ij}\frac{x_j}{r^5} \ . \tag{3.13}$$

The quadrupole moment can be brought to its principal axes; since it is traceless, only two diagonal components are independent. If the charge distribution is symmetric about the z-axis, we have

$$D_{xx} = D_{yy} = -\frac{1}{2}D_{zz} \tag{3.14}$$

and

$$\Phi_2 = \frac{1}{4r^3}D(3\cos^2\theta - 1) = \frac{1}{2r^3}DP_2(\cos\theta) \ , \tag{3.15}$$

where θ is the angle between $\mathbf{r}$ and the z-axis, $D = D_{zz}$ and P_2 is the Legendre polynomial of the 2-nd order.

If the total charge is zero, the dipole moment does not depend on the origin of coordinates; if the total charge and the dipole moment are zero, the quadrupole moment does not depend on the origin of coordinates.

In general, we have the expansion

$$\begin{aligned}\tfrac{1}{|\mathbf{r}-\mathbf{r}_0|} &= \textstyle\sum_{l=0}^{\infty} \tfrac{r_0^l}{r^{l+1}} P_l(\cos\Theta) = \\ &= \textstyle\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \tfrac{r_0^l}{r^{l+1}} \tfrac{4\pi}{2l+1} Y_{lm}(\theta_0,\varphi_0) Y_{lm}^*(\theta,\varphi)\end{aligned} \tag{3.16}$$

in spherical functions, which allows the representation

$$\Phi = \sum_{lm} \sqrt{\frac{4\pi}{2l+1}} \frac{1}{r^{l+1}} Q_{lm} Y_{lm}^*(\theta,\varphi) \ , \tag{3.17}$$

where

$$Q_{lm} = \sqrt{\frac{4\pi}{2l+1}} \sum_a q_a r_a^l Y_{lm}(\theta_a,\varphi_a) \tag{3.18}$$

is the electric moment of the 2^l-th order; it includes summation over all charges a. We have

$$\begin{aligned} &Q_{00} = \textstyle\sum_a q_a \ , \ Q_{10} = i \sum_a q_a r_a \cos\theta_a = i d_z \ , \\ &Q_{1\pm1} = \mp \tfrac{i}{\sqrt{2}} \textstyle\sum_a q_a r_a \sin\theta_a e^{\pm i\varphi_a} = \mp \tfrac{i}{\sqrt{2}} (d_x \pm i d_y) \end{aligned} \tag{3.19}$$

and

$$\begin{aligned} Q_{20} &= \tfrac{1}{2} \textstyle\sum_a q_a r_a^2 (1 - 3\cos^2\theta_a) = -\tfrac{1}{2} D_{zz} \ , \\ Q_{2\pm1} &= \pm\sqrt{\tfrac{3}{2}} \textstyle\sum_a q_a r_a^2 \cos\theta_a \sin\theta_a e^{\pm i\varphi_a} = \\ &= \pm \tfrac{1}{\sqrt{6}} (D_{xz} \pm i D_{yz}) \ , \\ Q_{2\pm2} &= -\tfrac{1}{2}\sqrt{\tfrac{3}{2}} \textstyle\sum_a q_a r_a^2 \sin^2\theta_a e^{\pm 2i\varphi_a} = \\ &= -\tfrac{1}{2\sqrt{6}} (D_{xx} - D_{yy} \pm 2i D_{xy}) \ . \end{aligned} \tag{3.20}$$

Let us assume that a charge distribution is placed in an external field with scalar potential Φ; the energy of the charge distribution in this external field is given by

$$U = \sum_a q_a \Phi(\mathbf{r}_a) \ . \tag{3.21}$$

We may expand $\Phi(\mathbf{r}_a)$ in powers of the coordinates x_{ai},

$$U = U_0 + U_1 + U_2 + \ , \tag{3.22}$$

where

$$U_0 = \Phi_0 \sum_a q_a \ , \tag{3.23}$$

$$U_1 = grad\Phi_0 \sum_a q_a \mathbf{r}_a = -\mathbf{d}\mathbf{E}_0 \tag{3.24}$$

and U_2 is the quadrupole contribution. The suffix 0 denotes the origin (around which the distribution is placed), $\mathbf{d}$ is the dipole moment and $\mathbf{E}_0$ is the electric field at the origin. Up to the first-order approximation the force acting upon the charge distribution is given by

$$\mathbf{F} = \mathbf{E}_0 \sum_a q_a + (\mathbf{d} grad)\left.\mathbf{E}\right|_0 + ... \tag{3.25}$$

and the torque is given by

$$\mathbf{K} = \sum_a q_a \mathbf{r}_a \times \mathbf{E}_0 = \mathbf{d} \times \mathbf{E}_0 \ . \tag{3.26}$$

The rotation of a rigid dipole $d = ql$ under the action of the torque of forces given by equation (3.26) implies the motion of the angular momentum $L = mvl$, $d\mathbf{L}/dt = \mathbf{K} = \mathbf{d} \times \mathbf{E}_0$. If we leave aside the azimuthal motion, the equation of motion is $ml^2\ddot{\theta} = -qlE_0 \sin\theta$, where θ is the angle between $\mathbf{d}$ and $\mathbf{E}_0$; for small angles θ and a constant field, this is the equation of motion of a harmonic oscillator with frequency $\omega = \sqrt{qE_0/ml} = \sqrt{dE_0/I}$, where $I = ml^2$ is the moment of inertia; the quantum counterpart reads $I\omega^2 = \omega L = dE_0$ $(L = I\omega)$ and $\omega = dE/\hbar$, where $\hbar$ is Planck's constant; such a frequency is known as the Rabi frequency.[1]

The energy of a dipole in the field generated by another dipole is

$$U = -\mathbf{d}_1\mathbf{E}_2 = \frac{(\mathbf{d}_1\mathbf{d}_2)r^2 - 3(\mathbf{d}_1\mathbf{r})(\mathbf{d}_2\mathbf{r})}{r^5} \ , \tag{3.27}$$

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[1] I. I. Rabi, "On the process of space quantization", Phys. Rev. **49** 324 (1936); I. I. Rabi, "Space quantization in a gyrating magnetic field", Phys. Rev. **51** 652 (1937).

where we have used the dipole field given by equation (3.9). Similarly, for a charge q in the field of a dipole we have the energy

$$U = q\frac{\mathbf{dr}}{r^3} \ . \tag{3.28}$$

The quadrupole contribution to the interaction energy is

$$U_2 = \tfrac{1}{2}\sum\nolimits_a q_a x_{ai} x_{aj} \tfrac{\partial^2 \Phi_0}{\partial x_i \partial x_j} = \tfrac{1}{2}\sum\nolimits_a q_a (x_{ai} x_{aj} - \tfrac{1}{3}\delta_{ij} r_a^2) \tfrac{\partial^2 \Phi_0}{\partial x_i \partial x_j} =$$
$$= \tfrac{1}{6} D_{ij} \tfrac{\partial^2 \Phi_0}{\partial x_i \partial x_j} \ . \tag{3.29}$$

In general, since

$$\Phi(\mathbf{r}_a) = \sum_{lm} r^l \sqrt{\frac{4\pi}{2l+1}} a_{lm} Y_{lm}(\theta_a, \varphi_a) \tag{3.30}$$

we get

$$U = \sum_a q_a \Phi(\mathbf{r}_a) = \sum_{lm} a_{lm} Q_{lm} \ \ , \tag{3.31}$$

where Q_{lm} is the moment given by equation (3.18) and a_{lm} are the coefficients of the expansion of the potential in spherical harmonics.

3.2 Magnetic Moments

With usual notations the vector potential is given by Kirchhoff's solution

$$\mathbf{A}(\mathbf{r}, t) = \frac{1}{c}\int d\mathbf{r}' \frac{\mathbf{j}(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|/c)}{|\mathbf{r} - \mathbf{r}'|} \ \ , \tag{3.32}$$

where $\mathbf{j}$ is the curent density (and c denotes the speed of light); it is a particular solution of the wave equation

$$\frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} - \Delta \mathbf{A} = \frac{4\pi}{c}\mathbf{j} \ . \tag{3.33}$$

In the quasi-static limit it becomes

$$\Delta \mathbf{A} = -\frac{4\pi}{c}\mathbf{j} \ , \tag{3.34}$$

hence

$$\mathbf{A}(\mathbf{r},t) \simeq \frac{1}{c}\int d\mathbf{r}'\frac{\mathbf{j}(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} \ ; \tag{3.35}$$

this is the Biot-Savart law for the magnetic field

$$\mathbf{H} = curl\mathbf{A} = \frac{1}{c}\int d\mathbf{r}'\frac{\mathbf{j}\times(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \ . \tag{3.36}$$

If we take the average of equation (3.33) over finite motion of charges in matter we get the static equation $\Delta\overline{\mathbf{A}} = 0$, since $\overline{\mathbf{j}} = 0$. It is worth noting that the quasi-static potentials Φ and $\mathbf{A}$ satisfy the Lorenz gauge $div\mathbf{A} + (1/c)\partial\Phi/\partial t = 0$ (due to the the continuity equation $\partial\rho/\partial t + div\mathbf{j} = 0$).

According to equation (3.35), the quasi-static vector potential $\mathbf{A}$ generated by a point charge q_a moving at $\mathbf{r}_a$ with velocity $\mathbf{v}_a$ *(i.e.* a current density $\mathbf{j}_a = q\mathbf{v}_a\delta(\mathbf{r}-\mathbf{r}_a)$) is given by

$$\mathbf{A}(\mathbf{r},t) = \frac{1}{c}q_a\frac{\mathbf{v}_a}{|\mathbf{r}-\mathbf{r}_a|} \ ; \tag{3.37}$$

far away from the charge we have the expansion

$$\mathbf{A} = \frac{1}{c}q_a\frac{\mathbf{v}_a}{r} + \frac{1}{c}q_a\frac{\mathbf{v}_a(\mathbf{r}_a\mathbf{r})}{r^3} + ..., \tag{3.38}$$

where we can write

$$\mathbf{v}_a(\mathbf{r}_a\mathbf{r}) = \frac{1}{2}\frac{d}{dt}[\mathbf{r}_a(\mathbf{r}_a\mathbf{r})] + \frac{1}{2}[\mathbf{v}_a(\mathbf{r}_a\mathbf{r}) - \mathbf{r}_a(\mathbf{v}_a\mathbf{r})] \ ; \tag{3.39}$$

the classical Electromagnetism admits that the macroscopic fields arise from macroscopic charges and currents, *i.e.* from microscopic charges and currents averaged over their finite motion in matter; consequently, we have $\overline{\mathbf{v}}_a = 0$ and

$$\overline{\mathbf{v}_a(\mathbf{r}_a\mathbf{r})} = \frac{1}{2}\overline{[\mathbf{v}_a(\mathbf{r}_a\mathbf{r}) - \mathbf{r}_a(\mathbf{v}_a\mathbf{r})]} = \frac{1}{2}\overline{(\mathbf{r}_a\times\mathbf{v}_a)}\times\mathbf{r} \ , \tag{3.40}$$

i.e.

$$\overline{\mathbf{A}} = \frac{1}{2c}q_a\frac{\overline{(\mathbf{r}_a\times\mathbf{v}_a)}\times\mathbf{r}}{r^3} = \frac{\overline{\mathbf{m}}\times\mathbf{r}}{r^3} \ , \tag{3.41}$$

where

$$\overline{\mathbf{m}} = \frac{1}{2c} q_a \overline{\mathbf{r}_a \times \mathbf{v}_a} \tag{3.42}$$

is the magnetic momentum of the charge q_a; we can sum over all charges (and can even admit a continuous charge and current distribution). From equation (3.41) we get easily the magnetic field

$$\overline{\mathbf{H}} = curl\overline{\mathbf{A}} = \frac{3(\overline{\mathbf{m}}\mathbf{r})\mathbf{r} - \overline{\mathbf{m}}r^2}{r^5} \tag{3.43}$$

(by using $\varepsilon_{ijk}\varepsilon_{ilm} = \delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}$), which indicates that the magnetic moment acts as a magnetic dipole. If the ratio charge-to-mass is the same for all particles (q/m) we can write

$$\overline{\mathbf{m}} = \frac{q}{2mc} \sum_a m_a \overline{\mathbf{r}_a \times \mathbf{v}_a} = \frac{q}{2mc}\mathbf{L}\ , \tag{3.44}$$

where $\mathbf{L}$ is the (mechanical) angular momentum. Since $(1/2)\mathbf{r} \times \mathbf{v} = \Delta S/\Delta t$, where ΔS is the area covered by a macroscopic rotation in time Δt, we get from equation (3.42) $m = I\Delta S/c$ for the magnetic moment of a macroscopic current $I = q/\Delta t$ (a coil). Indeed, the magnetic moment $m = IS/c = q\nu\pi r^2/c = q\omega r^2/2c$ of a charge q moving in a circular orbit (radius r, area $S = \pi r^2$, frequency $\nu = \omega/2\pi$, current $I = q\nu$) is related to the angular momentum $L = mvr = m\omega r^2$ through $m = (q/2mc)L$ (where m is the mass of the particle).

It is worth noting that a statistical average of the orbital currents or magnetic moments with classical statistics gives vanishing currents and magnetic moments, a result which is known as Bohr-van Leuween theorem (it is due to the kinetic energy in the classical statistical distribution, which is quadratic in velocities); classically, there is no magnetic moment (and no magnetism).[2] The quantum average of orbital currents (momenta) over bound states in centrally symmetric fields is also vanishing, due to the conservation of parity; in general, the (averaged) orbital currents in matter are "quenched", *i.e.* they are vanishing.

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[2] N. Bohr, Disertation, Copenhagen (1911); J. H. van Leeuwen, Disertation, Leiden (1919); J. H. van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford (1932).

The force acting upon an assembly of moving charges placed in a constant magnetic field **H** is zero:

$$\mathbf{F} = \sum_a \frac{q_a}{c}\overline{\mathbf{v}_a \times \mathbf{H}} = \sum_a \frac{q_a}{c}\overline{\frac{d}{dt}(\mathbf{r}_a \times \mathbf{H})} = 0 \; ; \tag{3.45}$$

the torque is given by

$$\begin{aligned}\mathbf{K} = \textstyle\sum_a \frac{q_a}{c}\overline{\mathbf{r}_a \times (\mathbf{v}_a \times \mathbf{H})} = \sum_a \frac{q_a}{c}\overline{\mathbf{v}_a(\mathbf{r}_a\mathbf{H}) - \frac{1}{2}\mathbf{H}\frac{d}{dt}(r_a^2)} = \\ = \textstyle\sum_a \frac{q_a}{c}\overline{\mathbf{v}_a(\mathbf{r}_a\mathbf{H})} \;\; ,\end{aligned} \tag{3.46}$$

or

$$\begin{aligned}\mathbf{K} = \textstyle\sum_a \frac{q_a}{2c}\overline{\mathbf{v}_a(\mathbf{r}_a\mathbf{H}) - \mathbf{r}_a(\mathbf{v}_a\mathbf{H})} = \\ = \textstyle\sum_a \frac{q_a}{2c}\mathbf{H} \times \overline{(\mathbf{v}_a \times \mathbf{r}_a)} = \overline{\mathbf{m}} \times \mathbf{H}\end{aligned} \tag{3.47}$$

(by using the same averaging procedure as given above for the magnetic moment); we can compare this magnetic torque with the electric torque acting upon a dipole as given by equation (3.26).

The lagrangian of the charges in a uniform magnetic field **H** with the vector potential $\mathbf{A} = (\mathbf{H} \times \mathbf{r})/2$ includes the additional term

$$L_H = \sum_a \frac{q_a}{c}\mathbf{A}\mathbf{v}_a = \sum_a \frac{q_a}{2c}(\mathbf{H} \times \mathbf{r})\mathbf{v}_a \;\; , \tag{3.48}$$

which, on averaging, leads to

$$L_H = \overline{\mathbf{m}}\mathbf{H} \; ; \tag{3.49}$$

the corresponding energy is

$$E_H = -\overline{\mathbf{m}}\mathbf{H} \; ; \tag{3.50}$$

it is similar with the dipole energy ($E_E = -\mathbf{d}\mathbf{E}$) in an electric field, as given by equation (3.24).

Let us assume an assembly of charges with the lagrangian

$$L = \sum_a \frac{1}{2}m_a v_a^2 - U \tag{3.51}$$

with usual notations, where U is their potential energy (including a centrally symmetric field and interaction). In a frame rotating with angular velocity $\overrightarrow{\Omega}$ the velocity is given by

$$\mathbf{v} = \mathbf{v}^{'} + \overrightarrow{\Omega} \times \mathbf{r}^{'} \ , \tag{3.52}$$

while the potential energy does not change. The lagrangian becomes

$$L = \sum_a [\frac{1}{2} m_a v_a^{'2} + m_a \overrightarrow{\Omega} (\mathbf{r}_a^{'} \times \mathbf{v}_a^{'}) + \frac{1}{2} m_a (\overrightarrow{\Omega} \times \mathbf{r}_a^{'})^2] - U \ ; \tag{3.53}$$

for the same ratio charge-to-mass (q/m) and for $\overrightarrow{\Omega} = \frac{q}{2mc}\mathbf{H}$ we can see that the lagrangian acquires a magnetic term $\overline{\mathbf{m}}\mathbf{H}$ (on averaging over the finite microscopic motion of charges), providing the magnetic field $\mathbf{H}$ (and angular velocity $\overrightarrow{\Omega}$) are sufficiently small as to neglect the quadratic term in H^2 (Ω^2). This is known as Larmor's theorem; the angular velocity $\Omega = |q| H/2mc$ is called the Larmor frequency.

The torque given by equation (3.47) moves the angular momentum,

$$\frac{d\mathbf{L}}{dt} = \mathbf{K} = \overline{\mathbf{m}} \times \mathbf{H} \ ; \tag{3.54}$$

using equation (3.44) (for the same ratio charge-to-mass) we get

$$\frac{d\overline{\mathbf{m}}}{dt} = \frac{q}{2mc} \overline{\mathbf{m}} \times \mathbf{H} \tag{3.55}$$

and

$$\frac{d\mathbf{L}}{dt} = \frac{q}{2mc} \mathbf{L} \times \mathbf{H} = -\overrightarrow{\Omega} \times \mathbf{L} \ . \tag{3.56}$$

Equation (3.55) is known as Larmor's equation of motion (precession); $\gamma = q/2mc$ is called the gyromagnetic ratio (factor).

It is worth noting that the motion of a charge q in a constant magnetic field H proceeds according to the equations $m\dot{v}_x = \frac{q}{c} v_y H$, $m\dot{v}_y = -\frac{q}{c} v_x H$, *i.e.* $\ddot{v}_x = (qH/mc)^2 v_x$; this motion oscillates with the frequency $\frac{qH}{mc}$, which is known as the cyclotron frequency. It is the average over microscopic motion which makes the magnetic moment and the angular momentum to precess with Larmor's frequency $\frac{qH}{2mc}$. Quasi-classical motion in matter in the presence of a magnetic field proceeds with cyclotron frequency.

3.3 Atoms and molecules

The motion of electrons in atoms is governed, mainly, by the non-relativistic Schrodinger equation with Coulomb interaction between electrons and nucleus (attraction) and between the electrons (repulsion). Usually, we eliminate the motion of the center of mass (practically the nucleus) and consider the nucleus as a fixed point charge. The electronic states are characterized by the (total, orbital) angular momentum $\mathbf{L}$, the (total) spin $\mathbf{S}$ (of the electrons) and parity; usually, we do not include the Planck's constant $\hbar$ in the definition of the angular momenta. The states are degenerate (their number is $(2L+1)(2S+1)$). The nucleus being much heavier than the electrons, it may be considered as being at rest. For heavier atoms, the relativistic effects become important, especially the spin-orbit coupling ($\sim \mathbf{LS}$); then, the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is a "good" quantum number (and $2\mathbf{LS} = \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2$, with the eigenvalues $J(J+1) - L(L+1) - S(S+1)$). The relativistic effects can be treated by perturbation theory; they split the degeneracy (multiplet splitting) and give the atomic states a fine structure. The atomic states are denoted by ${}^{2S+1}L_J$, where $L = S\,(L = 0)$, $P\,(L = 1)$, $D\,(L = 2)$, $F\,(L = 3), \ldots.$

The interaction in atoms is supposed to give rise to a mean field, *i.e.* a centrally symmetric, self-consistent field acting upon each electron (this is also known as the Hartree-Fock field); then, we can describe the atom as a collection of electron configuration (shells). Every electron has a definite angular momentum l, a principal quantum number n (increasing with increasing energy) and well-defined projections m and σ of the orbital momentum $\mathbf{l}$ and spin $\mathbf{s}$ ($s = 1/2$) on an axis. Electronic states are denoted by nl, where $l = s\,(l = 0)$, $p\,(l = 1)$, $d\,(l = 2)$, $f(l = 3), \ldots$ ($l = 0, 1, \ldots n - 1$, by analogy with the hydrogen atom). A full configuration is called a closed shell; it contains $2(2l+1)$ electrons (for a given n); it has a vanishing spin and a vanishing orbital momentum. In an open shell, we arrange electrons such as, first, get the highest spin S and then get the highest orbital momentum L: this ensures a highly symmetric wavefunction which minimizes the Coulomb repulsion between the electrons. The spin-orbit interaction is minimized by $J = |L - S|$ for less than half full shells and by $J = L + S$ for more than half full shells. This is known as Hund's rule. It amounts to putting as many unpaired electrons on the available levels as possible, and only thereafter to pair them. This way, open shells have always a non-vanishing spin. Anticipating, since the spin is related with the magnetic moment, we can say that, whenever possible, we have the highest magnetic moment.

In molecules the atomic nuclei are too heavy to move rapidly, and we have electronic energy levels (and states) depending parametrically on the nuclei positions; these are called electronic terms (this is known as the adiabatic, or Born-Oppenheimer approximation). If two electronic terms intersect each other, then the molecule gets distorted; this is known as the Jahn-Teller effect. In contrast with the atoms, in molecules the angular momentum $\mathbf{L}$ is not a "good" quantum number anymore (it is not conserved); the electronic spin remains a "good" quantum number (in non-relativistic approximation). In diatomic molecules we have an axial symmetry, as well as a reflection in any plane passing through this axis connecting the two nuclei. For identical atoms we can also have a spatial inversion symmetry. In general, the symmetry of the molecules is of great help in describing their properties. The main physics of the molecules is related to their vibrations and rotations (they can be viewed, approximately, as spherical, symmetrical or asymmetrical tops); rotation frequencies are smaller than vibration frequencies (microwave-far infrared to infrared range, $10^{11} - 10^{14}Hz$).

3.4 Atomic moments

The electric charge of the electron is $-e = 4.8 \times 10^{-10}esu$ ($1.6 \times 10^{-19}C$). Typical atomic distances are of the order of the Bohr radius $a_H = \hbar^2/me^2 = 0.53\text{Å}(1\text{Å} = 10^{-8}cm)$, where $\hbar \simeq 10^{-27}erg \cdot s$ is Planck's constant and $m \simeq 10^{-27}g$ is the electron mass (H stands for hydrogen, a_H is the "radius" of the hydrogen atom). An estimation of the atomic dipole moment is $d \simeq ea_H$. The atomic electric field is of the order $E = |e|/a_H^2$ ($\simeq 10^6 statvolt/cm$; $1statvolt/cm = 3 \times 10^4 V/m$), the dipole energy is of the order $\mathcal{E} = dE = e^2/a_H = 27.2eV$ ($1eV = 1.6 \times 10^{-19}J$; $-e^2/2a_H = -13.6eV$ is the ground-state energy of the hydrogen atom); the angular velocity of an electron in atom is of the order $\omega = \mathcal{E}/\hbar$, the corresponding action is of the order $\mathcal{E}/\omega = \hbar$. The motion of an atomic (or molecular) dipole (or quadrupole) is quantum-mechanical.

The wavefunctions may have a definite parity; then, the average of the dipole momentum over such a wavefunction is zero. Atoms in stationary states have not a dipole electric moment (except for excited hydrogen, or hydrogen-like excited atoms). The dipole moment has non-zero matrix elements only between states of different parity. Usually, in molecules this is not true, the molecules may have a nonvanishing dipole electric moment (polar molecules).

The quadrupole moment associated with the electrons in atom should be averaged over the electron motion. The resulting quantity can be expressed in terms of the total angular momentum **J** of the electrons (the only vector available for the atom); it is easy to see that we should have

$$Q_{ij} = \frac{3Q}{2J(2J-1)}(J_iJ_j + J_jJ_i - \frac{2}{3}\delta_{ij}J^2) \ , \tag{3.57}$$

where the distinction between D_{ij} and Q_{ij} arises from the averaging over quantum motion and the pre-factor in equation (3.57) has been chosen for convenience: we have

$$Q_{zz} = \frac{3Q}{J(2J-1)}[M^2 - \frac{1}{3}J(J+1)] \ , \tag{3.58}$$

where M is the quantum number of J_z, and $Q_{zz}(M = J) = Q$ (maximum value). In addition, we can see that $Q_{ij} = 0$ for $J = 0$ or $J = 1/2$, as expected. If the spin-orbit interaction can be neglected, a similar representation holds for Q_{ij} in terms of the angular momentum **L** of the electrons.

The moments described above are permanent electric moments. In the presence of an external electric field $\mathbf{E}_0$ we can compute the perturbation-theory contribution to the energy of an atom (Stark effect), for an interaction energy $-\mathbf{dE}_0$. Usually, since the diagonal matrix elements of $\mathbf{d}$ are zero we have a contribution $\mathcal{E} = -(1/2)\alpha_{ij}E_{01}E_{0j}$ of the second-order of the perturbation theory (not so for hydrogen!), so we have an induced dipole moment $d_i = -\partial\mathcal{E}/\partial E_{0i} = \alpha_{ij}E_{0j}$; α_{ij} is called the polarizability tensor. Typical values of atomic (or molecular) polarizabilities are of the order of the volume of the charge distribution. It is worth noting that we can also compute the contributions of the interaction energy $(1/6)Q_{ij}\partial^2\Phi_0/\partial x_i\partial x_j$, where Φ_0 is the scalar potential of the external field (and the derivatives are taken at the origin, where the charge distribution is placed), by means of the perturbation theory; then, we can have contributions linear in the external field (its spatial derivatives).

The quantum relativity gives particles a magnetic moment $\overrightarrow{\mu}$, which is related to the spin $\mathbf{s}$; this is the intrinsic magnetic moment. For an electron we have

$$\overrightarrow{\mu} = \frac{e\hbar}{mc}\mathbf{s} = \frac{e\hbar}{2mc}\overrightarrow{\sigma} \ , \tag{3.59}$$

where $\overrightarrow{\sigma}$ are Pauli's matrices;

$$\mu_B = \frac{|e|\,\hbar}{2mc} = 0.927\times10^{-20}erg/Gs \tag{3.60}$$

is called Bohr's magneton ($1Gs = 10^{-4}Ts$). We see that the intrinsic magnetic momentum of the electron is opposed to the intrinsic angular momentum (the spin) and the proportionality coefficient (e/mc) is twice as large as the proportionality coefficient corresponding to the angular momentum (gyromagnetic factor, $e/2mc$, equation (3.44)). In a mechanical model, the Bohr magneton corresponds to the quantization $\hbar/l = mv$ of the momentum mv for a particle with mass m and velocity v moving inside the length l.

The hamiltonian of the motion of a charge q with mass m in an electromagnetic field with potentials $\mathbf{A}$ and Φ is

$$\mathcal{H} = \frac{1}{2m}(\mathbf{p} - \frac{q}{c}\mathbf{A})^2 - \overrightarrow{\mu}\mathbf{H} + q\Phi \ , \tag{3.61}$$

where $\overrightarrow{\mu}$ is the magnetic moment of the particle and $\mathbf{H} = curl\mathbf{A}$ is the magnetic field (the product $\mathbf{pA}$ must be symmetrized; this is the quasi-non-relativistic approximation). The motion of an electron is governed by Dirac equation. In the classical limit this equation becomes the Schrodinger equation. The first-order relativistic corrections lead to the equation given above, which is known as Pauli's equation; it differs from Schrodinger's equation by the presence of the energy $-\overrightarrow{\mu}\mathbf{H}$ of a magnetic dipole in the external magnetic field $\mathbf{H}$. The equation (3.61) is extended to any other particle endowed with a magnetic moment. We note that the motion of the magnetic moment $i\hbar\dot{\overrightarrow{\mu}}=[\overrightarrow{\mu},\mathcal{H}]$ is governed by the same equation

$$\dot{\overrightarrow{\mu}}=\gamma\overrightarrow{\mu}\times\mathbf{H} \tag{3.62}$$

as in the classical motion; γ is the gyromagnetic factor, $\overrightarrow{\mu}=\gamma\hbar\mathbf{s}$ ($\overline{\mathbf{m}}=\gamma\mathbf{L}$); similarly, $\overrightarrow{\mu}\times\mathbf{H}$ is the torque of the forces acting upon the intrinsic angular momentum (the spin). For a uniform magnetic field we can take $A_x=-Hy/2$ and $A_y=A_z=0$; we can see that the motion along the y-axis is that of a harmonic oscillator with frequency $\Omega=|q|\,H/mc$, which is twice the Larmor frequency ($\Phi=0$); this is the cyclotron frequency; the corresponding energy levels are known as Landau levels. The motion of an atomic magnetic moment is, of course, quantum-mechanical. For an electron in a magnetic field $H=1Ts$ we get $\Omega=1.6\times10^{11}Hz$ and an energy $\hbar\Omega=10^{-4}eV\simeq1K$ ($1eV=1.16\times10^{4}K$) (twice the energy of its magnetic moment in that field).

Let us assume an atom in an external uniform magnetic field. We can take $\mathbf{A}=(1/2)\mathbf{H}\times\mathbf{r}$ and get immediately an interaction term $\overrightarrow{\mu_{at}}\mathbf{H}$, where $\overrightarrow{\mu_{at}}=-\mu_B(\mathbf{L}+2\mathbf{S})$; this interaction can be treated as a perturbation; it gives the energy levels $\Delta E=g\mu_BM_JH$, where $g=g(L,S,,J)$ is a numerical coefficient known as the Lande factor and M_J is the quantum number of the projection of the total angular momentum $\mathbf{J}$ on the z-axis. The magnetic field splits the atomic energy level (fine structure included); this is the Zeeman effect; the projection of the atomic magnetic moment $\overrightarrow{\mu}=-\partial\Delta E/\partial\mathbf{H}$ on an axis (the z-axis) is $-g\mu_BM_J$ (this is very similar with the electron magnetic moment for $g=2$ and M_J replaced by the spin 1/2). For $\mathbf{J}=0$ (but $\mathbf{L}$, $\mathbf{S}\neq0$) we should compute the second-order contribution of the interaction term $-\overrightarrow{\mu_{at}}\mathbf{H}$ (this is known as van Vleck's paramagnetism). If the magnetic field is strong enough as the splitting produced by it exceeds the fine structure, then the effect is known as the Paschen-Back effect; it remains linear in the magnetic field.

The Zeeman splitting of energy $E=-\overrightarrow{\mu}\mathbf{H}$ in a non-uniform magnetic field $\mathbf{H}$ gives rise to a force $grad\mathbf{E}$ which was used to visualize the magnetic moment (the spin) by Stern and Gerlach, as well as to measure the magnetic moments in molecular beams experiments by Rabi.

The derivation of the Lande factor assumes an average over all the orientations of the angular momenta; performing such an average we have

$$\Delta E = \mu_B H(J_z + S_z) \ , \tag{3.63}$$

where $S_z = C \cdot J_z$, $\mathbf{S} = C \cdot \mathbf{J}$ and

$$\mathbf{SJ} = C \cdot J(J+1) = \frac{1}{2}[J(J+1) - L(L+1) + S(S+1)] \ ; \tag{3.64}$$

we get the constant C from equation (3.64) and introduce it into $S_z = C \cdot J_z$ with $J_z = M_J$; the Lande factor is given by

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \ . \tag{3.65}$$

There is a second contribution to the hamiltonian of the atom in a magnetic field, given by

$$\frac{e^2}{8mc^2}\sum_a (\mathbf{H} \times \mathbf{r}_a)^2 \ ; \tag{3.66}$$

it is so small that its effect is relevant only for $\mathbf{L} = \mathbf{S} = 0$; it is given by

$$\Delta E = \frac{e^2}{12mc^2} H^2 \sum_a \overline{r_a^2} = -\frac{1}{2}\chi H^2 \ ; \tag{3.67}$$

χ (< 0) is called the diamagnetic susceptibility (magnetic moment $\mathbf{m} = \chi \mathbf{H}$); equation (3.67) is known as the Langevin formula (Langevin diamagnetism).

Finally we note that a charge q, with mass m and spin $\mathbf{s}$ in a magnetic field gives rise to a current density

$$\begin{aligned} \mathbf{j} = -\tfrac{iq\hbar}{2m}[\psi^* grad\psi - (grad\psi^*)\psi] - \\ -\tfrac{q^2}{mc}\mathbf{A}\psi^*\psi + \gamma\hbar c \cdot curl(\psi^* \mathbf{s}\psi) \ , \end{aligned} \tag{3.68}$$

where γ is the gyromagnetic factor ($\overrightarrow{\mu} = \gamma\hbar\mathbf{s}$); the first term in the *rhs* of equation (3.68) is the orbital quantum-mechanical current density, the second term can be viewed as a diamagnetic current, while the last term is a current associated with the spin (magnetic moment). Since the intrinsic magnetic moment ($\overrightarrow{\mu} = \gamma\hbar\mathbf{s}$) gives rise to a current, it follows that it produces also an electromagnetic field.

It is worth noting that a (microscopic) charge distribution can generate around it an electric field according to its multipole expansion; in general, an estimation of this field for atoms, molecules, etc is q/a^2, where q is an effective charge and a is a distance of the order of atomic distances. The magnetic field includes the factor v/c, where v stands for the velocity of the charges; usually, $v/c \ll 1$. For instance, the (dipolar) magnetic field $\sim \overrightarrow{\mu}/a^3$ of a magnetic moment $\mu = \mu_B$ is $\simeq 10^4 Gs$ at a distance 1Å (this is a rather high magnetic field). For comparison, an electron charge at the same distance (or an electronic dipole) yields an electric field $\simeq 10^6 statvolt/cm$.

In general, two neutral charge distributions interact mainly by their dipolar electric fields, which go like $1/r^3$; the main contribution to energy arises in the second-order of the perturbation theory (and is negative), where we get an energy $\Delta E \sim -1/r^6$ and an attractive force $F \sim -1/r^7$; this is known as the van der Waals-London force; the van der Waals energy is of the order of $0.1 - 0.01eV$ at distances a few times larger than atomic (molecular) distances (at short distances the atoms repel each other). A quadrupole-quadrupole interaction gives an energy $\Delta E \sim 1/r^5$ (in the first order of the perturbation theory). The dipole energy may also occur in the secular equation for two identical atoms, leading to an energy $\Delta E \sim 1/r^3$. Usually, it is of interest the average over all orientations of the angular momenta, so that the van der Waals formula holds (averaging over all orientations results in the vanishing of all moments; we are left with the second order of the perturbation theory for dipoles as the main contribution). It is worth noting the interaction of an ion, with electric field $\sim 1/r^2$, and the quadrupole of an atom: the energy is $\sim 1/r^3$, which, however, is vanishing by averaging over all directions of the total angular moment; the next-order contribution is a second-order perturbation with respect to the dipole moment, which goes like $1/r^4$; it can be written as $-(1/2)\alpha q^2/r^4$, where α is the polarizability of the atom; this gives an attractive force (which explains the attraction of an electron by neutral atoms, with binding energy in the $1eV$-range; though in fields which go like $-1/r^3$ (or $-1/r^4$) the number of bound states is finite, and it may even be zero).

In general, the vanishing of inter-atomic (molecular) forces at large distances means that they decrease exponentially, since the quantum-mechanical atomic (molecular) charge distribution decreases exponentially at large distances. At large distances we must include the effect of retardation (radiation), which (for dipolar interaction) gives an energy $\Delta E \sim -1/r^7$ and an attractive force $\sim -1/r^8$; this is known as the Casimir force.

3.5 Atomic nucleus and nuclear moments

The atomic nucleus consists of Z protons with mass $M_p \simeq 1.67 \times 10^{-24} g$ and charge $|e| = 4.8 \times 10^{-10} esu$ and $A - Z$ neutrons with mass $M_n \simeq M_p = M$ which are electrically neutral; both are called nucleons, and they have spin 1/2; the nucleus is surrounded by Z electrons; Z is the atomic number of the chemical element consisting of the corresponding atoms and A is the mass number; the nucleus extends over a few fm ($1fm = 10^{-13}cm$). The rest energy of a nucleon is $Mc^2 \simeq 1GeV$, such that, for any reasonable energy, the nucleon move non-relativistically. Strong (and short-range) forces act between the nucleons, attractive at large distances and repulsive at short distances; they have a saturation character, ensuring the nuclear cohesion (with an average cohesion energy $\simeq 7 - 8MeV$ per nucleon). These forces depend on position, spin and isospin, and they may not be two-body forces (the isospin is that quantum number which regards the proton and the neutron as two distinct states of the same particle). The radius of the nuclei is parametrized by $R = aA^{1/3}$, where $a \simeq 1.1fm$ is the nucleon "radius"; the Compton wavelength of a nucleon is $\hbar/Mc = 0.2fm$. A nuclear mean field can lead to nuclear shells, similar with the atomic electron shells, with a strong spin-orbit coupling. A pairing interaction acts between nucleons, whenever possible.

In general, the electric and magnetic moments of the nucleus are averaged over nuclear wavefunctions, according to equation (3.68) (as well as off-diagonal matrix elements of the corresponding operators; the nucleons move quantum-mechanically). In stationary states the nuclear dipole momentum is zero, due to the parity conservation. Since the total nuclear charge is non-zero (and since we are interested, in general, in intrinsic nuclear properties) we should eliminate the contribution of the center of mass by replacing the nucleon coordinates $\mathbf{r}_i$ by $\mathbf{r}_i - \mathbf{R}$ and the nucleon momenta $\mathbf{p}_i$ by $\mathbf{p}_i - \mathbf{P}/A$, where $\mathbf{R} = (1/A)(\sum_p \mathbf{r}_p + \sum_n \mathbf{r}_n)$ is the position of the center of mass (summation over protons p and neutrons n) and $\mathbf{P} = AM\mathbf{V}$ is the momentum of the center of mass (M is the nucleon mass and $\mathbf{V}$ is the velocity of the center of mass). In particular cases, like the quadrupole moment, we may use the representation in terms of the total angular momentum **J,** which avoids this point (since the nuclear forces depend on spin, the total spin $\mathbf{S}$ is not conserved - except its magnitude).

The nucleons have an intrinsic magnetic moment: $\mu_p = 2.79\mu_0$ (parallel to the spin) for the proton and $\mu_n = -1.91\mu_0$ for the neutron (antiparallel to the spin), where $\mu_0 = |e|\,\hbar/2M_pc = 5\times10^{-24}erg/Gs$ is the nuclear Bohr magneton (these moments come probably from the quarks, which are the constituents of the atomic nuclei). The magnetic moment of the nucleus can be written as $\overrightarrow{\mu} = g\mu_0\mathbf{J}$, where g, similar with Lande's factor, is called the gyromagnetic factor. The magnetic moment of the nucleus is produced by the nucleons outside the closed shells (the magnetic moments of the nucleons in closed shells cancel out). In general, we have for nucleons $\overrightarrow{\mu}/\mu_0 = g_l\mathbf{l} + g_s\mathbf{s}$, where $\mathbf{l}$ is the orbital angular momentum and $\mathbf{s}$ is the spin. For protons $g_l = 1$ and $g_s = 5.58$, for neutrons $g_l = 0$ and $g_s = -3.82$. We can write

$$g_j\mathbf{j} = g_l\mathbf{l} + g_s\mathbf{s} = \frac{1}{2}(g_l + g_s)\mathbf{j} + \frac{1}{2}(g_l - g_s)(\mathbf{l} - \mathbf{s}) \tag{3.69}$$

and multiply by $\mathbf{j} = \mathbf{l} + \mathbf{s}$ to get

$$g_j = g_l \pm \frac{g_s - g_l}{2l+1}\ ,\ j = l \pm 1/2 \tag{3.70}$$

(and $s = 1/2$). These formulae are useful for one or two nucleons outside a closed shell (with appreciable discrepancies with respect to the experimental values of the magnetic moments); for more nucleons outside a closed shell we should known the nuclear wavefunction. In addition, the spin-orbit interaction (which is of the first order in v/c, in contrast with atoms, because the nuclear forces depend on the spin) includes the velocity in the angular momentum, and, therefore, it includes the vector potential in the presence of an electromagnetic field; it is easy to see that it leads to an additional magnetic moment of the nucleons.

If we compare the nuclear Bohr magneton $\mu_0 = |e| \hbar/2M_pc = 5 \times 10^{-24} erg/Gs$ with a mechanical model for a particle with charge $|e|$ moving with velocity v in a nucleus with radius R, $\mu = |e| Rv/2c \simeq 10^{-25}(v/c) erg/Gs$, we get $\mu_0 \gg \mu$, *i.e.* $\hbar/R \gg M_pv$, which indicates that the nucleon moves over much shorter distances. In fact, the magnetic moment includes the Compton wavelength $\hbar/M_pc$, which for proton is $\hbar/M_pc = 0.2fm$, much smaller than the inter-nucleon separation in the nucleus.

Heavy nuclei are usually deformed, so they have a rotation spectrum; additional moments (quadrupole, magnetic moment) arise from rotation.

The atomic nucleus gives rise to effects on the electronic levels in the atom, called isotopic shifts. For light nuclei, the term

$$\frac{1}{2M}\left(\sum_i \mathbf{p}_i\right)^2 \tag{3.71}$$

appears in the hamiltonian, where M is the mass of the nucleus and $\mathbf{p}_i$ is the momentum of the i-th electron; this term can be treated by means of the perturbation theory; it produces an isotopic shift proportional to $1/M_1 - 1/M_2$ (*i.e.* it changes the difference between any two electronic levels on passing from an isotope with mass M_1 to another with mass M_2). For heavier nuclei, the finite extension of the nucleus gives an additional interaction

$$\Delta E = -e \int d\mathbf{r}(\phi + Ze/r)\psi^2(\mathbf{r}) \ , \tag{3.72}$$

where ϕ is the actual (Coulomb) potential of the extended nucleus, as distinct from the potential of a point-like nucleus and $\psi(\mathbf{r})$ is the wavefunction of the electron. We may put $\psi^2(\mathbf{r}) \simeq \psi^2(0)$ (for an s-state, which is the only state that have a non-zero value on the nucleus) and introduce $\triangle r^2 = 6$ in equation (3.72); we get easily

$$\Delta E = -\frac{2}{3}\pi e\psi^2(0)\int d\mathbf{r}\rho r^2 = \frac{2}{3}\pi Ze^2\psi^2(0)\overline{r^2} \ , \tag{3.73}$$

where ρ is the charge density and $\overline{r^2}$ is the proton mean square radius of the nucleus; for a spherical distribution $\overline{r^2} = 3R^2/5$, where R is the geometrical radius of the nucleus; since $\psi(0) \sim \sqrt{Z}$, the energy shift given by equation (3.73) goes like Z^2R^2 (without relativistic effects, *i.e.* for $Ze^2/\hbar c \ll 1$; $e^2/\hbar c = 1/137$ is the fine structure constant).

The atomic nucleus produces electric and magnetic fields acting upon the electrons in the atom; the main contribution comes from the electric field of the nuclear quadrupole $Q/r^4 \simeq |e|\, R^2/r^4$, which gives an energy $\simeq e^2R^2/r^3$, and from the nuclear magnetic dipole, which gives an interaction energy $\simeq \mu_0\mu_B/r^3$ (R is the radius of the nucleus). If we take for μ_0 its superior value $\simeq |e|\, Rv/2c$ discussed above, we can see that the dominant contribution is the magnetic one, by the virtue of the very small nuclear radius R; of course, this is valid for s-electrons, which have a non-zero probability of being at the position of the nucleus. These nuclear-electron interactions are called hyperfine interactions.[3] The magnetic hyperfine interaction can be represented as $a\mathbf{IJ}$, where $\mathbf{I}$ is the nuclear spin and $\mathbf{J}$ is the electronic spin (the coefficient a depends on the magnetic moments, distance, etc). It is easy to see that such an interaction produces a splitting of the electronic levels of the form $\Delta E = (a/2)F(F+1)$, where $\mathbf{F} = \mathbf{I} + \mathbf{J}$ is the total spin: $F = I+J, I+J-1, ...|I-J|$; for $I > J$ we have $2J+1$ hyperfine levels, for $J > I$ we have $2I+1$ hyperfine levels. The quadrupole hyperfine interaction can be represented as $\sim (I_iI_j + I_jI_i - 2I^2\delta_{ij}/3)J_iJ_j$, whose eigenvalues are

$$\sim \frac{1}{2}F^2(F+1)^2 + \frac{1}{2}F(F+1)[1 - 2J(J+1) - 2I(I+1)] \tag{3.74}$$

(the quadrupole interaction includes $\mathbf{I}^2\mathbf{J}^2$ and $\mathbf{IJ}$, since $\mathbf{I}$ commutes with $\mathbf{J}$).

An s electron has the (spherically symmetric) wavefunction $\psi(r)$, which is non-zero at the position of the nucleus (for non-relativistic regime $Ze^2/\hbar c \ll 1$). The electron generates a magnetic field

$$\mathbf{H} = \frac{1}{c}\int d\mathbf{r}\frac{\mathbf{n}\times\mathbf{j}}{r^2} \tag{3.75}$$

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[3] The hyperfine interaction arising from the effect of the nuclear magnetic moment on the motion of the electrons has been suggested by W. Pauli, "Zur Frage der theoretischen Deutung der Satelliten einiger Spektrallinien und ihrer Beeinflussung durch magnetische Felder", Naturwiss. **12** 741 (1924).

at the position of the nucleus, where $\mathbf{r}=\mathbf{n}r$ is oriented from the nucleus to the electron; the current density is given by

$$\mathbf{j}=-2\mu_B c\cdot curl(\psi^2\mathbf{s})=-2\mu_B c\frac{d\psi^2}{dr}\mathbf{n}\times\mathbf{s}\ , \tag{3.76}$$

where $\mathbf{s}$ is the electron spin; we have

$$\mathbf{H}=-2\mu_B\int_0^\infty dr\frac{d\psi^2}{dr}\int do\mathbf{n}\times(\mathbf{n}\times\mathbf{s})=-\frac{16\pi}{3}\mu_B\psi^2(0)\mathbf{s}\ . \tag{3.77}$$

The interaction energy (the energy of the nucleus in the magnetic field of the electron) is given by

$$\Delta E=-\overrightarrow{\mu}\mathbf{H}=\frac{16\pi}{3I}\mu\mu_B\psi^2(0)\mathbf{sI}\ , \tag{3.78}$$

where the magnetic moment of the nucleus is written as $\overrightarrow{\mu}=\mu\mathbf{I}/I$. If $J=S=1/2$, then $\mathbf{F}=\mathbf{I}+\mathbf{J}$ is $F=I\pm 1/2$, and we have the splitting

$$E_{I+1/2}-E_{I-1/2}=\frac{8\pi}{3I}\mu\mu_B\psi^2(0)(2I+1) \tag{3.79}$$

(where we have used $\mathbf{F}^2=\mathbf{I}^2+\mathbf{s}^2+2\mathbf{sI}$). Since $\psi(0)\sim\sqrt{Z}$, the magnitude of this splitting goes like Z.

Similarly, the nucleus produces a vector potential

$$\mathbf{A}=\frac{\overrightarrow{\mu}\times\mathbf{n}}{r^2} \tag{3.80}$$

and a magnetic field

$$\mathbf{H}=\frac{3(\overrightarrow{\mu}\mathbf{n})\mathbf{n}-\overrightarrow{\mu}}{r^3} \tag{3.81}$$

at $\mathbf{r}=r\mathbf{n}$ where and electron is placed; therefore, we have an interaction

$$\frac{|e|}{mc}\mathbf{Ap}+\frac{|e|\,\hbar}{mc}\mathbf{Hs}=\frac{2\mu_B}{r^3}\overrightarrow{\mu}[\mathbf{l}+3(\mathbf{ns})\mathbf{n}-\mathbf{s}]\ ; \tag{3.82}$$

here we average over all the directions, so that the expresssion in the bracket is proportional to $\mathbf{j}$; therefore, we have the interaction

$$\frac{2\mu_B}{\overline{r^3}j(j+1)}\overrightarrow{\mu}\mathbf{j}[\mathbf{lj}+3\overline{(\mathbf{ns})\mathbf{nj}}-\mathbf{sj}]\ , \tag{3.83}$$

where we average also over $n_i n_j$. This average can be written as

$$\overline{n_i n_j} - \frac{1}{3}\delta_{ij} = a[l_i l_j + l_j l_i - \frac{2}{3}\delta_{ij} l(l+1)] \tag{3.84}$$

for an electron with orbital momentum l (averaged over directions). In equation (3.84) we multiply on the left by l_i and on the right by l_j; since $\mathbf{n}$ is perpendicular to $\mathbf{l}$ we have $n_i l_i = 0$; in addition, $l_i l_i l_j L_j = (\mathbf{l}^2)^2 = [l(l+1)]^2$ and

$$\begin{aligned} l_i l_j l_i l_j = (\mathbf{l}^2)^2 + i\varepsilon_{jik} l_i l_k l_j = (\mathbf{l}^2)^2 - \tfrac{1}{2} i\varepsilon_{ijk} l_i (l_k l_j - l_j l_k) = \\ = (\mathbf{l}^2)^2 + \tfrac{1}{2}\varepsilon_{ijk}\varepsilon_{kjl} l_i l_l = (\mathbf{l}^2)^2 - \mathbf{l}^2 = [l(l+1)]^2 - l(l+1) \ ; \end{aligned} \tag{3.85}$$

we get

$$a = -\frac{1}{(2l-1)(2l+3)} \tag{3.86}$$

and the interaction from equation (3.83)

$$\frac{2\mu_B\mu}{\overline{r^3} j(j+1) I}\mathbf{Ij}\left[\mathbf{lj} + \frac{2l(l+1)\mathbf{sj} - 6(\mathbf{sl})(\mathbf{jl})}{(2l-1)(2l+3)}\right] \ ; \tag{3.87}$$

here we can eliminate $\mathbf{sj}$ and $\mathbf{sl}$ by using $\mathbf{j} = \mathbf{l} + \mathbf{s}$ and $\mathbf{Ij}$ by using $\mathbf{F} = \mathbf{I} + \mathbf{j}$; we get finally the hyperfine splitting

$$\frac{\mu_B \mu l(l+1)}{\overline{r^3} j(j+1) I} F(F+1) \tag{3.88}$$

($j = l \pm 1/2$).

We have derived above (equation (3.65)) the fine splitting of the electron energy levels $g\mu_B M_J H$, *i.e.* $g\mu_B J_z H$; similarly, the hyperfine splitting can be written as

$$g\mu_B \overline{J_z} H = g\mu_B (\mathbf{JF}/\mathbf{F}^2) M_F H = g_F \mu_B M_F H \tag{3.89}$$

by averaging J_z over all the orientations of $\mathbf{F}$; following the same procedure as before, and using $\mathbf{F} = \mathbf{J} + \mathbf{I}$, we get

$$g_F = g\frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} \ , \tag{3.90}$$

which is a generalized Lande factor.

3.6 Hyperfine splitting in molecules

Usually, molecules have a vanishing electronic spin; they have also a vanishing electronic orbital moment (in their ground-state). Consequently, their hyperfine splitting of the electronic levels is due to the quadrupole interaction of the nucleus with the electrons (for nuclei with spin $I \neq 0, 1/2$). This interaction is averaged over electronic states and over molecular rotations.

For a diatomic molecule the quadrupole hyperfine interaction (averaged over electron states) can be written as

$$bI_iI_j(n_in_j - \frac{1}{3}\delta_{ij}) \ , \tag{3.91}$$

where $\mathbf{n}$ is the unit vector along the molecular (z-) axis. For a given value I_z along this axis, the above operator can be written as $b[I_z^2 - I(I+1)/3]$. The average over molecular rotations implies the averaging over the directions of the molecular angular momentum $\mathbf{K}$; the average of n_in_j proceeds as in equation (3.84) above, and we get

$$-\frac{b}{(2K-1)(2K+3)}I_iI_j[K_iK_j + K_jK_i - \frac{2}{3}\delta_{ij}K(K+1)] \ . \tag{3.92}$$

The eigenvalues of this operator are similar with those given in equation (3.74).

For a polyatomic molecule we get $b_{ij}I_iI_j$ instead of equation (3.91), where b_{ij} is a traceless tensor expressing the electron state of the molecule. After averaging over the molecular rotations we get

$$b_{ij} = b[J_iJ_j + J_jJ_i - \frac{2}{3}\delta_{ij}J(J+1)] \ , \tag{3.93}$$

where $\mathbf{J}$ is the molecular angular momentum. The coefficient b can be expressed by means of the components b_i of the tensor b_{ij} with respect to the principal axes. Indeed, if we multiply equation (3.93) by J_i on the left and by J_j on the right and average over directions, we get

$$b_{ij}J_iJ_j = bJ(J+1)[\frac{4}{3}J(J+1) - 1] \tag{3.94}$$

by using the technique described above; now, we can expand

$$b_{ij}J_iJ_j = b_1J_1^2 + b_2J_2^2 + b_3J_3^2 \ , \tag{3.95}$$

where J_i are the components of the angular momentum along the principal axes (in equation (3.95) J_i^2 is the average over rotations; the average of cross products J_iJ_j is vanishing).

If the spins of the nuclei are 1/2, the nuclear quadrupole is zero; then, the main contribution to the molecular hyperfine splitting comes from the direct interaction between the magnetic moments of the nuclei; for two nuclei, this interaction is

$$\frac{\mu_1\mu_2}{r^3I_1I_2}[\mathbf{I}_1\mathbf{I}_2 - 3(\mathbf{I}_1\mathbf{n})(\mathbf{I}_2\mathbf{n})] \ , \tag{3.96}$$

where $\mathbf{r} = r\mathbf{n}$; it must be averaged over the molecular rotations.

For molecules containing heavier nuclei the relativistic effects are important; for instance, there exists an indirect interaction between nuclear magnetic moments in the second-order of the perturbation theory mediated by electrons; it is larger by a factor $(Ze^2/\hbar c)^2$ than the direct interaction between the nuclear magnetic moments.

There is also an interaction (leading to a hyperfine splitting) between the nuclear magnetic moments and the magnetic field of the rotating molecule; indeed, a rotating molecule gives rise to a current density $\mathbf{j} = \rho\overrightarrow{\Omega} \times \mathbf{r}$, where ρ is the charge density and $\overrightarrow{\Omega}$ is the angular velocity; this current generates a magnetic field and the nuclear magnetic moment has a certain energy in this field, which is the interaction energy of the hyperfine splitting (after averaging over molecular states).

3.7 Atomic polarizability

The electrons in an atom can be displaced by an external electric field E; the induced dipole moment $d = Zel$, where Z is the number of electrons, e $(= -4.8 \times 10^{-10} esu)$ is the electron charge and l is the displacement, is related to the electric field E. Using a classical model, the force acting upon the electrons is ZeE; the electrons are displaced by distance l, giving rise to an off-center charge $\simeq Zel^3/a^3$, where a

is the radius of the atom; and a Coulomb force with the nucleus $\simeq Z^2e^2l^3/a^3l^2 = Z^2e^2l/a^3$; the two forces should equilibrate each other, hence $l = a^3E/Ze$ and the induced dipole moment $d = Zel = a^3E$ (electron-electron interaction is neglected). This classical model led to the definition of an atomic polarizability α_a through $d = \alpha_a E$; we note that it is proportional to the atomic volume, $\alpha_a \simeq a^3$. This is a static polarizability; we can write the equation of motion

$$Zm\ddot{l} = -\frac{Z^2e^2}{a^3}l + ZeE \tag{3.97}$$

for the displacement of Z electrons, each with mass m ($\simeq 10^{-27}g$), which gives

$$l = -\frac{e}{m}E\frac{1}{\omega^2 - Ze^2/ma^3} \tag{3.98}$$

and the dipole moment

$$d = Zel = -\frac{Ze^2}{m}E\frac{1}{\omega^2 - Ze^2/ma^3} \tag{3.99}$$

(for the Fourier transforms); the static polarizability $\alpha_a = a^3$ is recovered for $\omega \to 0$; we can see that the atomic polarizability moves with a characteristic frequency $\omega_c = (Ze^2/\alpha_a m)^{1/2}$; making use of the Bohr radius $a_H = \hbar^2/me^2 \simeq 0.53\text{Å}$ for the atomic radius (polarizability) we get $\omega_c \simeq 10^{17}(Z/5)^{1/2}s^{-1}$, which is a very high frequency; it resembles the atomic plasma frequency $(4\pi ne^2/m)^{1/2}$ with $4\pi n = Z/a^3$ (electron density); this is why we may leave aside the frequency dependence of these polarizabilities and limit ourselves to static polarizabilities. It is worth estimating the displacement $l = a^3E/Ze$, in a typical field $E = 10^3V/m \simeq 3 \times 10^{-2}statvolt/cm$ ($1V/m = (1/3)10^{-4}statvolt/cm$); for $a = a_H$ we get $l \simeq 10^{-16}/Z\,cm$, which is a very small displacement. We note that the internal electric field of an atomic nucleus is very high, $Ze/a_H^2 \simeq 2 \times 10^7 Z\,statvolt/cm \simeq 6 \times 10^{11}V/m$; the macroscopic fields are extremely low in comparison with the atomic fields.

In general, an atom placed in an electric field changes its energy levels, which may get split; this is the Stark effect. Usually, the change in energy is quadratic in field, $\delta E = (1/2)\alpha E^2$, so we have a polarizability α (note the factor 1/2 as for an induced dipole moment); an exception is the hydrogen atom, where this effect is linear in field. Except for hydrogen and hydrogen-like atoms, in general, both the static and dynamic quantum polarizabilities do not differ appreciably from the classical estimations.

3.8 Molecular polarizability: orientational

In general, atoms have not a permanent electric dipole moment, except for excited hydrogen and similar hydrogen-like atoms. But there are many molecules where electronic charges are transferred between atoms (polar molecules), which possess a permanent electric dipole. It is worth noting that for two ions with mass m_1 and m_2 and charges $\pm q$, located at $\mathbf{R}+\frac{m_1}{M}\mathbf{r}$ and $\mathbf{R}-\frac{m_2}{M}\mathbf{r}$, where $\mathbf{R}$ is the position of the center of mass, $\mathbf{r}$ is the relative position and $M = m_1 + m_2$ is the total mass, the electric dipole moment is $\mathbf{d} = 2q\mathbf{r} = q\mathbf{l}$, where $\mathbf{l} = 2\mathbf{r}$. This dipole ($\mathbf{l}$) can rotate about the center of mass and it can be approximated by a spherical pendulum (rigid, spatial rotator, spherical top). A similar estimation for the magnetic moment $\frac{q}{2c}\overline{\mathbf{r}\times\mathbf{v}}$ gives $\frac{q}{2c}(\overline{\mathbf{R}\times\dot{\mathbf{r}}}+\overline{\mathbf{r}\times\dot{\mathbf{R}}})$, and we can see that it is vanishing (the classical model for a rotating molecule gives a vanishing magnetic moment).

At thermal equilibrium the permanent dipoles $\mathbf{d}$ are randomly oriented, but under the action of a uniform external electric field $\mathbf{E}$ they acquire an energy $-\mathbf{dE}$ (we neglect the interaction between oriented dipoles). The dipole mean value is given by

$$\overline{\mathbf{d}} = \int \frac{do}{4\pi}\mathbf{d}e^{\beta\mathbf{dE}}/Z = \frac{\partial}{\partial(\beta\mathbf{E})}\ln Z \ , \tag{3.100}$$

where

$$Z = \int \frac{do}{4\pi}e^{\beta\mathbf{dE}} = \frac{1}{\beta dE}\sinh\beta dE \tag{3.101}$$

is the sum of states, $\beta = 1/T$ is the inverse of the temperature T and o denotes the solid angle. Typical values of d are of the order $-e\cdot 1\text{Å} = 4.8\times10^{-18}$ (or $10^{-8}e\cdot cm$), where e is the electron charge. The temperature is so that $1.38\times10^{-16}erg$ equals $1K$ (the Boltzmann constant), for $T = 300K$ we get $\beta dE = 10^{-4}E$; it equals unity for $E = 10^4 statvolt/cm = 3\times10^8 V/m$, which is a very high electric field.

For usual electric fields (and not very low temperatures) $\beta dE \ll 1$ and $Z = 1 + \beta^2 d^2 E^2/6 + ...$; it follows

$$\overline{\mathbf{d}} = \frac{1}{3}\beta d^2 \mathbf{E} \ . \tag{3.102}$$

The dipole moment of the unit volume is called polarization. Therefore, there exists a static dipolar polarization $\mathbf{P}_0 = n\beta d^2 \mathbf{E}/3$ and a static polarizability $\chi_0 = n\beta d^2/3$, where n is the dipole density (concentration). Under the action of an external electric field matter gets polarized; this is an orientational polarization. Equation (3.102) is called the Langevin-Debye equation;[4] its temperature dependence may serve to determine the dipole d. The external electric field may be (slowly) time-dependent.

The relaxation of the dipoles is described by the typical equation

$$\frac{d}{dt}\mathbf{d} = -\gamma(\mathbf{d} - \overline{\mathbf{d}}) \ \ , \tag{3.103}$$

where $\tau = 1/\gamma$ is a relaxation time. We get

$$\mathbf{d}(\omega) = \frac{1}{3}\beta d^2 \mathbf{E}(\omega)\frac{\gamma}{\gamma - i\omega} = \frac{1}{3}\beta d^2 \mathbf{E}(\omega)\frac{1}{1 - i\omega\tau} \ ; \tag{3.104}$$

equation (3.104) is called the Debye relaxation law; usually, $\gamma = 1/\tau$ is much lower even than radio frequencies, so there is only a slight ω-dependence (and time-dependence) of the dipolar polarization.

3.9 Molecular polarizability: vibrational

The polar molecules rotate and vibrate; their dipole moment oscillates with rotation and vibration frequencies. Typically, the vibration spectrum is $\hbar\omega_v(n+1/2)$ and the rotation spectrum is $\hbar^2 n(n+1)/2I$, where n are quantum numbers (0, 1, etc), $\omega_v \simeq 10^{14} s^{-1}$ is the vibration frequency scale, I is the moment of inertia and $\hbar/2I \simeq 10^{12} - 10^{13} s^{-1}$.

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[4] P. Langevin, "Sur la theorie du magnetisme", J. Physique **4** 678 (1905); P. Langevin, "Magnetism et theorie des electrons", Ann. Chim. Phys. **5** 70 (1905); P. Debye, "Einige Resultate einer kinetischen Theorie der Isolatoren", Phys. Z. **13** 97 (1912).

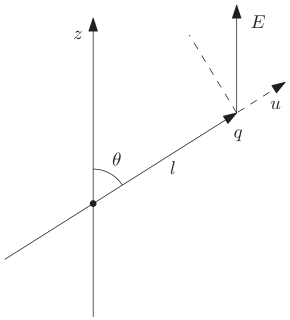

Figure 3.1: A dipole rotates and oscillates

These frequencies can be seen in the molecular absorption spectra, especially in Raman inelastic scattering (interaction with molecular vibrations and rotations). In the presence of an electric field molecular vibrations and rotations acquire new features. Usually, the electrons follow rapidly the vibrations of the nuclei so that the adiabatic approximation is valid, but an external field affects the nuclear vibrations.

Along the dipole axis the molecule vibrates under the action of an electric field, as shown in Fig.3.1; the equation of motion for the vibration displacement reads

$$m\ddot{u} = -m\omega_v^2 u + qE\cos\theta \ , \tag{3.105}$$

where m and q are generic mass and, respectively, charge of the dipole and ω_v is a vibration frequency (we leave aside the damping coefficient). The component u_z (along the field direction) obeys the equation

$$m\ddot{u}_z = -m\omega_v^2 u_z + qE\cos^2\theta \ . \tag{3.106}$$

We can assume that the dipoles are randomly distributed (by internal fields) such that we take the average of $\cos^2\theta$; we get $\overline{\cos^2\theta} = \frac{1}{3}$; we may take also the thermal average and get $\overline{\cos^2\theta} \simeq \frac{1}{3}$. Therefore, we have an induced dipole moment

$$d_v = -\frac{q^2 E}{3m}\frac{1}{\omega^2 - \omega_v^2} \tag{3.107}$$

and a molecular polarizability

$$\alpha_v = -\frac{q^2}{3m}\frac{1}{\omega^2 - \omega_v^2} \tag{3.108}$$

due to molecular vibrations; its static value is $q^2/3m\omega_v^2$.

The molecule rotates, together with its dipole. Leaving aside the azimuthal motion, under the action of an electric field the equation of motion for the angular moment is

$$ml^2\ddot{\theta} = -qlE\sin\theta \ , \tag{3.109}$$

where l is the length of the dipole moment. For constant fields, the molecule performs small oscillations about an equilibrium position (angle), with the frequency $\omega = \sqrt{qE/ml} = \sqrt{dE/ml^2}$; this is known as the Rabi frequency (it lies usually in the radio-frequency range). For a time-dependent field, equation (3.109) becomes a Hill (Mathieu) equation.

The Rabi frequencies may be given by a local field, which pins down the dipoles in various directions. An external electric field acts then, on the average, as an external force (torque) for the small oscillations of the angle θ in equation (3.109), independent of θ; we can have then a polarizability with a characteristic frequency (Rabi frequency).

Summarizing, we may have an atomic polarizability α_a, a molecular polarizability α_v, coming, for instance, from vibrations, another molecular polarizability of pinned molecules, a static orientational polarizability α_0 which depends on temperature, etc. The free or quasi-free charges in solids, liquids, etc, related to the chemical bonds, do contribute their own electronic polarizability (which, usually, does not depend on temperature); a similar situation occurs in plasmas, *e.g.* ionized gases.

3.10 Polarization of matter

With usual notations Maxwell's equations in vacuum read

$$\begin{gathered} div\mathbf{E} = 4\pi\rho_0 \ , \ div\mathbf{H} = 0 \ , \\ curl\mathbf{E} = -\tfrac{1}{c}\tfrac{\partial\mathbf{H}}{\partial t} \ , \ curl\mathbf{H} = \tfrac{1}{c}\tfrac{\partial\mathbf{E}}{\partial t} + \tfrac{4\pi}{c}\mathbf{j}_0 \ ; \end{gathered} \tag{3.110}$$

they lead to wave equations for the electromagnetic potentials Φ and $\mathbf{A}$ ($\mathbf{E}=-(1/c)\partial\mathbf{A}/\partial t-grad\Phi$, $\mathbf{H}=curl\mathbf{A}$ with Lorenz gauge $div\mathbf{A}+(1/c)\partial\Phi/\partial t=0$), whose solutions are given by Kirchhoff's formulae (only two equations are independent).

In matter, the magnetic field $\mathbf{H}$ is denoted by $\mathbf{B}$ and is called magnetic induction; it is also assumed that, in matter, there appears a polarization charge density $\rho_p=-div\mathbf{P}$ and a related current density $\mathbf{j}_p=\partial\mathbf{P}/\partial t$, where $\mathbf{P}$, which is a dipole moment of the unit volume, is called (electric) polarization; in addition, since the continuity equation $\partial\rho_0/\partial t+div\mathbf{j}_0=0$ ($\partial\rho_p/\partial t+div\mathbf{j}_p=0$) permits, it is assumed that a magnetization current $\mathbf{j}_m=c\cdot curl\mathbf{M}$ may occur in matter, where $\mathbf{M}$, which is a magnetic moment of the unit volume, is called magnetization ; indeed, we can check immediately

$$\frac{1}{2c}\int d\mathbf{r}\cdot\mathbf{r}\times\mathbf{j}_m=\int d\mathbf{r}\mathbf{M}\ . \tag{3.111}$$

Maxwell's equations become

$$\begin{gathered} div\mathbf{E}=4\pi\rho_0-4\pi div\mathbf{P}\ ,\ div\mathbf{B}=0\ , \\ curl\mathbf{E}=-\tfrac{1}{c}\tfrac{\partial\mathbf{B}}{\partial t}\ ,\ curl\mathbf{B}=\tfrac{1}{c}\tfrac{\partial\mathbf{E}}{\partial t}+ \\ +\tfrac{4\pi}{c}\mathbf{j}_0+\tfrac{4\pi}{c}\tfrac{\partial\mathbf{P}}{\partial t}+4\pi curl\mathbf{M}\ , \end{gathered} \tag{3.112}$$

or

$$\begin{gathered} div\mathbf{D}=4\pi\rho_0\ ,\ div\mathbf{B}=0\ , \\ curl\mathbf{E}=-\tfrac{1}{c}\tfrac{\partial\mathbf{B}}{\partial t}\ ,\ curl\mathbf{H}=\tfrac{1}{c}\tfrac{\partial\mathbf{D}}{\partial t}+\tfrac{4\pi}{c}\mathbf{j}_0\ , \end{gathered} \tag{3.113}$$

where $\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}$ is called the electric displacement and $\mathbf{H}=\mathbf{B}-4\pi\mathbf{M}$ is called magnetic field; here we have two independent equations ($\mathbf{E}=-(1/c)\partial\mathbf{A}/\partial t-grad\Phi$, $\mathbf{B}=curl\mathbf{A}$) and four unknowns ($\mathbf{E}$, $\mathbf{B}$, $\mathbf{D}$ and $\mathbf{H}$).

Under the action of an external electromagnetic field the elementary charges in matter acquire a displacement field $\mathbf{u}(\mathbf{r},t)$; it generates a polarization charge $\rho_p=-nqdiv\mathbf{u}$, where n is the concentration of elementary charges q, and a corresponding polarization current $\mathbf{j}_p=nq\dot{\mathbf{u}}$; obviously, $\mathbf{P}=nq\mathbf{u}$; in a generic model of homogeneous matter the displacement field obeys the equation of motion

$$m\ddot{\mathbf{u}}+m\omega_c^2\mathbf{u}+m\gamma\dot{\mathbf{u}}=q(\mathbf{E}_0+\mathbf{E}) \ , \tag{3.114}$$

where ω_c is a characteristic frequency associated with a restoring force, γ is a damping coefficient, $\mathbf{E}_0$ is the external field and $\mathbf{E}$ is the internal (polarization) field generated by the polarization charges and currents; $\mathbf{E}_t=\mathbf{E}_0+\mathbf{E}$ is the total electric field. The Lorentz force is omitted in equation (3.114) since the charge velocity in matter is usually much smaller than the speed of light. (An external magnetic field can be included in equation (3.114), leading to the Hall (galvanomagnetic) effect). Taking the Fourier transform of equation (3.114) we get

$$\begin{gathered}\mathbf{u}=-\tfrac{q}{m}\tfrac{\mathbf{E}_t}{\omega^2-\omega_c^2+i\omega\gamma} \ , \\ \mathbf{P}=nq\mathbf{u}=-\tfrac{\omega_p^2}{4\pi}\tfrac{\mathbf{E}_t}{\omega^2-\omega_c^2+i\omega\gamma} \ ,\end{gathered} \tag{3.115}$$

where $\omega_p=(4\pi nq^2/m)^{1/2}$ is called plasma frequency;

$$\chi_e=-\frac{\omega_p^2}{4\pi}\frac{1}{\omega^2-\omega_c^2+i\omega\gamma} \tag{3.116}$$

in $\mathbf{P}=\chi_e\mathbf{E}_t$ is called electric susceptibility; $\varepsilon=1+4\pi\chi_e$ in $\mathbf{D}=\varepsilon\mathbf{E}_t$ is called dielectric function; $\sigma=-i\omega\chi_e$ in $\mathbf{j}_p=-i\omega\mathbf{P}=-i\omega\chi_e\mathbf{E}_t=\sigma\mathbf{E}_t$ is called conductivity. It is easy to see that in the static limit ($\omega\rightarrow 0$) we have a conductivity for $\omega_c=0$; this case corresponds to conductors (free charges); $\omega_c\neq 0$ describes dielectrics (bound charges). This is the well-known Drude -Lorentz (plasma) model of polarizable matter.[5]

It is worth noting that equation of motion (3.114) supplies a third equation needed for solving Maxwell equations in matter. Indeed, in

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[5] P. Drude, "Zur Elektronentheorie der Metalle", Ann. Phys. **306** 566 (1900); P. Drude, "Zur Elektronentheorie der Metalle, 2. Teile. Galvanomagnetische und thermomagnetische Effecte", Ann. Phys. **308** 369-402 (1900); H. A. Lorentz, *The Theory of Electrons*, Teubner, Leipzig (1916). It seems that the equation of motion (3.114) which leads to the resonant dispersion equation (3.116) has been written for the first time by H. von Helmholtz, "Elektromagnetische Theorie der Farbenzerstreuung", Wied. Ann. **48** (Ann. Phys. **284**) 389 (1893) and E. Ketteler, "Notiz, betreffend die Moglichkeit einer zugleich den elastisch-optischen wie den elektromagnetischen Principien entsprechenden Dispersionsformel", Wied. Ann. **49** (Ann. Phys. **285**) 382 (1893).

the ideal case of quasi-static limit and infinite matter, the solution of equation $div\mathbf{E} = -4\pi div\mathbf{P}$ is $\mathbf{E} = -4\pi\mathbf{P}$ and, from $\mathbf{P} = \chi_e(\mathbf{E}_0 - 4\pi\mathbf{P})$ we get $\mathbf{P} = \alpha\mathbf{E}_0$, where $\alpha = \chi_e/(1 + 4\pi\chi_e)$ is called polarizability; for finite bodies in the quasi-static limit (wavelengths much longer than the dimensions of the bodies) we get $\mathbf{E} = -4\pi f\mathbf{P}$, where f is a numerical factor called (de-) polarizing factor; we get the polarizability

$$\alpha = \frac{\chi_e}{1 + 4\pi f\chi_e} = \frac{1}{4\pi} \cdot \frac{\varepsilon - 1}{f\varepsilon + 1 - f} \ ; \tag{3.117}$$

for a sphere[6] $f = 1/3$ and

$$\frac{4\pi\alpha}{3} = \frac{\varepsilon - 1}{\varepsilon + 2} \tag{3.118}$$

is known as the Lorentz-Lorenz[7] or Clausius-Mossotti equation.[8] In the quasi-static limit only the displacement field at the surface of the body is relevant. In general (leaving magnetization aside), we compute the electromagnetic potentials from Kirchhoff's formulae for the polarization charges and currents $\rho_p = -nqdiv\mathbf{u}$, $\mathbf{j}_p = nq\dot{\mathbf{u}}$, then compute the polarization field $\mathbf{E}$ and introduce it into the equation of motion (3.114); we get coupled (integral) equations for the components of $\mathbf{u}$, which, in principle, solve the problem (Maxwell equations in matter).

The displacement field $\mathbf{u}$ is sufficiently general to cover atomic, molecular, etc polarizabilities, as described previously; usually, the rotational motion of the dipoles leads to an eigenfrequency problem (Rabi frequencies), which does not contribute to polarizability. From equation (3.117) for a sphere we get

$$\chi_e = \frac{\alpha}{1 - \frac{4\pi}{3}\alpha} \ , \tag{3.119}$$

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[6] Similar factors occur in magnetostatics. For magnetized ellipsoids see, for instance, E. C. Stoner, "The demagnetizing factors for ellipsoids", Phil. Mag. **36** 803 (1945) and J. A. Osborne, "Demagnetizing factors for general ellipsoid", Phys. Rev. **67** 351 (1945).

[7] H. A. Lorentz, "Uber die Beziehung zwischen der Fortpflanzungsgeschwindigkeit des Lichtes und der Korperdichte", Ann. Physik **245** 641 (1880); L. Lorenz, "Uber die Refraktionsconstante", Ann. Physik **247** 70 (1880).

[8] R. Clausius, *Die mechanische Warmetheorie*, vol. 2, 2nd ed., Vieweg, Braunschweig (1879); O. F. Mossotti, Mem. Soc. Ital. Modena **14** 49 (1850); see also P. Debye, "Polar Molecules", Dover, NY (1929); A. von Hippel, "Dielectris and Waves", Artech House, Boston (1995).

and, for $\alpha = \alpha_0 + nd^2/3T$

$$\frac{4\pi}{3}\chi_e \simeq \frac{T_c}{T - T_c} \ , \tag{3.120}$$

where $T_c \simeq 4\pi nd^2/9$; α_0 ($\simeq 0$) is a polarizability independent of temperature (atomic, vibrational, etc) and $nd^2/3T$ is the orientational polarizability. Equation (3.120) is known as the Curie-Weiss law; here it indicates a "ferroelectric catastrophe", *i.e.* an unbounded increase of polarization for a certain critical temperature T_c, as if all the dipoles would align themselves along the same direction, similar with the magnetic moments in a ferromagnet. The critical temperature can be estimated as $T_c \simeq d^2/a^3 \simeq 10^3 K$, where typical values are $d = 10^{-18} esu$ and a is the mean separation distance of the dipoles. The corresponding electric field $d/a^3 \simeq 10^7 - 10^8 V/m$ is extremely high. Actually, the orientational polarizability $nd^2/3T$ leaves aside the internal (polarization) field (interaction between the dipoles); when this field is included, the ferroelectric catastrophe disappears (it is not α, but χ, which goes like $1/T$).

The electric susceptibility given by equation (3.116) can be generalized to

$$\chi_e = \chi_\infty + \frac{(\chi_s - \chi_\infty)(-\omega_c^2 + i\omega\gamma)}{\omega^2 - \omega_c^2 + i\omega\gamma} \ , \tag{3.121}$$

where χ_s is the static susceptibility ($\omega \rightarrow 0$) and χ_∞ is the high-frequency susceptibility ($\omega \rightarrow \infty$); both are phenomenological parameters. The damping coefficient γ may have a special role. If it is relevant, then we may neglect ω_c ($\omega_c = 0$) and write

$$\chi_e = \chi_\infty + \frac{\chi_s - \chi_\infty}{1 - i\omega\tau} \tag{3.122}$$

which is Debye's relaxation law (equation (3.104)) with $\tau = 1/\gamma$. The pole $\omega = 1/i\tau = -i\gamma$ indicates that the polarization decays like $\sim e^{-\gamma t}$, a law which can be obtained also from the equation of motion (3.114) $\ddot{u} + \gamma\dot{u} = 0$, which leads to $u \sim e^{-\gamma t}$. This is known as the Debye relaxation (saturation) law. An oscillating electric dipole emits electromagnetic radiation. The reaction field acts upon the dipole with a friction force (Lorentz damping), which results in the broadening of the spectral line (natural breadth). The motion of the molecules gives also a Doppler broadening, much larger than the natural breadth of the spectral line. The collisions between molecules and the corresponding mean free path and lifetime give also a line broadening, especially at low frequencies. The Debye relaxation contributes a distinct mechanism of broadening of the spectral line.

Finally, we note that for a permanent polarization (*i.e.* permanent dipoles) the density of the interaction energy is $\mathcal{E} = -\mathbf{P}\mathbf{E}_0$, while for an induced polarization the energy density is $\mathcal{E} = -(1/2)\alpha E_0^2$ (in general, $(-1/2)\alpha_{ij}E_{0i}E_{0j}$), where α is the polarizability (polarizability tensor α_{ij}); in general, $\delta\mathcal{E} = -\mathbf{E}_0\delta\mathbf{P}$. We must distinguish between the external energy $-\mathbf{E}_0\delta\mathbf{P}$ and the internal energy $\mathbf{E}\delta\mathbf{P}$, where the total electric field must be included. This later energy may give rise to a force density $-grad\mathcal{E}$, which is known as the ponderomotive force. Usually, this force is localized at the surface of the body (for conductors, for instance), and it gives rise to a pressure (an effect known as the electrostriction effect). The torque of the forces is defined as $\mathbf{K} = -\partial\mathcal{E}/\partial\overrightarrow{\alpha}$, where $\overrightarrow{\alpha}$ is the rotation angle; the change in the field is $\delta\mathbf{E} = \mathbf{E}\times\delta\overrightarrow{\alpha}$, so we have $\delta\mathcal{E} = (\partial\mathcal{E}/\partial\mathbf{E})(\mathbf{E}\times\delta\overrightarrow{\alpha})$, *i.e.* $\delta\mathcal{E} = -\mathbf{P}(\mathbf{E}\times\delta\overrightarrow{\alpha}) = -(\mathbf{P}\times\mathbf{E})\delta\overrightarrow{\alpha}$ and $\mathbf{K} = \mathbf{P}\times\mathbf{E}$. In general, from equations (3.112) we get the conservation of energy

$$\begin{gathered}\tfrac{1}{8\pi}\tfrac{\partial}{\partial t}(E^2+B^2) + \left[\mathbf{j}_0\mathbf{E} + \mathbf{E}\tfrac{\partial\mathbf{P}}{\partial t} + c\mathbf{E}curl\mathbf{M}\right] + \\ + \tfrac{c}{4\pi}div(\mathbf{E}\times\mathbf{B}) = 0\end{gathered} \tag{3.123}$$

and conservation of the momentum

$$\begin{gathered}\rho_0\mathbf{E} + \tfrac{1}{c}\mathbf{j}_0\times\mathbf{B} - \mathbf{E}div\mathbf{P} + \\ + \tfrac{1}{c}\tfrac{\partial\mathbf{P}}{\partial t}\times\mathbf{B} + curl\mathbf{M}\times\mathbf{B} = \\ = \tfrac{1}{4\pi}(\mathbf{E}div\mathbf{E} + \mathbf{B}div\mathbf{B} - \mathbf{E}\times curl\mathbf{E} - \\ -\mathbf{B}\times curl\mathbf{B}) - \tfrac{1}{4\pi c}\tfrac{\partial}{\partial t}(\mathbf{E}\times\mathbf{B})\ .\end{gathered} \tag{3.124}$$

The first term in equation (3.123) is the energy of the field, the second term, included in bracket, is the mechanical work done by field upon charges and currents (dissipated energy) and the third term is the radiated energy ($(c/4\pi)\mathbf{E}\times\mathbf{B}$ is the Poynting vector). It is worth noting that the energy of the field includes the internal (polarization) field, so the energy density of a polarizable (or polarized) body can be computed from $\delta\mathcal{E}=-(1/4\pi)\mathbf{E}\delta\mathbf{E}_i$, where $\mathbf{E}_i$ is the internal field ($\mathbf{E}$ in these equations is the total field, consisting of the external field $\mathbf{E}_0$ and the internal field $\mathbf{E}_i$); since $\delta\mathbf{E}_i=-4\pi\delta\mathbf{P}$ in the quasi-static limit, we get $\delta\mathcal{E}=\mathbf{E}\delta\mathbf{P}$. Here, it is important to include the surface contribution in the variation of the polarization. We can note the force $-\mathbf{E}div\mathbf{P}$ in equation (3.124) arising from the internal energy $-grad\mathcal{E}$. Similarly, from equation (3.123) we can see the energy $(1/4\pi)\mathbf{B}\delta\mathbf{B}_i=\mathbf{B}\delta\mathbf{M}$ of the magnetic field and, by conservation, $\delta\mathcal{E}=-\mathbf{B}\delta\mathbf{M}$ of a magnetized body in an external magnetic field (the magnetization implies $\mathbf{B}_i=4\pi\mathbf{M}$). A spatial variation of these energies (*e.g.* for an inhomogenous body) leads to a force, whose effect is usually sustained by elastic (or cohesion) forces (including electrostriction and magnetostriction effects).

In the *lhs* of equation (3.124) we have the Lorentz force, acting both on the external charges and currents (ρ_0 and $\mathbf{j}_0$) and on the polarization charges and currents ($\rho_p=-div\mathbf{P}$ and $\mathbf{j}_p=\partial\mathbf{P}/\partial t$) and magnetization currents ($\mathbf{j}_m=c\cdot curl\mathbf{M}$). The *rhs* of equation (3.124) contains the Maxwell stress $t_i=\partial_j\sigma_{ij}$, where

$$\sigma_{ij}=\frac{1}{4\pi}\left[E_iE_j+B_iB_j-\frac{1}{2}\delta_{ij}(E^2+B^2)\right] \tag{3.125}$$

and the variation in time of the electromagnetic momentum $\mathbf{g}=(1/4\pi c)\mathbf{E}\times\mathbf{B}$. These forces are in equilibrium, according to the principle of the action and reaction: the *lhs* of equation (3.124) contains forces by which the field acts upon charges and currents, while the *rhs* of equation (3.124) contains forces by which charges and currents act upon the field; and the reaction force of the field related to $\dot{\mathbf{g}}$. Therefore, the force acting upon matter is

$$\mathbf{f}=-\mathbf{E}div\mathbf{P}+\frac{1}{c}\frac{\partial\mathbf{P}}{\partial t}\times\mathbf{B}+curl\mathbf{M}\times\mathbf{B}\ , \tag{3.126}$$

where $\rho_0 = 0$, $\mathbf{j}_0 = 0$. Obviously, also we have

$$\begin{gathered}\mathbf{f} = \tfrac{1}{4\pi}(\mathbf{E}div\mathbf{E} + \mathbf{B}div\mathbf{B} - \mathbf{E} \times curl\mathbf{E} - \\ -\mathbf{B} \times curl\mathbf{B}) - \tfrac{1}{4\pi c}\tfrac{\partial}{\partial t}(\mathbf{E} \times \mathbf{B}) \ .\end{gathered} \tag{3.127}$$

It is worth noting that this force is different from the force given above; we note the torque

$$\int d\mathbf{r}\mathbf{r} \times (-\mathbf{E}div\mathbf{P}) = \int d\mathbf{r}\mathbf{P} \times \mathbf{E} \tag{3.128}$$

for a uniform $\mathbf{E}$. In general, the force acting upon polarized or magnetized matter includes the internal (interaction) forces, whose net effect is zero.

Bodies which possess a permanent polarization are called pyroelectric bodies (or electrets; the latter may include also bodies with a net charge). If the polarization gets singular near a critical temperature, the bodies are called ferroelectrics; if polarization appears through a mechanical stress and, conversely, a mechanical stress appears through an electric field (polarization), the bodies are called piezoelectrics. Similarly, there are piezomagnetic bodies and magnetoelectric bodies (where an electric field induces a magnetization and a magnetic field induces a polarization).

There exists a hybrid version of Maxwell's equations in matter, derived from equations (3.112) with $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$:

$$\begin{gathered} div\mathbf{E} = 4\pi\rho_0 - 4\pi div\mathbf{P} \ , \\ div\mathbf{H} = -4\pi div\mathbf{M} \ , \\ curl\mathbf{E} = -\tfrac{1}{c}\tfrac{\partial\mathbf{H}}{\partial t} - \tfrac{4\pi}{c}\tfrac{\partial\mathbf{M}}{\partial t} \ , \\ curl\mathbf{H} = \tfrac{1}{c}\tfrac{\partial\mathbf{E}}{\partial t} + \tfrac{4\pi}{c}\mathbf{j}_0 + \tfrac{4\pi}{c}\tfrac{\partial\mathbf{P}}{\partial t} \ ; \end{gathered} \tag{3.129}$$

it is worth noting that we have now a "magnetic charge" $\rho_m = -div\mathbf{M}$ and a "magnetic current" $\mathbf{j}_m = \frac{\partial M}{\partial t}$; the energy conservation reads

$$\begin{gathered}\tfrac{1}{8\pi}\tfrac{\partial}{\partial t}(E^2 + H^2) + \left[\mathbf{j}_0\mathbf{E} + \mathbf{E}\tfrac{\partial\mathbf{P}}{\partial t} + \mathbf{H}\tfrac{\partial\mathbf{M}}{\partial t}\right] + \\ + \tfrac{c}{4\pi}div(\mathbf{E} \times \mathbf{H}) = 0 \ ,\end{gathered} \tag{3.130}$$

where we can see both the "electric work" $\mathbf{E}\dot{\mathbf{P}}$ and "magnetic work" $\mathbf{H}\dot{\mathbf{M}}$ per unit time; in view of $\dot{\mathbf{M}} = \gamma\mathbf{M} \times \mathbf{B} = \gamma\mathbf{M} \times \mathbf{H}$, we can see that $\mathbf{H}\dot{\mathbf{M}} = 0$. The conservation of momentum gives

$$\begin{aligned} \rho_0\mathbf{E} + \tfrac{1}{c}\mathbf{j}_0 \times \mathbf{H} - \mathbf{E}div\mathbf{P} - \mathbf{H}div\mathbf{M} + \\ + \tfrac{1}{c}\tfrac{\partial\mathbf{P}}{\partial t} \times \mathbf{H} - \tfrac{1}{c}\tfrac{\partial\mathbf{M}}{\partial t} \times \mathbf{E} = \\ = \tfrac{1}{4\pi}(\mathbf{E}div\mathbf{E} + \mathbf{H}div\mathbf{H} - \\ -\mathbf{E} \times curl\mathbf{E} - \mathbf{H} \times curl\mathbf{H}) - \tfrac{1}{4\pi c}\tfrac{\partial}{\partial t}(\mathbf{E} \times \mathbf{H}) \ . \end{aligned} \tag{3.131}$$

We can see the internal energy $\mathbf{E}\delta\mathbf{P}$ and the force $-\mathbf{E}div\mathbf{P}$, as well as the part $\mathbf{H}\delta\mathbf{M}$ of the internal energy in the external field $\mathbf{H}$ and the corresponding force $-\mathbf{H}div\mathbf{M}$.

3.11 A fourth kind of polarization

Gases may get ionized and conduct electric current under the action of an electric field; they usually build a space charge, as in plasma. Such space charges are usual at the interface of two semiconductors. In liquids and solids there are defects: some atoms, molecules are missing (Schottky defects[9]), some others are displaced (Frenkel defects[10]); in electrolytes or ionic crystals such defects favour the migration of ionic charges and building-up of spatial charges. The conduction associated with such charges is very low, they are either quasi-free or may get bound, or quasi-bound, especially at interfaces. The after-effect, known also as the Maxwell-Wagner-Sillars effect,[11] in dielectrics is well known: after an initial discharge, the dielectric exhibits a weak

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[9] C. Wagner and W. Schottky, "Theorie der geordneten Mischphasen", Z. physik. Chemie **B11** 163 (1930).

[10] J. Frenkel, "Uber die Warmebewegung in festen und flussigen Korpern", Z. Phys. **35** 652 (1926); J. Frenkel, *Kinetic Theory of Liquids*, Dover, NY (1946).

[11] J. C. Maxwell, *Lehrbuch der Elektrizitat und der Magnetismus*, vol. 1, Art. 328-330, Berlin (1983); K. W. Wagner, "Erklarung der dielektrischen Nachwirkungsvorgange auf Grund Maxwellscher Vorstellungen", Electr. Eng. (Archiv fur Elektrotechnik) **2** 371 (1914); K. W. Wagner, *Die Isolierstoffe der Elektrotechnik*, H. Schering ed., Springer, Berlin (1924); R. W. Sillars, "The properties of a dielectric containing semiconducting particles of various

current which may last for months. The space charges and interfacial charges may give rise to a fourth kind of polarization. Some dielectrics, like the electrets, may retain a metastable polarization (*e.g.*, for years), some dielectrics may sustain an induced polarization due to the space and interfacial charges. Granular materials may exhibit such a polarization, usually with low characteristic frequencies (in the radio-frequency range).

3.12 Polarized sphere

We consider a (homogeneous) sphere of radius R subjected to a quasi-static electric field $\mathbf{E}_0$ directed along the z-axis. The field induces a displacement $\mathbf{u}$, which gives rise to a polarization $nq\mathbf{u}$, where n is the density of charges q. The polarization can be written as $\mathbf{P} = nq\mathbf{u}\theta(R-r)$, or $P = P_z = nqu\theta(R-r)$, where θ is the step function. The induced charge density is $\rho = -div\mathbf{P} = -div(nq\mathbf{u})\theta(R-r) + nqu\frac{z}{r}\delta(R-r)$. In the quasi-static limit the volume term $\sim \theta(R-r)$ may be neglected; we are left with a surface charge density $\sim \delta(R-r)$ and we have to solve Gauss's equation

$$div\mathbf{E} = 4\pi nqu\frac{z}{r}\delta(R-r) \ . \tag{3.132}$$

The polarization nqu is proportional to the external field, $nqu = \alpha E_0$, where α is the polarizability; introducing the potential Φ through $\mathbf{E} = -grad\Phi$, we have to solve Poisson's equation

$$\Delta\Phi = -4\pi\alpha E_0\frac{z}{r}\delta(R-r) \ , \tag{3.133}$$

whose solution is given by Kirchhoff' s formula

$$\Phi(\mathbf{r}) = \int d\mathbf{r}' \frac{\cos\theta' \delta(R-r')}{|\mathbf{r}-\mathbf{r}'|} \ . \tag{3.134}$$

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shapes", J. Inst. Electr. Engrs. (London) **80** 378 (1937); see also A. von Hippel, *Dielectrics and Waves*, Wiley, NY (1954) and D. E. Aspnes, Am. J. Phys. **50** 704 (1982).

Now we use the decomposition in spherical harmonics

$$\begin{gathered}\frac{1}{\left|\mathbf{r}-\mathbf{r}'\right|}=\sum_{l=0}\frac{r_<^l}{r_>^{l+1}}P_l(\cos\Theta)\ ,\\ P_l(\cos\Theta)=\frac{4\pi}{2l+1}\sum_{m=-l}^{m=l}Y_{lm}(\theta,\varphi)Y_{lm}^*(\theta',\varphi')\ ,\end{gathered}\tag{3.135}$$

where P_l is the Legendre polynomial and Θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$ $(\cos\Theta=\sin\theta\sin\theta'\cos(\varphi-\varphi')+\cos\theta\cos\theta')$. Making use of $Y_{10}=i\sqrt{\frac{3}{4\pi}}\cos\theta$ and the orthogonality of the spherical harmonics we get

$$\Phi=\frac{4\pi}{3}\alpha E_0\begin{cases}r\cos\theta\ ,\ r<R\ ,\\ \frac{R^3}{r^2}\cos\theta\ ,\ r>R\ .\end{cases}\tag{3.136}$$

We can see that the electric field is uniform inside the sphere and is a dipolar field outside the sphere. We get $E=-\frac{4\pi}{3}\alpha E_0$ inside, and we can see the (de-) polarizing factor $f=1/3$. From $P=\alpha E_0=\chi(E+E_0)=\chi(-\frac{4\pi}{3}\alpha+1)E_0$, we get the Clausius-Mossotti equation

$$\alpha=\frac{3}{4\pi}\frac{\varepsilon-1}{\varepsilon+2}\ .\tag{3.137}$$

3.13 Magnetization in Matter

It would be desirable to have an equation for the magnetization $\mathbf{M}$, such that to get four equations for the four unknowns of the Maxwell's equations in matter. An immediate suggestion is the Larmor equation

$$\frac{\partial\mathbf{M}}{\partial t}=\gamma\mathbf{M}\times\mathbf{B}\ ,\tag{3.138}$$

where γ is a gyromagnetic factor; for elementary charges in matter $\gamma=q/2mc$; for atomic, molecular or nuclear magnetic moments the magnetic moment is proportional to an angular momentum, and, from the interaction energy $-\mathbf{MB}$ and the commutation relations of the angular momentum we get a Larmor equation (3.138). It is assumed that such an equation holds also for the magnetizaton in matter, and in general, the magnetization is proportional to the magnetic field, $\mathbf{M}=\chi_m\mathbf{H}$; χ_m is called magnetic susceptibility. In general, such a relationship is obtained by estimating the energy $\delta\mathcal{E} = -\mathbf{M}\delta\mathbf{B}$ and by using $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$; it follows $\mathbf{B} = \mu\mathbf{H}$, where $\mu = 1 + 4\pi\chi_m$ is called the magnetic permeability (of course, if necessary, the anisotropy is introduced, and we have then a tensor of magnetic susceptibility and permeability). In general, there is a diamagnetic magnetization which opposes an external magnetic field, an alignment of magnetic moments which gives a paramagnetism, a spin magnetization of the electrons (Zeeman splitting) called Pauli paramagnetism, an orbital diamagnetism of the electrons called Landau diamagnetism, etc; all of these effects are very small, so, in fact, we may neglect this magnetization. There is one exception, that of ferromagnetic bodies (and those related to ferromagnetism), where the magnetizaton is high.

In general, the Larmor equation leads to an eigenvalue problem, which does not give a magnetization; it gives the motion of the magnetization as, for instance, in the motion of the ferromagnetic magnetization (ferromagnetic resonance, spin waves); a similar motion may also appear in paramagnetic bodies, under special circumstances. The magnetization, at least the static magnetization, is obtained by estimating the interaction energy of the motion of the charges with an external magnetic field (magnetic induction) as in the cases mentioned above (and described below). It is worth noting that the presence of a local angular velocity $\overrightarrow{\Omega}$ in matter (vortex) leads to a displacement field $\mathbf{u}$ which obeys the laws of motion in a rotating frame (including Coriolis and centrifugal forces) and, through $\rho_p = -nqdiv\mathbf{u}$ and $\mathbf{j_p} = nq\dot{\mathbf{u}}$, to a local magnetic field which is the magnetization; now, a local angular velocity can be related to an external magnetic field through Larmor's theorem, so we have access to a magnetic susceptibility of an induced magnetization (diamagnetism). Such a point can be included more generally into a non-inertial electromagnetism (rotation can induce a magnetization and a magnetic field can induce a rotation; these are known as gyromagnetic effects or Einstein-de Haas and Barnett effects).

3.14 Diamagnetism

Making use of $curl\mathbf{E} = -(1/c)(\partial\mathbf{H}/\partial t)$, we can see that a point charge q moving in a circular orbit of radius r in an uniform magnetic field H experiences an electric field given by $2\pi rE = -(\pi r^2/c)(dH/dt)$ and a torque $qEr = -(qr^2/2c)(dH/dt)$; the latter changes the orbital angular momentum by $\Delta L = -(qr^2/2c)H$; therefore, we get an induced magnetic moment $\mu = (q^2r^2/4mc^2)H$. This is the diamagnetic moment. It is convenient to use the average of $r^2 = x^2 + y^2$ (*i.e.* the projection along the axis of the magnetic field), which is $2a^2/3$, where a^2 is the average of the square radius of the orbit; we get the diamagnetic susceptibility $\chi = -q^2a^2/6mc^2$ $(\mu = \chi H)$.

The rotation of a charge q with Larmor's frequency $\omega = \frac{|q|H}{2mc}$ $(\nu = \frac{|q|H}{4\pi mc})$ gives rise to a current $I = q\nu = \frac{q|q|H}{4\pi mc}$ and a magnetic moment $\mu = \frac{1}{c}I \cdot \pi r^2 = \frac{q|q|H}{4mc^2}r^2$ (or $\frac{q}{2c}\omega r^2$); for electrons, we get the diamagnetic susceptibility $\chi = -\frac{e^2a^2}{6mc^2}$. This is known as Langevin's diamagnetism. The diamagnetism arises from the change in the orbital moment induced by an applied magnetic field.

Let us assume that a uniform external magnetic field is applied; the magnetic induction $\mathbf{B}$ comes from a vector potential

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r} \ . \tag{3.139}$$

The energy of a charge q with mass m is

$$\begin{aligned} E &= \tfrac{1}{2m}p^2 - \tfrac{q}{mc}\mathbf{pA} + \tfrac{q^2}{2mc^2}A^2 = \\ &= \tfrac{1}{2m}p^2 - \tfrac{q}{2mc}\mathbf{B}(\mathbf{r}\times\mathbf{p}) + \tfrac{q^2}{2mc^2}A^2 \ , \end{aligned} \tag{3.140}$$

which indicates that there appears an intrinsic (or orbital) magnetic moment

$$\overrightarrow{\mu_i} = \frac{q}{2mc}(\mathbf{r}\times\mathbf{p}) = \frac{q}{2c}(\mathbf{r}\times\mathbf{v}) + \frac{q^2}{4mc^2}[\mathbf{r}\times(\mathbf{B}\times\mathbf{r})] \ , \tag{3.141}$$

proportional to the angular momentum. It differs from the magnetic moment

$$\overrightarrow{\mu} = \frac{q}{2c}(\mathbf{r}\times\mathbf{v}) = \overrightarrow{\mu_i} - \frac{q^2}{4mc^2}[\mathbf{r}\times(\mathbf{B}\times\mathbf{r})] \tag{3.142}$$

by a quantity induced by the external field. The variation of the energy is

$$\begin{aligned}\delta E = -\tfrac{q}{2mc}(\mathbf{r}\times\mathbf{p})\delta\mathbf{B} + \tfrac{q^2}{2mc^2}\mathbf{A}(\delta\mathbf{B}\times\mathbf{r}) = \\ = -\tfrac{q}{2mc}(\mathbf{r}\times\mathbf{v})\delta\mathbf{B} = -\vec{\mu}\,\delta\mathbf{B}\ .\end{aligned} \tag{3.143}$$

Let $\vec{\mu_i} = 0$, as for a vanishing angular momentum (for several charges the ratio q/m should be the same). We are left with the induced term, whose average can be written as

$$\begin{aligned}\overline{\vec{\mu}} = -\tfrac{q^2}{4mc^2}\overline{[\mathbf{r}\times(\mathbf{B}\times\mathbf{r})]} = \\ = -\tfrac{q^2}{4mc^2}[\overline{r^2}\mathbf{B} - \overline{\mathbf{r}(\mathbf{rB})}] = -\tfrac{q^2}{6mc^2}\overline{r^2}\mathbf{B}\ .\end{aligned} \tag{3.144}$$

It follows that the induced magnetic moment opposes the (external) magnetic field. This magnetism is called diamagnetism; its opposition in sign to the external field is known as Lenz's law.

The magnetic moment of the unit volume is called magnetization. From equation (3.144) the magnetization is given by

$$\mathbf{M} = \overline{\vec{\mu}}/v = -\frac{nq^2}{6mc^2}\overline{r^2}\mathbf{B} = -\frac{nq^2}{6mc^2}\overline{r^2}(\mathbf{H}+4\pi\mathbf{M})\ , \tag{3.145}$$

where n is the density of particles (of volume v); which leads to

$$\mathbf{M} = -\frac{nq^2\overline{r^2}/6mc^2}{1+2\pi nq^2\overline{r^2}/3mc^2}\mathbf{H} \simeq -\frac{nq^2\overline{r^2}}{6mc^2}\mathbf{H} \tag{3.146}$$

and to the diamagnetic susceptibiliy ($\mathbf{M} = \chi\mathbf{H}$)

$$\chi = -\frac{nq^2\overline{r^2}}{6mc^2} \tag{3.147}$$

(and $\mathbf{M} = \chi\mathbf{B}$); its ratio to density is independent of temperature; by definition ($\mathbf{B} = \mu\mathbf{H}$) the magnetic permeability is given by

$$\mu = 1 + 4\pi\chi = \frac{1}{1+2\pi nq^2\overline{r^2}/3mc^2} \simeq 1 - \frac{2\pi nq^2\overline{r^2}}{36mc^2} < 1\ . \tag{3.148}$$

The highest diamagnetic susceptibility belongs to bismuth, $\chi = -1.3 \times 10^{-6}$ (and decreases with rising temperature, due to quantum effects). The diamagnetism is a small effect. From $\delta E = -\overrightarrow{\mu}\delta\mathbf{B} = -\mathbf{M}\delta\mathbf{B}/n$ and $E = -\chi B^2/2n$ we can see that the diamagnetic bodies ($\chi < 0$) are repelled by regions where the magnetic field is higher. The magnetic permeability $\mu = 1+4\pi\chi$ is smaller than unity for diamagnetic bodies. In this respect, the diamagnetic bodies resemble the dielectrics, since $H = B/\mu > B$ like $D = \varepsilon E > E$. It is worth noting that the ratio of the diamagnetic susceptibility to static electric susceptibility is

$$\chi/\chi_e \simeq \frac{nq^2\overline{r^2}}{mc^2} / \frac{nq^2}{m\omega_c^2} = \frac{\overline{r^2}\omega_c^2}{c^2} = \frac{\overline{v^2}}{c^2} \ , \tag{3.149}$$

where ω_c is the characteristic frequency of the electric polarization (equation (3.116)) and v is of the order of the particle velocity; we can see that diamagnetism is a relativistic effect.

3.15 Paramagnetism

In general, atoms with an odd number of electrons in the outer (open) shells have a magnetic moment. Usually, these electrons pair up their spins in molecules, so the molecules do not have permanent magnetic moments arising from electronic spin. In their ground state, the orbital electronic momentum is zero, the orbital motion of the ions gives a vanishing magnetic moment; the origin of molecular magnetic moments resides in nuclear spins. Let us suppose that there is a non-vanishing intrinsic magnetic moment $\overrightarrow{\mu_0}$, with an energy $-\overrightarrow{\mu_0}\mathbf{B}$. By analogy with the permanent electric dipoles, its mean value at temeprature $T = 1/\beta$ is (see equation (3.102))

$$\overline{\overrightarrow{\mu_0}} = \frac{1}{3}\beta\mu_0^2\mathbf{B} \ , \tag{3.150}$$

giving rise to a magnetization

$$\mathbf{M} = \frac{1}{3}\beta n\mu_0^2\mathbf{B} \ , \tag{3.151}$$

where n is the density of magnetic moments; a magnetic susceptibility

$$\chi = \frac{\beta n\mu_0^2/3}{1 - 4\pi\beta n\mu_0^2/3} \simeq \frac{1}{3}\beta n\mu_0^2 > 0 \tag{3.152}$$

and a magnetic permeability

$$\mu = 1 + 4\pi\chi = \frac{1}{1 - 4\pi\beta n\mu_0^2/3} \simeq 1 + \frac{4\pi}{3}\beta n\mu_0^2 > 1 \ . \tag{3.153}$$

This is paramagnetism, the magnetization is parallel with the external magnetic field. Since $\mu_0/d \simeq v/c \simeq 10^{-2} - 10^{-3}$, where d is an electric dipole and v denotes a particle velocity, we can see that one needs magnetic fields of the order $10^6 Gs = 100Ts$ to get the paramagnetic susceptibility unity at usual temperatures; *i.e.*, the paramagnetic susceptibility is typically small. The ratio of paramagnetic susceptibility to diamagnetic susceptibility is

$$\chi_p/\chi_d = \frac{mv^2}{T} \ ; \tag{3.154}$$

the energies of the atomic charges are of the order $10eV$ ($1eV = 1.6 \times 10^{-19}J = 1.1 \times 10^4 K$); at room temperature $mv^2/T \simeq 100$, which is a pretty good estimate (the liquid oxygen has a paramagnetic susceptibility $\chi = 3 \times 10^{-4}$). The paramagnetism is typically a small effect. The $1/T$-law of paramagnetic susceptibility is known as Curie's law.[12] A relaxation Debye law can also be written for the paramagnetic magnetization.

Aligned magnetic moments in a magnetic field have a low entropy, so a decrease of the magnetic field increases the entropy and lowers the temperature; the disorder of the magnetic moments implies a work done against the magnetic field, which is done at the cost of the thermal motion of the substance; the isolated substance gets cool by adiabatic demagnetization.

3.16 Molecular paramagnetism

Paramagnetism arises from spins and orbital moments. Atoms with closed shells have zero total spin and zero total orbital moment, consequently they have not a permanent magnetic moment; a similar

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[12] P. Curie, "Lois experimentales du magnetisme. Proprietes magnetiques des corps a diverses temperatures", Ann. Chim. Phys. **5** 289 (1895).

situation is encountered in the ground-state of the molecules. Diamagnetism can, however, be induced in these cases; collisions in condensed matter do not affect, usually, the diamagnetism, which is a quasi-classical motion. An instance of strong diamagnetism is the superconductors. The angular moment L and one of its components, say L_z, are conserved in central fields; but L_z is not anymore in lower-symmetry fields, as the crystal field in solids; the orbital moment is quenched in this case.

By analogy with the electric (dipole) moment, a molecule placed in a magnetic field H has its ground-state φ_0 and one excited state φ_e perturbed; these states become

$$\varphi_0^{'} = \varphi_0 + \frac{H}{\Delta}(m_z)_{e0}\varphi_e \ , \ \varphi_e^{'} = \varphi_e - \frac{H}{\Delta}(m_z)_{0e}\varphi_0 \ , \tag{3.155}$$

where Δ is the energy separation between the two states and m_z is the component of the magnetic moment along the z-direction of the field; we may include all the states connected by the matrix elements of the m_z. The mean value of the magnetic moment is

$$(m_z)_{00} = \frac{2H}{\Delta}\left|(m_z)_{e0}\right|^2 \ , \ (m_z)_{ee} = -\frac{2H}{\Delta}\left|(m_z)_{0e}\right|^2 \ . \tag{3.156}$$

The thermal ratio of the populations of the two states is $n_0/n_e = e^{\beta\Delta}$, $\beta = 1/T$, T being the temperature; the average magnetization is

$$M = \frac{2nH}{\Delta}\left|(m_z)_{e0}\right|^2 \frac{1 - e^{-\beta\Delta}}{1 + e^{\beta\Delta}} \ , \tag{3.157}$$

where n is the concentration of moments; for high temperatures $\beta\Delta \ll 1$ we get a Curie-type law

$$M = \frac{nH}{T}\left|(m_z)_{e0}\right|^2 \ ; \tag{3.158}$$

for lower temperatures $\beta\Delta \gg 1$ we get a temperature-independent magnetization

$$M = \frac{2nH}{\Delta}\left|(m_z)_{e0}\right|^2 \ ; \tag{3.159}$$

this is known as the van Vleck magnetization (susceptibility).

3.17 Magnetism in metals

Quasi-free electrons in metals behave as a Fermi liquid, subjected to the Fermi statistics. The Fermi surface is only sligthly blurred by a temperature which is small in comparison with the Fermi energy (chemical potential) $\varepsilon = \hbar^2 k_F^2/2m$, where k_F is the Fermi wavevector. The number of electrons is

$$N = 2\frac{V}{(2\pi)^3}\int d\mathbf{k} = \frac{V}{3\pi^2}k_F^3 \tag{3.160}$$

and the total energy per spin is

$$E_0 = \frac{V}{(2\pi)^3}\int d\mathbf{k}\frac{\hbar^2 k^2}{2m} = \frac{V}{10\pi^2}\frac{\hbar^2 k_F^5}{2m} = \frac{3}{10}N\varepsilon_F \ , \tag{3.161}$$

where V is the volume. In the presence of a magnetic field H the energy for spin down is

$$E_0(1+p)^{5/3} - \frac{1}{2}N\mu_B H(1+p) \tag{3.162}$$

and the energy of the spin up is

$$E_0(1-p)^{5/3} + \frac{1}{2}N\mu_B H(1-p) \ , \tag{3.163}$$

where p is the fraction of electrons whose spin is reversed by the magnetic field and μ_B is Bohr's magneton. The total energy given by equations (3.162) and (3.163) has a minimum $2E_0 - 3N\mu_B^2 H^2/4\varepsilon_F$ for $p = 3\mu_B H/10\varepsilon_F$; the magnetization is

$$M = \mu_B p N = \frac{3N\mu_B H}{2\varepsilon_F} \ ; \tag{3.164}$$

this is known as the Pauli magnetization (susceptibility).[13]

The orbital diamagnetism for the Fermi liquid is known as the Landau diamagnetism;[14] it is 1/3 of Pauli paramagnetism; therefore, the total magnetization in metals is $N\mu_B H/\varepsilon_F$. This result is usually affected by the diamagnetism of the ionic cores, band effects and electron interaction.

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[13] W. Pauli, "Uber Gasentartung und Paramagnetismus", Z. Phys. **41** 81 (1927).

[14] L. Landau, "Diamagnetismus der Metalle", Z. Phys. **64** 629 (1930).

3.18 Ferromagnetism

Let us assume that $\mathbf{B}=\mathbf{H}+4\pi\mathbf{M}$ is replaced by

$$\mathbf{B}=\mathbf{H}+\lambda\mathbf{M} \ , \tag{3.165}$$

where λ is a constant. This is known as Weiss's hypothesis of molecular (internal) field. [15] The energy of the intrinsic magnetic moment is $-\overrightarrow{\mu_0}\mathbf{B}$; we assume two orientations of $\overrightarrow{\mu_0}$, parallel and antiparallel with $\mathbf{B}$ (in accordance to a one-half quantum spin). The mean value of the moment is

$$\overline{\overrightarrow{\mu_0}}=\mu_0\frac{e^{\beta\mu_0 B}-e^{-\beta\mu_0 B}}{e^{\beta\mu_0 B}+e^{-\beta\mu_0 B}}=\mu_0\tanh\beta\mu_0 B \ , \tag{3.166}$$

where $\beta=1/T$ is the inverse of the temperature T. The magnetization is given by

$$M=n\overline{\overrightarrow{\mu_0}}=n\mu_0\tanh\beta\mu_0 B=n\mu_0\tanh\beta\mu_0(H+\lambda M) \ , \tag{3.167}$$

where n is the density of moments. For $H=0$, this equation can be rewritten as

$$\frac{M}{n\mu_0}=\tanh\left(\frac{T_c}{T}\frac{M}{n\mu_0}\right) \ , \tag{3.168}$$

where $T_c=n\mu_0^2\lambda$. (The Boltzmann distribution gives $\frac{x}{x^2+T/T_c}=\tanh(T_c x/T)$ instead of equation (3.168), where $x=M/n\mu_0$; the discussion does not change qualitatively). We can see that there exists a critical temperature below which the body exhibits a spontaneous magnetization (less than $n\mu_0$). This critical temperature is called the Curie temperature; it is of the order of 10^3K; for $T\ll T_c$, all the moments are practically lined up, as in a permanent magnet. Above the critical temperature a magnetic field is required to produce magnetization. For $T\gg T_c$ we have approximately

$$\frac{M}{n\mu_0}=\frac{\mu_0 H}{T}+\frac{T_c}{T}\frac{M}{n\mu_0} \ , \tag{3.169}$$

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[15] P. Weiss, "La variation du ferromagnetisme avec la temperature", Compt. Rend. **143** 1136 (1906); P. Weiss, "L'hypothese du champ moleculaire et la propriete ferromagnetique", J. Physique **6** 661 (1907).

or

$$M = \frac{n\mu_0^2}{T - T_c} H = \frac{1}{\lambda} \frac{T_c}{T - T_c} H \ , \tag{3.170}$$

a result valid for

$$\frac{\mu_0 H}{T - T_c} \ll 1 \ ; \tag{3.171}$$

this is called the Curie-Weiss law.

It is worth estimating the parameter λ, using $\mu_0 \simeq qrv/c$:

$$T_c = n\mu_0^2\lambda = n\frac{q^2r^2v^2}{c^2}\lambda = (nr^3)\frac{q^2}{r}\frac{v^2}{c^2}\lambda \ ; \tag{3.172}$$

at the atomic scale $nr^3 \simeq 1/10$, $q^2/r \simeq 1eV = 10^4K$; with $T_c = 10^3K$ we get $\lambda = c^2/v^2 \ (10^4 - 10^6)$; which shows that ferromagnetism is an electric, not magnetic, effect. The quantum exchange forces introduced by Heisenberg to explain λ may indicate the same conclusion, although the sign of the coupling λ is usually wrong.

The exchange interaction of the conduction electrons may lead to an increase of the paramagnetism and even to ferromagnetism; this is known as Stoner (or band) ferromagnetism.[16] Localized magnetic moments and narrow d- and f-bands are described by what is known as Anderson's hamiltonian.[17]

The magnetic moments are aligned in ferromagnetics, usually in domains, more or less randomly oriented. Domain order is a frequent occurrence in condensed matter. Two sub-lattices with magnetic moments ordered in opposite directions give antiferromagnetics, with total moment saturated to zero (antiferromagnets) or to a non-zero value (ferrites); various other ordering of the magnetic moments may appear in condensed matter; the Curie temperature is negative in antiferromagnetics.

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[16] E. C. Stoner, "Collective electron ferromagnetism", Proc. Roy. Soc. London **A165** 372 (1938).

[17] P. W. Anderson, "Localized magnetic states in metals", Phys. Rev. **124** 41 (1961).

4 Classical Limit

4.1 Electromagnetic field

As it is well known, the electromagnetic field is emitted and absorbed by quantum transitions (jumps) in matter. Motion in matter is mainly non-relativistic (or quasi non-relativistic). The relativistic energy $E = \sqrt{m^2c^4 + c^2p^2}$ of a charge q with mass m and momentum $\mathbf{p}$ becomes

$$\frac{1}{2m}\left(mc + \frac{E - q\Phi}{c}\right)^2 - \frac{1}{2}mc^2 = \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}\right)^2 \qquad (4.1)$$

in the presence of an electromagnetic field with potentials Φ and $\mathbf{A}$ (energy measured from mc^2). The leading non-relativistic approximation gives

$$E \simeq \frac{1}{2m}p^2 - \frac{q}{mc}\mathbf{pA} + q\Phi \ , \qquad (4.2)$$

where the momentum $\mathbf{p} = m\mathbf{v} + \frac{q}{c}\mathbf{A}$ includes the electromagnetic contribution $q\mathbf{A}/c$ besides the mechanical momentum $\mathbf{p} = m\mathbf{v}$, $\mathbf{v}$ being the particle velocity. We get

$$E \simeq \frac{1}{2m}p^2 - \frac{1}{c}\mathbf{JA} + q\Phi \ , \qquad (4.3)$$

where $\mathbf{J} = q\mathbf{v}$ is the electric current. E in equation (4.3) can be viewed as a hamiltonian H, equation (4.3) can be written for many particles, an external potential or an interaction between particles can be added, a particle hamiltonian H_0 can be formed, the scalar potential can be included in the particle hamiltonian and $-\frac{1}{c}\mathbf{JA}$ in

$$H = H_0 - \frac{1}{c}\mathbf{JA} \qquad (4.4)$$

can be viewed as a perturbation; for many charges it includes a summation over all charges, $-\frac{1}{c}\sum\mathbf{JA}$.

In relativistic theories the electromagnetic potential is a four-vector written in the second quantization (with creation and annihilation operators), the current density is also a four-vector written with the particle field density of the form $\overline{\psi}\psi$ and the interaction has exactly the linear form given by equation (4.4). However, the current includes now the spin current too, which in the (quasi) non-relativistic limit either is preserved as a current or it is transformed to lead to an interaction $-\overrightarrow{\mu}\mathbf{H}$, where $\mathbf{H}$ is the magnetic field and $\overrightarrow{\mu}$ is the magnetic moment of the particle; including this interaction in Schrodinger's equation leads to Pauli's equation. In addition, for a purely radiation field, the interaction term in equation (4.4) can be transformed in the action function through

$$-\frac{1}{c}\mathbf{JA} = -\frac{q}{c}\mathbf{vA} \to \frac{q}{c}\mathbf{r}\frac{\partial \mathbf{A}}{\partial t} = -\mathbf{dE} \ , \tag{4.5}$$

where $\mathbf{d}$ is the dipole moment and $\mathbf{E}$ is the electric field; this is known as the dipolar interaction. A similar interaction can also arise from the scalar potential; it is particularly relevant if permanent dipoles exist in matter.

In the next-order approximation we get from equation (4.1) another interaction, given by $\frac{q^2}{2mc^2}A^2$, which should be combined with $-\frac{q^2}{mc^2}A^2$ from $-\frac{q}{mc}\mathbf{pA}$; it can be viewed as corresponding to a diamagnetic current. We can write in general

$$H \simeq H_0 - \frac{1}{c}\sum \mathbf{JA} - \sum \mathbf{dE} - \sum \overrightarrow{\mu}\mathbf{H} - \sum \frac{q^2}{2mc^2}A^2 \ , \tag{4.6}$$

where various terms are included according to the specific characteristics of the problem.

As it is well known, the quantum transitions in matter involve emission and absorption of photons, which are quanta of electromagnetic field. The quantum states of the electromagnetic field, in particular the radiation field, are defined by the number of photons with monochromatic frequencies, the photons being harmonic oscillators. A similar representation holds also for a general electromagnetic field. The matrix elements of the electromagnetic potential $\mathbf{A}$, as well as the fields $\mathbf{E}$ and $\mathbf{H}$, are only non-vanishing between states n and $n \pm 1$, where n is the photon numbers in a state with a given frequency; they are proportional to $\sqrt{n}$, $\sqrt{n \pm 1}$. In general, with usual notations, a wavefunction can be written as $\psi = \sum a_n \varphi_n e^{-\frac{i}{\hbar} E_n t}$, and the mean value of an operator f reads

$$\begin{aligned} \overline{f} &= \sum\nolimits_{nm} a_n^* a_m f_{nm} e^{\frac{i}{\hbar}(E_n - E_m)t} = \\ &= \sum\nolimits_{ns} a_n^* a_{n+s} f_{n,n+s} e^{\frac{i}{\hbar}(E_n - E_{n+s})t} \ ; \end{aligned} \tag{4.7}$$

for photons $E_n = \hbar\omega(n + \frac{1}{2})$ and $s = \pm 1$. In usual experiments we have many atomic constituents, each emitting a photon with the same frequency ω, so that we get a quantum state of the electromagnetic field with a very large value of n. In fact, we have such a state only if we wait a sufficiently long time. For shorter times we have a superposition of such states, corresponding to a variation of the quantum number n between $n_0 - \Delta n$ and $n_0 + \Delta n$, usually with $1 \ll \Delta n \ll n_0$; we may assume that the coefficients a_n and the wavefunctions φ_n depend weakly on n in this Δn-range, and the coefficients a_n are vanishing outside this range of n-values. The corresponding wavefunction reads

$$\psi \simeq a_{n_0} \varphi_{n_0} e^{-i\omega n_0 t} \frac{\sin \omega(\Delta n + \frac{1}{2})t}{\sin \frac{\omega t}{2}} \ . \tag{4.8}$$

This is a (periodic) wavepacket, oscillating very rapidly between time moments given by $\omega t(\Delta n + \frac{1}{2}) = k\pi$, exhibiting sharp peaks $\delta(t - kT)$ for any integer k, $T = 2\pi/\omega$ (beats), where T is the period corresponding to the frequency ω; the peak value of the wavefunction is proportional to $a_{n_0} \Delta n \simeq 1$. Similarly, the peak probability density goes like $(a_{n_0} \Delta n)^2 \simeq 1$. The matrix elements $f_{n,n+s}$ vary slowly in the range $n_0 - \Delta n < n, n + s < n_0 + \Delta n$, so that we get from equation (4.7),

$$\overline{f} \simeq \sum_s f_{n_0 n_0 + s} e^{-is\omega t} \ , \tag{4.9}$$

which is the Fourier transform of a classical quantity. It follows that the mean values of quantum quantities (operators) become classical quantities (*i.e.*, they do not depend anymore on the quantum state) for a wavefunction corresponding to a wavepacket. This is the classical limit of the quantum motion. For n photons the potential of the electromagnetic field is written as $A = \sum_{i=1}^{n} A(x_i)$ and the wavefunction is written as $\varphi_n(x_1, x_2, ...x_n)$. The main conclusion is that the electromagnetic field is a classical electromagnetic field when it is produced by a large number of quantum jumps n, all of them in the vicinity of the same large value n_0, $n_0 - \Delta n < n < n_0 + \Delta n$, $1 \ll \Delta n \ll n_0$. We emphasize that under these circumstances the field is either incoherent or coherent, in the sense that the photons have distinct, random phases or they have the same phase, respectively. In usual experiments we may consider the electromagnetic field a classical electromagnetic field.

4.2 Matter

The quantum nature of the condensed matter has certain particularities. Since the number of particles (degrees of freedom) in condensed matter is very large, the energy levels are extremely (exponentially) dense. Consequently, it is practically impossible to define stationary quantum states in condensed matter. Indeed, on one side we have an interaction with the surrounding environment, which is much greater than the gap between the energy levels, so we have always a broadening of the quantum states; on the other side, a similar interaction is implied whenever we try to prepare a sample of condensed matter in a given stationary state; the uncertainty in energy $\Delta E \simeq \hbar/\Delta t$ can only be minimized for a practically infinite interval of time $\Delta t \to \infty$. We may say that the condensed matter is usually in classical (or quasi-classical) states.

This is true for usual conditions. At low temperatures, we may encounter quantum states for condensed matter, like superfluidity, superconductivity, ferromagnetism, etc.

On the other hand, there are excited states in condensed matter, consisting of elementary excitations, either single-particle or collective, which have a finite lifetime (and a mean free path, if propagating), which may have a quantum character. However, when such elementary excitations imply a large number of degrees of freedom, the amount of action involved (number of quanta $\hbar$) is large, and they behave (quasi-) classically. In the first approximation, the interaction, in general, of a classical electromagnetic field with matter falls in this category. Plasmons, polaritons, polarization of matter in general, motion of electric dipole moments and magnetic moments generated by a classical electromagnetic field (or by other classical means) are (quasi-) classical motions. Similarly, the interaction of a classical electromagnetic field with a classical material motion is a classical interaction. In all these cases, the quanta of mechanical action implied by the interaction is compared with the energy levels of the condensed matter, and it is much smaller than the latter. However, in emission or absorption of electromagnetic radiation, the quanta of mechanical action is compared with the difference in the energy levels of condensed matter, and, in these cases, the motion is, in general, quantum-mechanical.

The quantum motion of the elementary excitations in condensed matter is conveniently described by field-theoretical methods, in particular by means of the Green functions, since many degrees of freedom are involved. In particular, correlations and fluctuations are amenable to these methods. The large number of degrees of freedom in condensed matter brings other particularities. A sample of condensed matter is not entirely and perfectly isolated from the rest; even if the whole assembly is described by a quantum wavefunction, that sample has not a wavefunction, because the wavefunction of the assembly is not, in general, a product of wavefunctions of the sample and the rest of the ensemble. The sample still admits a quantum, probabilistic description, since all the quantities pertaining to the sample are represented as averages of the form $\overline{f}=\sum_{nm}\rho_{nm}f_{mn}$, where ρ is the density matrix; it goes like $e^{-\frac{i}{\hbar}(E_n-E_m)t}$, including damping factors. The rate of transitions between quantum states are such averages; they may serve to write down kinetic equations for state populations, damping factors included. The state populations are classical, macroscopic variables, the corresponding kinetic equations are classical equations. In addition, the macroscopic quantities associated with condensed matter are usually statistical averages of the form $\overline{f}=\sum_{nm}w_{nm}f_{mn}$, where w is the statistical matrix; in the energy representation w is diagonal and $w_{nn}\sim e^{-\beta E_n}$, where $\beta=1/T$ is the reciprocal of the temperature T.

Consider a set of N quantum systems (*e.g.*, particles), not necessarily identical, distributed in a spatial region and labelled by $i=1,2...N$. A physical quantity f can be written as $f=\sum_{i=1}^{N}f_i$. The assembly has a set of stationary states $\psi_n(\mathbf{r}_1,..\mathbf{r}_N)$, where $n=(n_1,...n_N)$ is a set of quantum numbers and $\mathbf{r}_i$ denote the systems positions; $\mathbf{r}_i$ may include spin variables. We can represent ψ_n as $\psi_n = \prod_i \varphi^i_{n_i}(\mathbf{r}_i)$, though it is not necessary to have individual wavefunctions $\varphi^i_{n_i}$ (nor the wavefunction ψ_n). We can write another state as ψ_m, where $m = (n_1, ...m_i, ...n_N)$, such that a matrix element of f reads $f_{nm} = \sum_i f_{i,n_i m_i}$; some m_i can be identical with n_i, the state m can contain several $m_i \neq n_i$. The energy of the state n is $E_n = \sum_i E_{n_i}$. We note that for large values of N the energy E_n is large and there are a large number of states with energy close to the value E_n. We may restrict the summation in $\Psi = \sum_n a_n \psi_n e^{-\frac{i}{\hbar}E_n t}$ to an interval Δn around some value n, such that $1 \ll \Delta n \ll n$. Under these circumstances we can see that Ψ is a wavepacket and the mean value $\overline{f} = \sum a^*_n a_m f_{nm} e^{\frac{i}{\hbar}(E_n - E_m)t}$ behaves as a classical quantity; if the wavefunction does not exist, the mean value is $\overline{f} = \sum \rho_{mn} f_{nm} e^{\frac{i}{\hbar}(E_n - E_m)t}$ (or $\overline{f} = \sum \rho_{mn}(t) f_{nm}$) and the conclusion is preserved. We can write $E_m \simeq E_n + \frac{\partial E_n}{\partial n}(m - n)$ and, in the first approximation,

$$\overline{f} \simeq \rho_{nn} f_{nn} \Delta n \frac{\sin \omega_n (\Delta n + \frac{1}{2})t}{\sin \frac{\omega_n t}{2}} \ , \tag{4.10}$$

where n is fixed and $\omega_n = \frac{\partial E_n}{\hbar \partial n}$. This is a wavepacket, exhibiting beats (arising from the superposition of close frequencies). The next-order terms in the expansion of E_m flattens the packet through a factor $\sim 1/\sqrt{t}$, which indicates that this classical limit[1] in condensed matter must be viewed as producing in fact elementary excitations with a finite lifetime. A long-lasting wavepacket would correspond to a coherent state.[2]

The assembly of N systems (particles) can be viewed as corresponding to a local density of such assemblies (dividing by N, or by the volume), so that we arrive at the classical, macroscopic description of matter. The only thing reminiscent of quantum behaviour is the time dependence governed by term differences $(E_n - E_m)/\hbar = \omega_{nm}$,

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[1] P. Debye, "Wellenmechanik und Korespondenzprinzip", Phys. Z. **28** 170 (1927); C. G. Darwin, "Free motion in the Wave Mechanics", Proc. Roy. Soc. London **A117** 258 (1927).

[2] E. Schrodinger, "Der stetige Ubergang von der Mikro- zur Makromechanik", Naturwiss. **14** 664 (1926); E. H. Kennard, "Zur Quantemechanik einfacher Bewegungstypen", Z. Phys. **44** 326 (1927).

actually by frequencies $\omega_n = \frac{\partial E_n}{\hbar \partial n}$ which produce the classical beats. We can notice here the correspondence principle leading to classical limit. For statistical ensembles, the time dependence is lost, the matrix density becomes statistical matrix, the latter is diagonal in the energy representation and the mean value becomes a statistical mean value ($\rho_{mn} \rightarrow w_{nn} \sim e^{-\beta E_n}$).

4.3 Perturbations and transitions

Consider a quantum system with stationary states φ_n, energies E_n and hamiltonian H_0, $H_0\varphi_n = E_n\varphi_n$. We assume that at the initial moment the system is in state φ_n, with the wavefunction $\psi_n = \varphi_n e^{-\frac{i}{\hbar}E_n t}$; for convenience we choose the initial moment $t = -\infty$ and we introduce slowly ("adiabatically") an interaction

$$V(t) = \frac{1}{2}\left(Ve^{-i\omega t} + V^{+}e^{i\omega t}\right)e^{\alpha t} \ \ , \tag{4.11}$$

where $\alpha = 0^{+}$ ($\omega > 0$); it can be of the form $-\frac{1}{c}\mathbf{JA}$ discussed before. The wavefunction becomes $\phi_n = \varphi_n e^{-\frac{i}{\hbar}E_n t} + \chi_n$ and Schrodinger equation reads

$$\begin{gathered} i\hbar\tfrac{\partial\chi_n}{\partial t} = H_0\chi_n + V(t)\varphi_n e^{-\frac{i}{\hbar}E_n t} + ... = \\ = H_0\chi_n + \tfrac{1}{2}(V\varphi_n e^{-\frac{i}{\hbar}(E_n+\hbar\omega)t+\alpha t} + \\ + V^{+}\varphi_n e^{-\frac{i}{\hbar}(E_n-\hbar\omega)t+\alpha t}) \end{gathered} \tag{4.12}$$

in the first order of approximation in V, which is considered as a small perturbation. Obviously, χ_n is of the form

$$\chi_n = \chi_n^{(+)}e^{-\frac{i}{\hbar}(E_n+\hbar\omega)t+\alpha t} + \chi_n^{(-)}e^{-\frac{i}{\hbar}(E_n-\hbar\omega)t+\alpha t} \ \ , \tag{4.13}$$

where

$$\begin{gathered} (E_n + \hbar\omega + i\hbar\alpha)\chi_n^{(+)} = H_0\chi_n^{(+)} + \tfrac{1}{2}V\varphi_n \ , \\ (E_n - \hbar\omega + i\hbar\alpha)\chi_n^{(-)} = H_0\chi_n^{(-)} + \tfrac{1}{2}V^{+}\varphi_n \ . \end{gathered} \tag{4.14}$$

The solutions are

$$\begin{aligned} \chi_n^{(+)} &= \tfrac{1}{2}\sum\nolimits_m' \tfrac{V_{mn}}{E_n-E_m+\hbar\omega+i\hbar\alpha}\varphi_m \ , \\ \chi_n^{(-)} &= \tfrac{1}{2}\sum\nolimits_m' \tfrac{V_{nm}^*}{E_n-E_m-\hbar\omega+i\hbar\alpha}\varphi_m \end{aligned} \tag{4.15}$$

and

$$\begin{aligned} \phi_n = \varphi_n e^{-\frac{i}{\hbar}E_n t} + \tfrac{1}{2}\sum\nolimits_m' \tfrac{V_{mn}e^{-\frac{i}{\hbar}(E_n+\hbar\omega)t+\alpha t}}{E_n-E_m+\hbar\omega+i\hbar\alpha}\varphi_m + \\ +\tfrac{1}{2}\sum\nolimits_m' \tfrac{V_{nm}^* e^{-\frac{i}{\hbar}(E_n-\hbar\omega)t+\alpha t}}{E_n-E_m-\hbar\omega+i\hbar\alpha}\varphi_m \ , \end{aligned} \tag{4.16}$$

where $\sum'$ means $m \neq n$; a second-order change appears in φ_n, such that ϕ_n be normalized. This perturbation procedure can be carried out to higher orders and for various temporal variations of the perturbation.[3] Similar calculations can be performed for any state $\varphi_n \to \Phi_n$. We can see that there is a transition $n \to m$, given by the coefficient

$$c_{nm} = \frac{1}{2}\frac{V_{mn}e^{-\frac{i}{\hbar}(E_n-E_m+\hbar\omega)t+\alpha t}}{E_n-E_m+\hbar\omega+i\hbar\alpha} \ ; \tag{4.17}$$

the transition rate is

$$\begin{aligned} \tfrac{\partial |c_{nm}|^2}{\partial t} = \left|\tfrac{1}{2}V_{nm}\right|^2 \tfrac{2\alpha}{(E_n-E_m+\hbar\omega)^2+\hbar^2\alpha^2} \to \\ \to \tfrac{2\pi}{\hbar}\left|\tfrac{1}{2}V_{nm}\right|^2 \delta(E_n-E_m+\hbar\omega) \ ; \end{aligned} \tag{4.18}$$

a quantum $\hbar\omega$ is absorbed (*e.g.*, a photon) to pass from E_n to $E_m = E_n + \hbar\omega$. A similar reverse transition $m \to n$ takes place with the coefficient

$$c_{mn} = \frac{1}{2}\frac{V_{mn}^* e^{-\frac{i}{\hbar}(E_m-E_n-\hbar\omega)t+\alpha t}}{E_m-E_n-\hbar\omega+i\hbar\alpha} \ , \tag{4.19}$$

where a quantum $\hbar\omega$ is emitted to pass from $E_m = E_n + \hbar\omega$ to E_n; it is obtained from the second summation in equation (4.16) by interchanging $n \leftrightarrow m$. We can see that the two transition rates, the

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[3] E. Schrodinger, "Quantisierung als Eigenwertproblem", Ann. Physik **81** 109 (1926).

direct one ($n \rightarrow m$) and the reverse one ($m \rightarrow n$) are equal. This is an illustration of the detailed balancing principle, which indicates that statistical equilibrium is possible.[4] At equilibrium there is a probability for the state with n photons; the perturbation contains the creation and annihilation photon operators a^+ and a, whose matrix elements are given by $a^+ \left| n \right\rangle = \sqrt{n+1} \left| n+1 \right\rangle$ and $a \left| n \right\rangle = \sqrt{n} \left| n-1 \right\rangle$; the ratio of the absorption to emission coefficients should equal the statistical weight, $\frac{\overline{n}}{\overline{n}+1} = e^{-\beta\hbar\omega}$, hence the Bose-Einstein distribution $\overline{n} = (e^{\beta\hbar\omega} - 1)^{-1}$ for the mean number of photons in the black-body radiation. While $\partial \left| c_{nm} \right|^2 / \partial t$ and $\partial \left| c_{mn} \right|^2 / \partial t$ above are illustrative for induced rates of absorption and emission of radiation (at statistical equilibrium proportional to $\overline{n}$) the 1 in $\overline{n}+1$ is responsible for the rate of stimulated emission.[5] We can see that the statistical behaviour implies a different picture than that offered by perturbation theory: the (quantum) mechanical description is only compatible to statistical behaviour, but does not lead to it.

The mean value of an operator F over state ϕ_n given by equation (4.16) is

$$\begin{aligned} F_{nn}(t) = F_{nn} + \tfrac{1}{2} {\sum_m}' \tfrac{F_{nm} V_{mn} e^{-i\omega t + \alpha t}}{E_n - E_m + \hbar\omega + i\hbar\alpha} + \\ + \tfrac{1}{2} {\sum_m}' \tfrac{F_{nm} V_{nm}^* e^{i\omega t + \alpha t}}{E_n - E_m - \hbar\omega + i\hbar\alpha} + \\ + \tfrac{1}{2} {\sum_m}' \tfrac{F_{mn} V_{mn}^* e^{i\omega t + \alpha t}}{E_n - E_m + \hbar\omega - i\hbar\alpha} + \\ + \tfrac{1}{2} {\sum_m}' \tfrac{F_{mn} V_{nm} e^{-i\omega t + \alpha t}}{E_n - E_m - \hbar\omega - i\hbar\alpha} \ ; \end{aligned} \tag{4.20}$$

hence we can deduce the density matrix $\rho_{nn}(t) \simeq 1$ and

$$\begin{aligned} \rho_{nm}(t) = \tfrac{1}{2} \tfrac{V_{nm} e^{-i\omega t + \alpha t}}{E_n - E_m - \hbar\omega - i\hbar\alpha} + \\ + \tfrac{1}{2} \tfrac{V_{mn}^* e^{i\omega t + \alpha t}}{E_n - E_m + \hbar\omega - i\hbar\alpha} \ , \ n \neq m \ ; \end{aligned} \tag{4.21}$$

indeed, according to its definition, the density matrix obeys the equation of motion

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho] \ ; \tag{4.22}$$

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[4] L. Boltzmann, "Vorlesungen uber Gastheorie", Barth, Leipzig (1896, 1898).

[5] A. Einstein, "Zur Quantentheorie der Strahlung", Phys. Z. **18** 121 (1917).

writing $H = H_0 + V(t)$ and $\rho = \rho^{(0)} + \rho^{(1)}$ we get equation (4.21), in the first order of the perturbation theory. This result is obtained for the initial condition $\rho^{(0)}_{nn} = 1$; in general, in equation (4.21) occurs the factor $\rho_{nn} = \rho^{(0)}_{nn}$ (or $\rho_{nm} = \rho^{(0)}_{nm}$), according to the conditions in which the system is prepared initially. For initial conditions $\rho^{(0)}_{nn} = \rho_{nn}$, $\sum \rho_{nn} = 1$, for any n we get $\rho_{nn}(t) \simeq \rho_{nn}$ and

$$\begin{gathered}\rho_{nm}(t) = \tfrac{1}{2}[\tfrac{V_{nm}e^{-i\omega t+\alpha t}}{E_n - E_m - \hbar\omega - i\hbar\alpha} + \\ + \tfrac{1}{2}\tfrac{V^*_{mn}e^{i\omega t+\alpha t}}{E_n - E_m + \hbar\omega - i\hbar\alpha}](\rho_{nn} - \rho_{mm}) \ , \ n \neq m \ .\end{gathered} \tag{4.23}$$

We consider a macroscopic assembly; it has not a wavefunction, since it is part of a larger assembly; its energy levels E_n have a finite uncertainty $\Delta E_n = -i\hbar\gamma/2$, where γ is a damping (relaxation) coefficient. The assembly is originally prepared in a state defined by the density ρ_{nn}. We assume that the assembly is subject to a perturbation $V(t)$ (introduced adiabatically from t$\rightarrow -\infty$). The density matrix evolves according to equation (4.23), in the first order of the perturbation theory. Making use of this density matrix we can calculate the average of any physical quantity F. If, in addition, the assembly is in statistical equilibrium, then we replace ρ_{nn} in equation (4.23) by the statistical weight $w_n \sim e^{-\beta E_n}$, and get the statistical average of any quantity F (in general, such averages depend on the time, and it is assumed that the time dependence is sufficiently slow to preserve the statistical equilibrium).

Let us consider an assembly of N (identical) particles (quantum systems) and an electromagnetic interaction $V(t) = -\frac{1}{c}\mathbf{JA}(t)$, which can also be put in the form $V(t) = -\mathbf{dE}(t) = -\mathbf{dE}\cos\Omega t$; the Fourier transform of the electric field $\mathbf{E}(t)$ is $\mathbf{E}(\omega) = \pi\mathbf{E}[\delta(\omega - \Omega) + \delta(\omega + \Omega)]$. The Fourier transform of $\rho_{nm}(t)$ is

$$\rho_{nm}(\omega) = -\frac{d_{nm}}{E_n - E_m - \hbar\omega - i\hbar\alpha}(\rho_{nn} - \rho_{mm})E(\omega) \ , \tag{4.24}$$

where d is the dipole moment along $\mathbf{E}$. We calculate the average dipole moment induced by $\mathbf{E}$ and the polarizability

$$\alpha(\omega) = -\sum_{nm} \frac{|d_{nm}|^2}{E_n - E_m - \hbar\omega - i\hbar\alpha}(\rho_{nn} - \rho_{mm}) \ , \tag{4.25}$$

or

$$\alpha(\omega) = -\tfrac{1}{V}\sum_{nm} \tfrac{2|d_{nm}|^2(E_n-E_m)}{(E_n-E_m)^2-(\hbar\omega+i\hbar\alpha)^2}\rho_{nn} = \ , \\ = -\tfrac{N^2}{V}\sum_{nm} \tfrac{2q^2|u_{nm}|^2(E_n-E_m)}{(E_n-E_m)^2-(\hbar\omega+i\hbar\alpha)^2}\rho_{nn}\ \ , \tag{4.26}$$

where V is the volume of the assembly and q is the charge of each particle; here we have transitions $n \to m$, so that we may put $E_m = E_n + \hbar\omega_0$, $\omega_0 > 0$, for a (large) subset of states, where ω_0 is a fixed frequency; of course, we can have several such frequencies. On the other hand, we have for these excitations

$$\frac{\hbar^2}{2m\left|u_{nm}\right|^2} = E_m - E_n = \hbar\omega_0\ ; \tag{4.27}$$

we get from equation (4.26)

$$\alpha(\omega) = -\tfrac{N^2}{V}\sum_n \rho_{nn}\tfrac{q^2}{(\omega+i\alpha)^2-\omega_0^2} \simeq \\ \simeq -\tfrac{nq^2}{m}\tfrac{1}{\omega^2-\omega_0^2+i\omega\gamma}\ \ , \tag{4.28}$$

since $N\sum_n \rho_{nn}$can be approximated by unity; we replaced 2α by a damping coefficient γ. We can see that we arrived at the classical polarizability derived from the classical equation of motion

$$m\ddot{\mathbf{u}} + m\omega_0^2\mathbf{u} + m\gamma\dot{\mathbf{u}} = q\mathbf{E}(t)\ . \tag{4.29}$$

The derivation described above is the classical dispersion theory, which marked the beginning of the Quantum Mechanics.[6]

4.4 Orientational polarizability

In the previous section we have analyzed the polarization induced by the electromagnetic interaction $-\frac{1}{c}\mathbf{JA}$ or $-\mathbf{dE}$ upon mobile charges in

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[6] H. A. Kramers and W. Heisenberg, "Uber die Streuung von Strahlen durch Atome", Z. Phys. **31** 681 (1925); W. Heisenberg, "Uber quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen", Z. Phys. **33** 879 (1925).

condensed matter; we represented the dipole moment as $\mathbf{d} = q\mathbf{u}$ and the current as $\mathbf{J} = q\dot{\mathbf{u}}$, where q is an elementary electric charge and $\mathbf{u}$ is a displacement field ($\mathbf{A}$ is the vector potential and $\mathbf{E}$ is the electric field). We arrived at the conclusion that the electric polarization in condensed matter is satisfactorily described by the classical motion of a displacement field $\mathbf{u}$. There may exist restrictions to the motion of mobile charges, like, for instance, in (permanent) electric dipoles. Such dipoles are usually associated with the molecular constituents of the condensed matter; they are usually represented as rigid (spatial) rotators; a rigid rotator is also known as a spherical pendulum, or a spherical top; another representation is provided by a symmetrical or asymmetrical top.

A rigid rotator has the hamiltonian $L^2/2I$, where L is the angular (orbital) momentum and I is the moment of inertia. The rotation energy levels are $\hbar^2 l(l+1)/2I$, $l = 0, 1, 2...$; the rotation quanta $\hbar^2/2I$ is of the order of $10K$ $(1eV = 1.1 \times 10^4 K)$, *i.e.* $10^{11} - 10^{12}Hz$, for molecular rotators. We can see that free molecular rotations, in condensed matter, as far as the lowest-energy states are involved, are quantum-mechanical. A typical external electric field is of the order $E = 10^2 V/m$, *i.e.* $\simeq 10^{-2} statvolt/cm (1 statvolt/cm = 3 \times 10^4 V/m)$, a typical dipole moment is of the order $10^{-18}esu$, its energy in an external electric field is $10^{-20}erg \simeq 10^{-8}eV$ $(1eV = 1.6 \times 10^{-12}erg)$, which is an extremely small energy. Perturbation calculations can be performed for estimating the effect of an external electric field upon the molecular rotation energy levels. The effect is usually of the second-order (non-degenerate levels), in some (degenerate) cases it is of the first order. The perturbation energy dE may give the quanta of Rabi oscillations[7] $dE/\hbar \simeq 10^7 Hz$. We can compute the quantum-mechanical and thermal averages of the dipole moment for a time-dependent dipolar perturbation as in the previous section; for usual field strengths the results are, practically, those of classical dynamics. The main picture is that of an orientational Langevin effect in the presence of an external electric field.[8]

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[7] I. I. Rabi, "On the process of space quantization", Phys. Rev. **49** 324 (1936); I. I. Rabi, "Space quantization in a gyrating magnetic field", Phys. Rev. **51** 652 (1937).

[8] P. Langevin, "Sur la theorie du magnetisme", J Physique **4** 678 (1905); P. Langevin, "Magnetism et theorie des electrons", Ann. Chim. Phys. **5** 70

Molecules can also vibrate, like harmonic oscillators in the first approximation, with energies $\hbar\omega(n+1/2)$, $n=0,1,2...$; the vibration quanta is usually of the order of $\hbar\omega \simeq 0.1eV$ $(10^{13}-10^{14}Hz)$. These vibrations can be seen in the Raman spectra. A macroscopic (or locally macroscopic) collection of such vibrating molecules obeys also a classical, or quasi-classical, dynamics, according to our previous discussion.

Molecular dipoles may generate high, rapidly oscillating (in space and time) electromagnetic fields in condensed matter. The rapid oscillations may be averaged out, since they have little influence on the usual dynamics (this is the macroscopic average of the classical Electromagnetism). The local (averaged) environment of a molecular dipole may be often anisotropic. In granular matter electric charge can be accumulated at the interfaces. Such circumstances may generate high electric fields, acting upon the dipoles. We consider a rigid rotator with mass m, length R and charge q, subjected to such a local electric field $\mathbf{E}_0$. The hamiltonian is given by

$$H=\frac{1}{2}mR^2(\dot{\theta}^2+\sin^2\theta\dot{\varphi}^2)-qE_0R\cos\theta \tag{4.30}$$

and the equations of motion are

$$\begin{gathered} mR^2\ddot{\theta}=mR^2\sin\theta\cos\theta\dot{\varphi}^2-qE_0R\sin\theta\ , \\ \tfrac{d}{dt}(mR^2\sin^2\theta\dot{\varphi})=0\ . \end{gathered} \tag{4.31}$$

We can see that an integral of motion is the angular momentum L along the z-axis (coordinate φ); another integral of motion is the energy $\mathcal{E}$, such that

$$\mathcal{E}=\frac{1}{2}mR^2\dot{\theta}^2+\frac{L^2}{2mR^2\sin^2\theta}-qE_0R\cos\theta\ ,\ \dot{\varphi}=\frac{L}{mR^2\sin^2\theta}\ . \tag{4.32}$$

The effective potential energy

$$U=\frac{L^2}{2mR^2\sin^2\theta}-qE_0R\cos\theta \tag{4.33}$$

(1905); P. Debye, "Einige Resultate einer kinetischen Theorie der Isolatoren", Phys. Z. **13** 97 (1912).

exhibits a minimum for $0 < \theta_0 < \pi/2$; the rotator executes small θ-oscillations around this θ_0-minimum, while φ-precessing around the z-axis. The minimum is given by

$$U^{'} = -\frac{L^2}{mR^2 \sin^3\theta_0}\cos\theta_0 + qE_0R\sin\theta_0 \ , \tag{4.34}$$

while the expansion in powers of θ around this minimum leads to

$$\begin{aligned} U \simeq \tfrac{1}{2}L\sqrt{\tfrac{qE_0}{mR}}\tfrac{1}{\sqrt{\cos\theta_0}} - qE_0R\cos\theta_0 + \\ +\tfrac{1}{2}\left[4qE_0R\cos\theta_0 + L\sqrt{\tfrac{qE_0}{mR}}\tfrac{1}{\sqrt{\cos\theta_0}}\right]\theta^2 + ... \ . \end{aligned} \tag{4.35}$$

We may assume that $L^2/mqE_0R^3 \ll 1$, *i.e.* the strength E_0 of the electric field is sufficiently high, so that the effects of this field are much larger than, for instance, the effects of the thermal agitation (the dipoles are quenched along the direction of the field). In this case the solution of equation (4.34) is $\theta_0 \simeq (L^2/mqE_0R^3)^{1/4}$ and the energy becomes

$$\mathcal{E} \simeq \frac{1}{2}mR^2\dot{\theta}^2 - qE_0R + 2qE_0R\theta^2 + ... \ . \tag{4.36}$$

We can see that the θ-oscillations have frequency $2\sqrt{qE_0/mR}$, while the precession has frequency $\dot{\varphi} = \sqrt{qE_0/mR}$ (correction to this precession is called nutation). These are typical Rabi frequencies. The case $\dot{\varphi} = 0$ ($L = 0$) is also acceptable as a solution; it implies oscillations about $\theta_0 = 0$. The physical picture described here for a spatial rotator acted by an external field is related to the rotation of molecules in crystals.[9]

It is worth emphasizing that electric dipoles associated with the molecular constituents of the condensed matter may be pinned down by local electric fields, arising, for instance, from environmental anisotropies; they may be randomly distributed. Their precession may give rise to magnetic moments, oriented along randomly distributed θ angles;

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[9] L. Pauling, "The rotational motion of molecules in crystals", Phys. Rev. **36** 430 (1930); T. E. Stern, "The symmetrical spherical oscillator, and the rotational motion of homopolar molecules in crystals", Proc. Roy. Soc. **A130** 551 (1931).

their average is zero. An external electric field E along the z-axis acts with a force $qE\sin\theta$ upon a dipole pointing along the θ-direction; this force acts upon an oscillatory displacement $R\delta\theta = \delta u$, which has an eigenfrequency ω_0 of the order of $\sqrt{qE_0/mR}$ (Rabi frequency); this displacement contributes a component $\sim qE\sin^2\theta$ to the electric polarization, whose averaged value is $2qE/3$. Therefore, these bound dipoles can generate a polarization through their rotation, which can be described by an equation of motion of the type $\ddot{\mathbf{u}} + \omega_0^2\mathbf{u} + \gamma\dot{\mathbf{u}} = q\mathbf{E}/m$, where $\mathbf{E}$ is the electric field acting upon the displacement $\mathbf{u}$ and ω_0 is a characteristic frequency originating in the "bound" motion of the dipoles.

4.5 Absorption and emission of radiation

Under the action of radiation, as described by the interacting hamiltoniain $-\frac{1}{c}\mathbf{JA}$, the condensed matter gets polarized; mobile charges are displaced from their equilibrium positions and induced dipoles arise; the induced rotation of the permanent dipoles implies a charge displacement; to the current $\mathbf{J}$ contribute the spins also (spin current). All these currents can be represented as $\mathbf{J} = q\dot{\mathbf{u}}$, where the displacement field $\mathbf{u}$ obeys the classical equation of motion of a harmonic oscillator; the elementary charges q and mass m of the particles are parameters. Under these circumstances, the interaction $-\frac{1}{c}\mathbf{JA}$ can be written as $-\mathbf{dE}$, where $\mathbf{E}$ is the electric field and $\mathbf{d}$ is the dipole moment. A distribution of charges in the interaction $\sum q\Phi$ may also lead to a dipolar interaction.

The equation of motion for the displacement field $\mathbf{u}$ in a monochromatic field reads

$$m\ddot{\mathbf{u}} + m\omega_0^2\mathbf{u} + m\gamma\dot{\mathbf{u}} = q\mathbf{E}\cos\omega t \ ; \tag{4.37}$$

the solution is given by

$$\begin{gathered} \mathbf{u} = \mathbf{a}\cos\omega t + \mathbf{b}\sin\omega t \ , \\ \mathbf{a} = -\tfrac{q}{m}\mathbf{E}\tfrac{\omega^2-\omega_0^2}{(\omega^2-\omega_0^2)^2+\omega^2\gamma^2} \ , \ \mathbf{b} = \tfrac{q}{m}\mathbf{E}\tfrac{\omega\gamma}{(\omega^2-\omega_0^2)^2+\omega^2\gamma^2} \end{gathered} \tag{4.38}$$

(as usually we consider a non-relativistic motion). The power absorbed by the sample per unit volume is $\mathbf{jE}$, where $\mathbf{j} = nq\dot{\mathbf{u}}$, n being the charge density. We get

$$\overline{\mathbf{jE}} = \frac{nq^2}{2m} E^2 \frac{\omega^2 \gamma}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2} \ , \tag{4.39}$$

where the temporal average has been performed. We can see that the absorbed power exhibits a typical resonance behaviour.

From equation (4.37) we get

$$\frac{d}{dt}\left(\frac{1}{2} m \dot{\mathbf{u}}^2 + \frac{1}{2} m \omega_0^2 u^2\right) + m\gamma \dot{\mathbf{u}}^2 = q\mathbf{E}\dot{\mathbf{u}} \cos \omega t \ , \tag{4.40}$$

where we can see that the pure oscillations do not absorb energy; the absorbed energy $\overline{\mathbf{jE}}$, which is the work done by the field upon the charges, is the dissipated energy $\overline{mn\gamma \dot{\mathbf{u}}^2}$. In the absence of dissipation the energy $\overline{\mathbf{jE}}$ ($\overline{\mathbf{E}\dot{\mathbf{P}}}$) is zero (the polarization is $\mathbf{P} = nq\mathbf{u}$). The general solution of equation (4.37) includes the damped oscillations with frequency ω_0, which allow initial conditions to be imposed. Since this damped solution is transient and disappears after a while, we restrict ourselves here to the particular solution of forced oscillations given by equations (4.38). The average energy per cycle

$$\frac{1}{2} mn \dot{\mathbf{u}}^2 + \frac{1}{2} mn \omega_0^2 u^2 = \frac{nq^2}{4m} E^2 \frac{\omega^2 + \omega_0^2}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2} \tag{4.41}$$

stored by the oscillators in the transient regime should be compared with the dissipated energy $\overline{\mathbf{jE}}/\omega$ per cycle, given by equation (4.39); we get the quality factor $Q = (\omega^2 + \omega_0^2)\omega / 2\omega^2 \gamma \simeq \omega_0 / \gamma$.

The induced current $\mathbf{j}$ generates a vector potential

$$\mathbf{A}(\mathbf{r}, t) = \frac{1}{c} \int d\mathbf{r}' \frac{\mathbf{j}(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'| / c)}{|\mathbf{r} - \mathbf{r}'|} \ ; \tag{4.42}$$

we assume that the dimensions of the body are small in comparison with the wavelength and we are far away from the body in the wave zone; we get approximately

$$\mathbf{A}(\mathbf{r}, t) = \frac{nqv\omega}{cr} \left[-\mathbf{a} \sin \omega (t - r/c) + \mathbf{b} \cos \omega (t - r/c) \right] \tag{4.43}$$

and, from $div\mathbf{A}+\frac{1}{c}\frac{\partial\Phi}{\partial t}=0$ we get the scalar potential

$$\Phi(\mathbf{r},t)=\frac{nqv\omega}{cr^2}\left[-\mathbf{ar}\sin\omega(t-r/c)+\mathbf{br}\cos\omega(t-r/c)\right]\ \ , \tag{4.44}$$

where v is the volume of the body. We get also the emitted electric field $\mathbf{E}_e=-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}-grad\Phi$,

$$\begin{gathered}\mathbf{E}_e=\tfrac{nqv\omega^2}{c^2r^3}\{\mathbf{r}\times[\mathbf{r}\times\mathbf{a}\cos\omega(t-r/c)]+\\ +\mathbf{r}\times[\mathbf{r}\times\mathbf{b}\sin\omega(t-r/c)]\}\ \ ,\end{gathered} \tag{4.45}$$

the emitted magnetic field $\mathbf{H}_e=curl\mathbf{A}$

$$\mathbf{H}_e=\frac{nqv\omega^2}{c^2r^2}\left\{\mathbf{r}\times\mathbf{a}\cos\omega(t-r/c)]+\mathbf{r}\times\mathbf{b}\sin\omega(t-r/c)]\right\} \tag{4.46}$$

and the Poynting vector $\mathbf{S}=\frac{c}{4\pi}\mathbf{E}_e\times\mathbf{H}_e$,

$$\begin{gathered}\mathbf{S}=\tfrac{c}{4\pi}\left(\tfrac{nqv\omega^2}{c^2r}\right)^2[(\mathbf{r}\times\mathbf{a})^2\cos^2\omega(t-r/c)+\\ (\mathbf{r}\times\mathbf{b})^2\sin^2\omega(t-r/c)]\tfrac{\mathbf{r}}{r^3}\ \ ;\end{gathered} \tag{4.47}$$

averaging over time,

$$\overline{\mathbf{S}}=\frac{c}{8\pi}\left(\frac{nq^2v\omega^2}{mc^2r}\right)^2E^2\frac{1}{(\omega^2-\omega_0^2)^2+\omega^2\gamma^2}\sin^2\theta\frac{\mathbf{r}}{r}\ \ , \tag{4.48}$$

where θ is the angle between $\mathbf{E}$ and $\mathbf{r}$; the energy radiated per unit time and unit area is $\overline{\mathbf{S}}r^2do$, where o is the solid angle; the total energy radiated per unit time is

$$I=d\mathcal{E}/dt=\frac{c}{3}\left(\frac{nq^2v\omega^2}{mc^2}\right)^2E^2\frac{1}{(\omega^2-\omega_0^2)^2+\omega^2\gamma^2}\ . \tag{4.49}$$

This is the radiation of an induced dipole which exhibits a resonance phenomenon. The wave-zone approximation gives the exact result for a point body. It is known as Rayleigh (elastic) scattering of radiation, which exhibits the fluorescence resonance for $\omega=\omega_0$; for $\omega_0=0$ it is known as Thomson scattering; $q^2/mc^2=r_0$ is the (classical) electromagnetic radius of the charge. In molecules, the (electronic) displacement given by equation (4.38) may acquire a dependence on the ionic coordinates (through ω_0^2), of the form $u \sim E\cos\Omega t\cos\omega t$, where Ω is a vibration (or rotation) frequency, even for $\omega_0 = 0$; then, the dipole emits radiation with frequency $\omega \pm \Omega$ (and ω), which is known as the (inelastic) Raman scattering (not necessarily of a resonance character). The response in equation (4.37) of the electronic oscillations to an external electric field can also be affected (modulated) by collective motions like phonons, etc, which lead again to an inelastic scattering of the radiation, known as Brillouin scattering.

It is worth noting the conservation of energy. The temporal average of $\partial(E^2+H^2)/\partial t$ (where $\mathbf{E}$ and $\mathbf{H}$ are total fields) is zero; the time average of $div\mathbf{S}$ is also zero; in the energy balance we should add the oscillator energy given by equation (4.40); we can see that the Joule term $\overline{\mathbf{jE}}$ compensates the dissipation term $\overline{mn\gamma\dot{\mathbf{u}}^2}$. In order to maintain the external field $\mathbf{E}$ we spend the energy $\overline{\mathbf{jE}}$ and the radiated energy given by equation (4.49). Usually, the radiated energy is much smaller than the dissipated Joule energy, at least in view of the quadratic dependence on the body volume v in equation (4.49) in comparison with the linear dependence in equation (4.39). For numerical estimations it is convenient to note that vE^2 is the field energy in the volume of the body, $4\pi nq^2/m$ is the square of a plasma frequency ω_p (with typical values $\omega_p \simeq 10^{15}Hz$) and, usually, the ratio γ/ω_0 is of the order of 10^{-3}.

4.6 Motion of magnetization

The magnetic moment $\overrightarrow{\mu}$ is related to the spin $\mathbf{s}$ by $\overrightarrow{\mu} = \gamma\hbar\mathbf{s}$, where γ is the gyromagnetic factor (for electron $\gamma = e/mc = -2\mu_B/\hbar$, where e is the electron charge, m is the electron mass and μ_B is the Bohr magneton). In general, an angular momentum $\mathbf{L}$ is related to a magnetic moment $\mathbf{m}$ by such an equation ($\mathbf{m} = \gamma\mathbf{L}$), with various gyromagnetic factors γ. The magnetization $\mathbf{M}$ is the magnetic moment of the unit volume. Making use of the commutation relations of the angular moment ($e.g.$,$[s_i, s_j] = i\varepsilon_{ijk}s_k$) we get

$$\dot{\mathbf{M}} = \gamma\mathbf{M}\times\mathbf{H} \tag{4.50}$$

for a density $-\mathbf{MH}$ of (interaction) hamiltonian, where $\mathbf{H}$ is a magnetic field; precisely the same equation of motion exists in classical Electromagnetism (the Larmor equation).

We can see from equation (4.50) that $\mathbf{M}\dot{\mathbf{M}} = 0$, *i.e.* $M^2 = const$, which means that the vector $\mathbf{M}$ only rotates under the action of a magnetic field. Let $\mathbf{H}$ be directed along the z-axis; then $M_z = const$ and

$$\dot{M}_x = \gamma M_y H \ , \ \dot{M}_y = -\gamma M_x H \ ; \tag{4.51}$$

the solutions of these equations are

$$\begin{aligned} M_x &= M_\perp \sin\left(\gamma \int^t dtH + \alpha\right) \ , \\ M_y &= M_\perp \cos\left(\gamma \int^t dtH + \alpha\right) \ , \end{aligned} \tag{4.52}$$

where $M_\perp = \sqrt{M^2 - M_z^2} = const$ and α is an initial phase; we can see that for a constant magnetic field the magnetization precesses about the magnetic field with the frequency γH (Larmor's precession); for electron $\gamma H = eH/mc$ is the cyclotron frequency (twice the Larmor frequency).

Equations (4.52) are valid both classically and for matrix elements. In condensed matter we may consider locally a large number of "atomistic" magnetic moments; then we can see that the motion of such a quantity proceeds by wavepackets, therefore it is classical; in addition, the number of quantum states generated by the interaction $-\mathbf{MH}$ is small; it follows that magnetization in condensed matter behaves classically.

We consider now a uniform and constant induction B_0 in matter, oriented along the z-axis, and an additional, small, transverse induction $\mathbf{B}$. Equation (4.50) can be linearized,

$$\begin{aligned} \dot{M}_x &\simeq \gamma B_0 M_y - \gamma M_z B_y \ , \\ \dot{M}_y &\simeq \gamma M_z B_x - \gamma B_0 M_x \ , \\ \dot{M}_z &= \gamma M_x B_y - \gamma M_y B_x \simeq 0 \ ; \end{aligned} \tag{4.53}$$

this is the typical situation in magnetic (spin) resonance. We can see that $M_z = const$; we get

$$M_\pm = \frac{\omega_s}{\omega_0 \mp \omega} B_\pm \ , \tag{4.54}$$

where $M_\pm = M_x \pm iM_y$, $B_\pm = B_x \pm iB_y$ and $\omega_0 = \gamma B_0$, $\omega_s = \gamma M_z$. We assume now that $\mathbf{B}$ is generated by a radiation field, such that

$$\begin{gathered} div\mathbf{E} = 0 \ , \ div\mathbf{B} = 0 \ , \\ curl\mathbf{E} = -\tfrac{1}{c}\tfrac{\partial \mathbf{B}}{\partial t} \ , \ curl\mathbf{B} = \tfrac{1}{c}\tfrac{\partial \mathbf{E}}{\partial t} + 4\pi curl\mathbf{M} \ ; \end{gathered} \tag{4.55}$$

making use of $div\mathbf{B} = 0$ and $div\mathbf{M} = 0$ (equations (4.54)) we get

$$\Delta\mathbf{B} = \frac{1}{c^2}\frac{\partial^2 \mathbf{B}}{\partial t^2} + 4\pi\Delta\mathbf{M} \ , \tag{4.56}$$

or, making use of equations (4.54),

$$\omega^2 = c^2k^2\left(1 - \frac{4\pi\omega_s}{\omega_0 \mp \omega}\right) \ , \tag{4.57}$$

where $\mathbf{k}$ is the wavevector. Equation (4.57) gives the elementary excitations of the electromagnetic field (photons) coupled with magnetization; they resemble the polaritons, and we may call them photomagnons; the elementary excitations of the magnetization are called magnons. Equation (4.57) has two dispersion branches; one goes from $\omega = \omega_0 = \gamma B_0$ for $k \to 0$ and approaches asymptotically $\omega = ck$; another goes like $\omega = vk$, $v = c/\sqrt{\mu}$ for $k \to 0$ and tends asymptotically to $\omega = \omega_0 - 4\pi\omega_s = \gamma H$ for $k \to \infty$, where μ is the magnetic permeability and $H = B_0 - 4\pi M_z$ is the magnetic field (for an isotropic body).

Equation (4.50) can also be written as

$$\ddot{\mathbf{M}} = \gamma^2\mathbf{B}(\mathbf{MB}) - \gamma^2\mathbf{M}B^2 + \gamma\mathbf{M}\times\dot{\mathbf{B}} \ , \tag{4.58}$$

where $\mathbf{B}$ is the local (total) magnetic field called magnetic induction; if the external (applied) field is denoted by $\mathbf{B}_0$ (actually an $\mathbf{H}$), then $\mathbf{B}$ contains also an internal $\mathbf{B}_i$, which may include various magnetic effects (diamagnetic, paramagnetic, ferromagnetic, etc), in general anisotropic. In the quasi-static limit the internal field generated by the magnetization is given by equation $curl\mathbf{B}_i = 4\pi curl\mathbf{M}$ (current density $c \cdot curl\mathbf{M}$), so $\mathbf{B}_i = 4\pi\mathbf{M}$; for finite-size bodies (de-) magnetizing factors f appear, leading to $\mathbf{B}_i = 4\pi f\mathbf{M}$ (in general anisotropic).[10] Usually, they are generated by diamagnetic surface effects, so that they are negative. Let us assume that there exists an internal field $\mathbf{B}_i$, originating in ferromagnetic domains, or in various local anisotropies, such as $\mathbf{B}$ in equation (4.58) is $\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_i$; we assume further that $\mathbf{B}_i$ is randomly oriented, with constant magnitude. We average equation (4.58) with respect to the orientation of the internal magnetic field $\mathbf{B}_i$ and get

$$\ddot{\mathbf{M}} + \frac{2}{3}B_i^2\mathbf{M} = \gamma^2\mathbf{B}_0(\mathbf{M}\mathbf{B}_0) - \gamma^2\mathbf{M}B_0^2 + \gamma\mathbf{M} \times \dot{\mathbf{B}}_0 \ . \tag{4.59}$$

Equation (4.59) implies, in general, coupled Mathieu-Hill equations; we may consider $\mathbf{B}_0$ very weak and restrict ourselves to the linear term in $\mathbf{B}_0$, which can be treated as a perturbation; denoting $\omega_0^2 = \frac{2}{3}B_i^2$, equation (4.59) becomes

$$\ddot{\mathbf{M}} + \omega_0^2\mathbf{M} = \gamma\mathbf{M}_0 \times \dot{\mathbf{B}}_0 \ , \tag{4.60}$$

where $\mathbf{M}_0$ is the solution of the equation $\ddot{\mathbf{M}}_0 + \omega_0^2\mathbf{M}_0 = 0$. For a harmonic oscillation $\mathbf{B}_0 \sim \cos\Omega t$, equation (4.60) has, beside the solution $\mathbf{M}_0\cos(\omega_0 t + \alpha)$, particular harmonic oscillations with frequencies $\omega_0 \pm \Omega$. Usually, the motion of $\mathbf{M}_0$ should be thermaly averaged, which makes $\overline{\mathbf{M}}_0 = 0$. If, for some reasons $\mathbf{M}_0$ exists and is independent of time, for instance it is directed along a certain direction, say the z-axis, then, assuming the field $\mathbf{B}_0$ directed along the x-axis, we get small induced oscillations for M_y, whose Fourier transform obeys a dispersion-like equation

$$M_y(\omega) = \gamma M_0 B_0(\omega)\frac{i\omega}{\omega^2 - \omega_0^2} \ ; \tag{4.61}$$

a damping coefficient can be included. This is a magnetic resonance.

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[10] E. C. Stoner, "The demagnetizing factors for ellipsoids", Phil. Mag. **36** 803 (1945); J. A. Osborne, "Demagnetizing factors for general ellipsoid", Phys. Rev. **67** 351 (1945).

The typical magnetic (spin) resonance is based on equation (4.53), where $\mathbf{B}$ is a transverse quasi-static external field; we denote it by $H_x(t) = H\cos\omega t$. In general, in the equation of motion $\dot{\mathbf{M}} = \gamma\mathbf{M}\times\mathbf{B}$ we may use the external field $\mathbf{H}$ instead of $\mathbf{B}$. Equations (4.53) become

$$\dot{M}_x = \omega_0 M_y \ , \ \dot{M}_y = \omega_s H\cos\omega t - \omega_0 M_x \ , \tag{4.62}$$

or

$$\begin{gathered} \ddot{M}_x + \omega_0^2 M_x = \omega_0\omega_s H\cos\omega t \ , \\ \ddot{M}_y + \omega_0^2 M_y = -\omega\omega_s H\sin\omega t \ , \end{gathered} \tag{4.63}$$

where $\omega_0 = \gamma H_0$ and $\omega_s = \gamma M_z$ ($= \frac{\chi}{\mu}\omega_0$, where χ is the magnetic susceptibility and μ is the magnetic permeability, for an isotropic body). A damping coefficient α should be included in these equations,

$$\begin{gathered} \ddot{M}_x + \omega_0^2 M_x + \alpha\dot{M}_x = \omega_0\omega_s H\cos\omega t \ , \\ \ddot{M}_y + \omega_0^2 M_y + \alpha\dot{M}_y = -\omega\omega_s H\sin\omega t \ , \end{gathered} \tag{4.64}$$

which amounts to

$$\dot{\mathbf{M}} = \gamma\mathbf{M}\times\mathbf{H} - \alpha\mathbf{M} \tag{4.65}$$

for the Larmor equation (the coefficient α for the transverse x, y-components is different, in general, from the damping coefficient for the longitudinal z-component). In this form, the Larmor equation is known as Bloch equations.[11] The solution of equations (4.64),

$$\begin{gathered} M_x = a_x\cos\omega t + b_x\sin\omega t \ , \\ M_y = -\tfrac{\omega}{\omega_0}a_x\sin\omega t + \tfrac{\omega}{\omega_0}b_x\cos\omega t \ , \end{gathered} \tag{4.66}$$

where

$$\begin{gathered} a_x = -\omega_0\omega_s H\tfrac{\omega^2-\omega_0^2}{(\omega^2-\omega_0^2)^2+\alpha^2\omega^2} \ , \\ b_x = \omega_0\omega_s H\tfrac{\alpha\omega}{(\omega^2-\omega_0^2)^2+\alpha^2\omega^2} \ , \end{gathered} \tag{4.67}$$

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[11] F. Bloch, "Nuclear induction", Phys. Rev. **70** 460 (1946).

exhibits the (magnetic, spin) resonance phenomenon. The average dissipated power (per unit volume) is given by

$$\begin{gathered}P_x = H\overline{\cos\omega t \cdot \dot{M}_x} = \tfrac{1}{2}\omega_0\omega_s H^2 \tfrac{\alpha\omega^2}{(\omega^2-\omega_0^2)^2+\alpha^2\omega^2} \ , \\ P_y = -H\overline{\sin\omega t \cdot \dot{M}_y} = \tfrac{1}{2}\omega_s H^2 \tfrac{\alpha\omega^3}{(\omega^2-\omega_0^2)^2+\alpha^2\omega^2}\end{gathered} \tag{4.68}$$

and

$$\begin{gathered}P = P_x + P_y = \tfrac{1}{2}\omega_s H^2 \tfrac{\alpha\omega^2(\omega+\omega_0)}{(\omega^2-\omega_0^2)^2+\alpha^2\omega^2} \simeq \\ \simeq \tfrac{1}{2}\tfrac{(\alpha/2)\omega_s\omega_0 H^2}{(\omega-\omega_0)^2+\alpha^2/4} \ .\end{gathered} \tag{4.69}$$

We can check that the motion of the magnetization in the absence of dissipation does not absorb energy, *i.e.* $\mathbf{H}\dot{\mathbf{M}} = 0$ for $\alpha = 0$.

We note that the induced magnetization $\mathbf{M}$ generates a current $\mathbf{j} = c \cdot curl\mathbf{M}$ and a vector potential

$$\mathbf{A} = \frac{1}{c}\int d\mathbf{r}' \frac{\mathbf{j}(\mathbf{r}', t - |\mathbf{r}-\mathbf{r}'|/c)}{|\mathbf{r}-\mathbf{r}'|} = \int d\mathbf{r}' \frac{\mathbf{M}\times(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \ , \tag{4.70}$$

which, in the quasi-static limit, becomes

$$\mathbf{A} = v\frac{\mathbf{M}(t-r/c)\times\mathbf{r}}{r^3} = -v\mathbf{M}\times grad\frac{1}{r} \ ; \tag{4.71}$$

it is easy to see that $div\mathbf{A} = 0$, so that $\Phi = 0$ (in agreement with the fact that the current $c \cdot curl\mathbf{M}$ has no associated charge). Both the electric field and the magnetic field go like $1/r^2$ for large distances, and the Poynting vector is vanishing; the motion of the induced magnetization does not radiate energy. At small distances from the body the dipolar magnetic field is the leading contribution.

We assume now that at the initial moment of time we have a magnetization $M_y(x)$, $M_z(x)$ in a ferromagnet; we apply a magnetic field $H_0 + h(t)$ along the z-axis; $M_y(x)$ starts to rotate; we get a component $M_x(x)$, which generates a magnetic field $H_x(x) = -4\pi M_x(x)$ according to $div\mathbf{H} = -4\pi div\mathbf{M}$; we consider $M_{x,y}$ small and, similarly, h small in comparison with H_0; the leading contributions to the motion of the magnetization give

$$\begin{aligned} \dot{M}_x \simeq \omega_0 M_y \ , \ \dot{M}_y \simeq -\omega_0 M_x \ , \\ \dot{M}_z = -\gamma M_y H_x = 4\pi\gamma M_x M_y \ ; \end{aligned} \tag{4.72}$$

we get $M_x = m\sin\omega_0 t$, $M_y = m\cos\omega_0 t$ and $\dot{M}_z = 4\pi\gamma m^2 \sin\omega_0 t\cos\omega_0 t$ (where $m = m(x)$). The absorbed power is $P = (H_0 + h)\dot{M}_z$; we see that we can get a finite pumping power for $h(t) = h\sin 2\omega_0 t$; we get an average power $P = \pi\gamma m^2 h$. The absorbed energy (per unit volume) is $\mathcal{E} \simeq -H_0 M_z = -H_0(M^2 - m^2)^{1/2} \simeq -H_0 M + H_0 m^2/2M$; its kinetic equation reads

$$\begin{aligned} \tfrac{d\mathcal{E}}{dt} = -\alpha(\mathcal{E} - \overline{\mathcal{E}}) + \pi\gamma h m^2 \ , \\ \tfrac{dm^2}{dt} = -\alpha(m^2 - \overline{m^2}) + \tfrac{2\pi\gamma h M}{H_0} m^2 \ \ , \end{aligned} \tag{4.73}$$

where α is a damping coefficient; we can see that the static solution can increase indefinitely for $2\pi\gamma h M/H_0 \to \alpha$; this is a ("parallel") ferromagnetic pumping.

Finally we note that the temporal Fourier transforms of the magnetization are of the form $M_x \sim aH_x - bH_y$, $M_y \sim aH_y + bH_x$, according to equation (4.53), where a and b are coefficients related to ω_0 and ω_s. Consequently, the induction has the form $B_x = \mu H_x - \nu H_y$, $B_y = \mu H_y + \nu H_x$, where μ is the magnetic permeability and ν is a coefficient related to b. Now we can set $H = -grad\varphi$ and solve the equation $div\mathbf{B} = 0$, $\mu(\partial^2\varphi/\partial x^2 + \partial^2\varphi/\partial y^2) + \partial^2\varphi/\partial z^2 = 0$, in the quasi-static limit ($curl\mathbf{H} = 0$). The boundary conditions require the continuity of the tangential component of $\mathbf{H}$ and the normal component of $\mathbf{B}$. The solutions are known as magnetostatic modes.

4.7 A quasi-classical note

We consider a collection of N "quatum systems" (particles), not necessarily identical, labelled by $i = 1, 2...N$, each with a set of quantum states labelled by quantum numbers n_i; we consider stationary energy states, with energy ε_{n_i}, such as the total energy of the collection is

$E_n = \varepsilon_{n_1} + \varepsilon_{n_2} + ... + \varepsilon_{n_N}$; we can see that it is convenient to denote the states of the collection by $n = (n_1, n_2, ...n_N)$. Now we see that another energy $E_{n'}$ is obtained by changing at least by a unity at least one of the quantum numbers n_i, for instance $E_{n'} = \varepsilon_{n_1} + ... + \varepsilon_{n'_i} + ... + \varepsilon_{n_N}$, where $n'_i = n_i \pm 1$. Such a change implies a small difference in energy, $E_{n'} - E_n \simeq \hbar/\Delta t$, where $\hbar$ is Planck's constant and Δt is the time needed for the change. The quantum dynamics of each of the quantum systems implies small changes in the action function s_i, of the order of the Planck's constant. Now we can see that for a large number of quantum systems, *i.e.* for large N, $N \gg 1$, we have a large number of states with the same energy. Therefore, a macroscopic body has a dense distribution of energy levels, practically a continuum of energy, and, in addition, a multitude of densely distributed wavefunctions. As far as the distinction is preserved between the members of the collection of the systems, at least nominally, and their dynamics is distinct for each system, a macroscopic set of quantum sytems has not a well-defined wavefunction, nor well-defined energy levels.

Indeed, let us consider the motion of an operator O for macroscopic quantum states n,

$$i\hbar\dot{O} = [O, H] \ , \ i\hbar\dot{O}_{nm} = (E_m - E_n)O_{nm} \ , \tag{4.74}$$

where H is the hamiltonian of the assembly of quantum systems; or

$$\hbar^2\ddot{O}_{nm} + (E_m - E_n)^2 O_{nm} = 0 \ , \ \ddot{O}_{nm} + \omega_{mn}^2 O_{nm} = 0 \ , \tag{4.75}$$

where $\omega_{mn} = (E_m - E_n)/\hbar$. Since the states are dense, we can choose an n and construct around it a wavepacket ; and we can choose an m and construct around it a wavepacket; then we set $m = n + s$ and note that $O_{nm} = O_{n,n+s}$ depends practically only on s, $O_{n,n+s} \simeq O_s$, and $\omega_{mn} = \omega_{n+s,n}$ depends practically only on s, $\omega_{n+s,n} \simeq \omega_s$; equation (4.75) becomes

$$\ddot{O}_s + \omega_s^2 O_s = 0 \ , \tag{4.76}$$

which is the classical equation of a harmonic oscillator. Usually, the range of the variable s is not very large, since the quantum deviation $O_{nm}O_{mn} - O_{nn}^2$ should be small if we are going to attribute to the quantum operator O any relevant meaning. On the other hand, equations similar with equation (4.76) can be written for other regions of the quantum numbers n, m, which amounts to distinct initial conditions for O. Since $\omega_s \simeq (\partial\omega/\partial s)s{=}\omega s$, we can see that s labels the temporal Fourier transforms of O, which is, practically, a classical quantity ($O_s \sim e^{\pm i\omega st}$).

The wavefunction of the collection of quantum systems can be written as $\psi_n(1,2,...N) = \varphi_{n_1}(1)\varphi_{n_2}(2)...\varphi_{n_N}(N)$, symmetrized as necessary for identical systems, where $\varphi_{n_i}(i)$ are the wavefunctions of individual systems i; we denote by i the coordinates (spin included) of the system i. In general, the existence of distinct $\varphi_{n_i}(i)$ is an idealization, implying the absence of any interaction between the systems; such an assembly behaves incoherently, with the interaction residue accounted by a finite lifetime (in this sense, any distinct system i in the assembly is an elementary excitation, a quasi-particle). Genuine entanglement in a wavefunction $\psi_n(1,2,...N)$ corresponds to coherence. A quantum change in φ_{n_i} implies a small change in $\psi_n(1,2,...N)$. In general, it is conceivable that a change in the dynamics of the i-th system implies a small change in $\psi_n(1,2,...N)$, although it is not necessary that n be represented as a multiplicity $(n_1, n_2, ...n_N)$. An operator O can be written as $O = O_1(1) + O_2(2) + ...O_N(N)$ (a one-particle operator); its matrix elements can be represented as $O_{nm} = (O_1)_{n_1m_1} + (O_2)_{n_2m_2} + ...(O_N)_{n_Nm_N}$; for instance, $O_{nn'} = (O_1)_{n_1n_1} + ... + (O_i)_{n_in_i'} + ... + (O_N)_{n_Nn_N}$.

According to the discussion made above, we can take for the assembly $1, 2, ...N$ a local collection of particles; we can divide their number by the volume they occupy, and get a particle density (which can change in space and time). We can divide any operator of the form $O = O_1(1){+}O_2(2){+}...O_N(N)$ by N and get densities of physical quantities. This way, if N is sufficiently large and the particles sufficiently close to each other, *i.e.* if we have a sample of condensed matter, we get a macroscopic continuum described by classical quantities obeying a classical dynamics.

The lack of a wavefunction for condensed matter means that there is not a complete measuring process whose result is predictable, *i.e.* there is not a complete set of operators with eigenfunctions. Although wavefunctions are missing, we can speak of mean values of operators over states defined by a density matrix. For instance, instead of $O_{nn} = \int d\tau\psi_n^*(\tau)O(\tau)\psi_n(\tau)$ we write $\overline{O} = \sum_n \rho_n O_{nn} = \sum_{nm} \rho_{nm}\delta_{nm}O_{mn}$, with $\rho_n = \rho_{nn}$; we can see that ρ_n are statistical weights of the n-

states, such as $\sum_n \rho_n = \sum_n \rho_{nn} = tr(\rho) = 1$; ρ is the density matrix, it is positive definite, and, in general, $\rho_{nm} = \int d\tau \psi_n^*(\tau)\rho(\tau)\psi_n(\tau)$, $\overline{O} = \sum_{nm} \rho_{nm} O_{mn}$; if the assembly has a wavefunction $\psi = \sum_n c_n \psi_n$ then it is easy to see that $\rho_{nm} = c_m^* c_n$ and $(\rho^2)_{nm} = \rho_{nm}$; in this later case we have a "pure" state, while in the former case we have a "mixed" state.

The density matrix reflects the statistical character of the quantum behaviour, ρ_n being the probability density of the state n, although it is not factorizable in wavefunctions. Another statistical behaviour occurs in macroscopic bodies, related to the thermal (statistical) equilibrium; the averages are given by $\overline{O} = \sum_n w_n O_{nn}$, where $w_n \sim e^{-\beta E_n}$ is the Gibbs distribution ($\beta = 1/T$ being the inverse of the temperature); w_n is the statistical matrix, diagonal in the energy representation (the necessary representation for statistical description); if the wavefunction exists, $w_n \psi_n^* \psi_n \sim e^{-\beta E_n} \psi_n^* \psi_n$ is the probability density.

4.8 Macroscopic motion

The usual measurements made upon matter imply macroscopic samples, either of material bodies or fields. In this respect matter consists of local, continuous, macroscopic "subsystems", whose behaviour, in the first approximation, is averaged over the quantum motion of their atomistic constituents. According to the discussion above, this "macroscopic" matter obeys a classical dynamics, which is an emergent behaviour with respect to the underlying quantum dynamics. In addition, macroscopic matter is at thermal (statistical) equilibrium, or tends to equilibrium; it may happen that particular subsystems be not at equilibrum and tend to equilibrium, usually through a damping (relaxation) kinetics.

With usual notations we consider a damped harmonic oscillator

$$\ddot{u} + \omega_0^2 u + \gamma \dot{u} = 0 \; ; \tag{4.77}$$

for $\gamma \ll \omega_0$ the solution is given by the damped oscillations $u = const \cdot \cos(\omega t + \delta) e^{-\gamma t/2}$, where $\omega = (\omega_0^2 - \gamma^2/4)^{1/2} \simeq \omega_0$ and δ is a phase. At equilibrium, the initial conditions (represented by *const* and δ) are distributed statistically, and so are the solutions u; the equilibrium statistical distribution is the Gibbs distribution $\sim e^{-\frac{1}{2}\beta u^2}$, where $\beta = 1/T$ is the inverse of the temperature. We can see that the mean value of the coordinate u is zero, $\overline{u} = 0$. If the damping coefficient γ dominates, *i.e.* $\gamma \gg \omega_0$, we may have $\ddot{u} + \gamma\dot{u} = 0$, or $\dot{u} + \gamma u = A$, with the solution $u = A/\gamma + Be^{-\gamma t}$, where A and B are constants. We can see that we can have a relaxation to zero ($A = 0$), or to $A/\gamma \neq 0$, for $t \to \infty$, where equilibrium is attained. A special damped solution $u = (A + Bt)e^{-\gamma t/2}$ occurs for $\omega_0 = \gamma/2$.

An external force F,

$$\ddot{u} + \omega_0^2 u + \gamma\dot{u} = F/m \ , \tag{4.78}$$

where m is the particle mass, makes the solution to consist of the solution u_0 of the homogeneous equation (4.77) and a particular solution u of equation (4.78); u_0 is subjected to thermal averaging, so for damped oscillations it is vanishing; we are left with the particular solution u, which, usually, since F depends on the time, is expressed conveniently through temporal Fourier transforms. If the damping coefficient dominates, besides the relaxation solution of the homogeneous equation, we have the particular solution $\dot{u} = F/m\gamma$; for charges q acted by an external, constant electric field E, this solution is the drift (diffusion) current $j = nq\dot{u} = (nq^2/m\gamma)E$, where $nq^2/m\gamma$ is the static conductivity (n being the charge density).

Usually, the particular solution driven by an external agent survives the statistical equilibrium. This holds also for the motion of magnetization, which is that of (damped) harmonic oscillators.

However, this is not always true; for instance, a dipole $\mathbf{d}$ acted by an external electric field $\mathbf{E}$ rotates according to

$$I\ddot{\theta} = -dE\sin\theta \ , \tag{4.79}$$

where θ is the angle between $\mathbf{d}$ and $\mathbf{E}$ and I is the moment of inertia. We can see that the external field occurs as a term which contains the coordinate of motion θ (this is true for the spatial rotator too). Consequently, the external field manifests itself in the statistical equilibrium. As it is well known, the energy $-\mathbf{dE}$ leads to the statistical weight $\sim e^{\beta dE\cos\theta}$ and to the average value $\overline{\cos\theta} = \beta dE/3$; we get $\mathbf{d} = \frac{1}{3}\beta d^2\mathbf{E}$ and the Langevin polarizability (susceptibility)$\chi = \frac{1}{3}n\beta d^2$. This is true even for time-dependent fields, since, usually, the thermal equilibrium is very quickly established. Now, the dipoles are oriented in average along an angle θ_0 (given by $\overline{\cos\theta_0} = \beta dE/3$), though with large fluctuations, since $\beta dE \ll 1$; we can expand the equation of motion (4.79) around this angle and get free oscillations with the frequency $\sqrt{dE_0/I}$, under the action of another (constant) external field E_0. These are Rabi oscillations; they are vanishing upon thermal averaging (similar Hill-Mathieu oscillations occur for time-dependent fields, with zero thermal averages too). However, a dynamics imposed upon statistical behaviour is not consistent.

It may happen that the dipole moments are pinned down by local fields $\mathbf{E}_i$ oriented along randomly distributed directions corresponding to angles θ_0. Then, the dipoles execute free oscillatios according to $I\ddot{\theta} + dE_i\theta = 0$ around these directions (leaving aside the rotations). Under the action of an external field E oriented along the z-axis the equation of motion becomes $ml\ddot{\theta} + (dE_i/l)\theta = qE\sin\theta_0$, where l is the dipole length and q is the dipole charge. The projection of these oscillations along the direction of the external field obeys the equation of motion $m\ddot{u} + (dE_i/l^2)u = qE\sin^2\theta_0$, where $u = l\theta\sin\theta_0$; averaging over θ_0 we get $m\ddot{u} + m\omega_0^2 u = \frac{2}{3}qE$, where $\omega_0 = \sqrt{dE_i/I}$ is the Rabi frequency (of the internal field). The particular solution of this equation leads to a (rotational) polarization for matter in thermal equilibrium. Similarly, if the dipoles are not rigid, we get a vibrational polarization too.

5 Magnetic Resonance I

5.1 Nuclear magnetic resonance

The nuclear magnetic moments are measured usually in nuclear Bohr magnetons. The nuclear Bohr magneton is $\mu_0 = |e|\,\hbar/2M_pc$, where $e = -4.8\times10^{-10}esu$ ($statcoulomb$, $e = -1.6\times10^{-19}C$) is the electron charge ($|e|$ is the proton charge), $M_p = 1.67\times10^{-24}g$ is the proton mass, $\hbar \simeq 10^{-27}erg\cdot s$ is Planck's constant and $c = 3\times10^{-10}cm/s$ is the speed of light in vacuum. The nuclear Bohr magneton is $\mu_0 \simeq 5\times19^{-24}erg/Gs$. The nuclear magnetic moments are written as $\overrightarrow{\mu} = g\mu_0\mathbf{I}$, where g is called the gyromagnetic (Lande) factor and $\mathbf{I}$ is the nuclear spin (in $\hbar$ units); g can be positive or negative; for instance, the magnetic moment of the proton is $\mu_p = 2.79\mu_0 \simeq 1.4\times10^{-23}erg/Gs$ and the magnetic moment of the neutron is $\mu_n = -1.91\mu_0 \simeq -0.96\times10^{-23}erg/Gs$. The nuclear magnetic moments vary approximately between $-2\mu_0$ and $6\mu_0$ (and the nuclear spin may go up to 9/2 or higher). It is also convenient to write the magnetic moments as $\overrightarrow{\mu} = \gamma\hbar\mathbf{I}$, where γ ($= g\mu_0/\hbar$) is also called the gyromagnetic factor (or magnetogyric factor, coefficient, ratio). For proton $\gamma \simeq 2.7\times10^4s^{-1}Gs^{-1}$ ($I = 1/2$); $\overrightarrow{\mu} = \gamma\hbar\mathbf{I}$ incorporates the angular moment $\mathbf{J} = \hbar\mathbf{I}$.

In an external magnetic field $\mathbf{H}_0$ the magnetic moment acquires the Zeeman energy $U = -\overrightarrow{\mu}\mathbf{H}_0 = -\gamma\hbar\mathbf{I}\mathbf{H}_0$; we can see that the spin tends to align itself along the magnetic field; for instance, if initially the spins are distributed equally among the states $m = I_z = \pm1/2$ for spin 1/2, in the presence of an external field H_0 oriented along the z-axis the level $m = 1/2$ will be more populated, being lower in energy (for $g, \gamma > 0$). At thermal equilibrium the ratio of the two populations is $N_{1/2}/N_{-1/2} = e^{\beta\gamma\hbar H_0}$, where $\beta = 1/T$ is the inverse of the temperature. It is convenient to introduce the frequency $\omega_0 = \gamma H_0$ (usually positive); for proton and $H_0 = 1Ts$ we get $\omega_0 = 2.7\times10^8Hz$

or $\nu_0 = \omega_0/2\pi = 4.3 \times 10^7 Hz$.

Therefore, on applying a constant external field H_0 directed along the z-axis the component M_z of the magnetization (magnetic moment of the unit volume) relaxes towards the lower energy state, where it acquires the mean value $M_0 = n\mu^2 H_0/3T$, n being the density of moments (the Curie law for the Langevin paramagnetism);[1] its kinetic equation reads

$$\frac{dM_z}{dt} = -\alpha_1(M_z - M_0) \ , \tag{5.1}$$

where α_1 is a damping (relaxation) coefficient; the solution is $M_z = M_0(1 - e^{-\alpha_1 t})$, for zero initial magnetization. The released energy goes to the environment, for instance to the solid lattice. Indeed, a change in magnetization gives rise to an electric field which acts upon the neighbouring ions and generates vibrations (phonons). Therefore, during the relaxation of the magnetization a phonon can be created, or a phonon can be inelastically scattered (phonon Raman scattering), or an electron (in metals) can be inelastically scattered, or various other processes may occur, by wich the magnetic energy is released to the environment. This is why α_1 is also called a spin-latice relaxation coefficient. In general, it depends on the temperature; usually, an uncertainty in energy is associated with T; for phonons we should note that their number goes like T^3 and their energy goes like T^4 , so that for Raman scattering we may have $\alpha_1 \sim T^7$; for other processes we may have other temperature-dependence laws.

The average transverse magnetization is vanishing; if, by external means, we take the transverse magnetization out of equilibrium ($M_{x,y0} \neq 0$ initially), it will relax according to

$$\frac{dM_x}{dt} = -\alpha_2 M_x \ , \ \frac{dM_y}{dt} = -\alpha_2 M_y \ , \tag{5.2}$$

where α_2 is a transverse damping coefficient; by contrast, α_1 is called the longitudinal damping coefficient. The solution is $M_{x,y} = M_{x,y0} \cdot \cdot e^{-\alpha_2 t}$. This relaxation does not imply an energy flow.

Let us consider that, besides the constant magnetic field H_0 oriented along the z-axis, we apply a transverse time-dependent magnetic field

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[1] M_0 is proportional to $N_{1/2} - N_{-1/2}$ for spin 1/2; in general, μ^2 in $M_0 = n\mu^2 H_0/3T$ is replaced by $[I(I+1)/I^2]\mu^2 = [(I+1)/I]\mu^2$.

$H_x(t) = H\cos\omega t$ along the x-direction. The equation of motion for the magnetization is Larmor's equation $\dot{\mathbf{M}} = \gamma(\mathbf{M}\times\mathbf{B})$ plus the relaxation terms; in the magnetic induction $\mathbf{B}$ we may keep only the magnetic field. The equations of motion are

$$\begin{gathered}\tfrac{dM_x}{dt} = \gamma M_y H_0 - \alpha_2 M_x\ ,\\ \tfrac{dM_y}{dt} = \gamma(M_0 H\cos\omega t - M_x H_0) - \alpha_2 M_y\ ,\\ \tfrac{dM_z}{dt} = -\gamma M_y H\cos\omega t - \alpha_1(M_z - M_0)\ .\end{gathered}\tag{5.3}$$

We assume the field H suficiently small as to replace M_z in the equations for M_x and M_y by a constant value M_0; at the same time we neglect the field contribution to the equation for M_z, since it is quadratic in field H. This way, the equations for $M_{x,y}$ are decoupled from the equation for M_z. In general, if we make abstraction of the damping coefficients, Larmor's equations imply $M = (M_x^2+M_y^2+M_z^2)^{1/2} = const$. The initial longitudinal magnetization M_z decreases on applying the field H, while the transverse magnetization increases, such as to preserve the total magnitude M constant. Consequently, and rigourously, M_0 in equations (5.3) is not the equilibrium value of the longitudinal magnetization. However, since the field H is small, we may disregard this small variation. This approximation, which amounts to a linearization of the Larmor equations, is known as the Holstein-Primakoff approximation, in a different context.[2] Introducing $\omega_0 = \gamma H_0$ and $\omega_s = \gamma M_0$, we get

$$\dot{M}_x = \omega_0 M_y - \alpha_2 M_x\ ,\ \dot{M}_y = -\omega_0 M_x + \omega_s H\cos\omega t - \alpha_2 M_y\ \ , \tag{5.4}$$

or

$$\begin{gathered}\ddot{M}_x + \omega_0^2 M_x + \alpha_2\dot{M}_x = \omega_0\omega_s H\cos\omega t\ ,\\ \ddot{M}_y + \omega_0^2 M_y + \alpha_2\dot{M}_y = -\omega\omega_s H\sin\omega t\ \ ,\end{gathered}\tag{5.5}$$

where we may neglect $\alpha_2 M_{x,y}$ since $\alpha_2 \ll \omega_0, \omega_s$. Equations (5.5) are equations of motion for damped harmonic oscillators. They are

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[2] T. Holstein and H.Primakoff, "Field dependence of the intrinsic domain magnetization of a ferromagnet", Phys. Rev. **58** 1098 (1940); the motion of the transverse magnetization can be quantized in magnons.

equivalent with the original equations (5.4) providing we redefine the small damping parameter α_2. The solution of equations (5.4) consists of free damped oscillations and forced damped oscillations. The free oscillations are given by

$$\begin{aligned} M_x &= (A_x \cos\omega_0 t + B_x \sin\omega_0 t)e^{-\alpha_2 t} \ , \\ M_y &= (-A_x \sin\omega_0 t + B_x \cos\omega_0 t)e^{-\alpha_2 t} \ , \end{aligned} \tag{5.6}$$

where A_x and B_x are constants. The particular solution is given by

$$\begin{aligned} M_x &= a\cos\omega t + b\sin\omega t \ , \\ M_y &= \tfrac{-a\omega+b\alpha_2}{\omega_0}\sin\omega t + \tfrac{b\omega+a\alpha_2}{\omega_0}\cos\omega t \ , \end{aligned} \tag{5.7}$$

where

$$\begin{aligned} a &= -\omega_0\omega_s H \tfrac{\omega^2-\omega_0^2-\alpha_2^2}{(\omega^2-\omega_0^2-\alpha_2^2)^2+4\omega^2\alpha_2^2} \ , \\ b &= \omega_0\omega_s H \tfrac{2\omega\alpha_2}{(\omega^2-\omega_0^2-\alpha_2^2)^2+4\omega^2\alpha_2^2} \ . \end{aligned} \tag{5.8}$$

We can simplify these solutions by assuming $\alpha_2 \ll \omega_0$, ω_s and ω close to ω_0. We get

$$M_x \simeq a\cos\omega t + b\sin\omega t \ , \ M_y \simeq -a\sin\omega t + b\cos\omega t \ , \tag{5.9}$$

where

$$a \simeq -\tfrac{1}{2}\omega_s H \tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha_2^2} \ , \ b \simeq \tfrac{1}{2}\omega_s H \tfrac{\alpha_2}{(\omega-\omega_0)^2+\alpha_2^2} \ . \tag{5.10}$$

The same solutions are obtained from the oscillator equations (5.5) with $\alpha_2 \to \alpha_2/2$ in equations (5.10). We can see that the magnetization performs a Larmor precession about the z-axis. The power absorbed from the field and dissipated by the motion of the transverse magnetization can be obtained from equations (5.5), through

$$\begin{aligned} \tfrac{d}{dt}\left(\tfrac{1}{2}\dot{M}_x^2 + \tfrac{1}{2}\omega_0^2 M_x^2\right) + \alpha_2\dot{M}_x^2 &= \omega_0\omega_s H\dot{M}_x\cos\omega t \ , \\ \tfrac{d}{dt}\left(\tfrac{1}{2}\dot{M}_y^2 + \tfrac{1}{2}\omega_0^2 M_y^2\right) + \alpha_2\dot{M}_y^2 &= -\omega_0\omega_s H\dot{M}_y\sin\omega t \ . \end{aligned} \tag{5.11}$$

We get

$$P = \overline{H\dot{M}_x \cos\omega t} = \frac{1}{2}Hb\omega = \frac{1}{4}\omega_s H^2 \frac{\omega\alpha_2}{(\omega-\omega_0)^2+\alpha_2^2} \qquad (5.12)$$

(where we left aside the damped oscillations).

These are typical solutions of damped harmonic oscillators exhibiting resonance for $\omega = \omega_0$. This is the nuclear magnetic resonance (NMR).[3] Equations (5.3) are called Bloch equations.[4] The nuclear magnetic resonance was suggested by Gorter.[5] It was previously used by Rabi and others to estimate the nuclear magnetic moments in molecular beam resonance.[6]

The constants A_x and B_x are determined from the initial conditions. We can see from equations (5.9) that the transverse magnetization rotates with constant magnitude $M_x^2 + M_y^2 \simeq a^2 + b^2 \simeq (\omega_s H/2\alpha_2)^2$. In the total magnetization M given by $M^2 = M_x^2 + M_y^2 + M_z^2 \simeq (\omega_s H/2\alpha_2)^2 + M_0^2$ we may neglect the H^2-term.

The Larmor equations discussed above are classical equations of motion for magnetization. With energy $-\mathbf{MH}$, where $\mathbf{H}$ is an external magnetic field, with $\mathbf{M} = \gamma\hbar\mathbf{I}$ and the commutation relations $[I_i, I_j] = i\varepsilon_{ijk}I_k$ for the spin operators we get the same equations of motion for $\mathbf{I}$ and for $\mathbf{M}$. For the constant field $\mathbf{H}_0$ these equations of motion are equivalent to the diagonalization of the energy $-\mathbf{MH}_0$;

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[3] E. M. Purcell, H. C. Torrey, R. V. Pound, "Resonance absorption by nuclear magnetic moments in a solid", Phys. Rev. **69** 37 (1946); F. Bloch, W. W. Hansen and M. Packard, "Nuclear induction", Phys. Rev. **69** 127 (1946); F. Bloch, W. W. Hansen and M. Packard, "The nuclear induction experiment", Phys. Rev. **70** 474 (1946).

[4] F. Bloch, "Nuclear induction", Phys. Rev. **70** 460 (1946).

[5] C. J. Gorter, "Paramagnetic relaxation", Physica **3** 503 (1936); "Negative result of an atempt to detect nuclear magnetic spins", Physica **3** 995 (1936); C. J. Gorter and L. J. F Broer, "Negative results of an attempt to observe nuclear magnetic resonance in solids", Physica **9** 591 (1942).

[6] See, for instance, J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, "An electrical quadrupole moment of the deuteron", Phys. Rev **55** 318 (1939); J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, "The magnetic moments of the proton and the deuteron. The radiofrequency spectrum of H_2 in various magnetic fields", Phys. Rev. **56** 728 (1939); J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, "An electrical quadrupole moment of the deuteron. The radiofrequency spectra of HD and D_2 molecules in a magnetic field", Phys. Rev. **57** 677 (1940).

the energy levels are $-\gamma\hbar H_0 m = -\hbar\omega_0 m$, where m is the quantum number of the component I_z. The external time-dependent field $H_x(t) = H\cos\omega t$, with an interaction hamiltionian $-\gamma\hbar I_x H\cos\omega t$ produces quantum transitions between states m and $m\pm1$, according to the selection rules for I_x. Usually, the states m are populated thermally, and the energy is absorbed from the field H in transitions from each m to $m+1$, separated by energy $\hbar\omega_0$. The absorbed energy can be computed from the corresponding transition probabilities, which involve the matrix element $(I_x)_{m,m+1}$. The result is a resonance spectral power of the form given by equation (5.12). This suggests that a quasi-classical dynamics may govern the motion of the magnetization. As it is well known, in a quasi-classical dynamics the matrix elements $O_{m,m+s}$ of an operator O depend slightly on m and fall off abruptly to zero for large s; this is consistent with the selection rules and one resonance line ω_0 in case of the NMR.

5.2 Emitted field

The absorbed power given by equation (5.12), exhibiting a resonance at $\omega = \omega_0$, can be used for identifying the resonance phenomenon. Similarly, the field emitted by the induced magnetization can also be used.

A magnetization $\mathbf{M}$ induces a current density $\mathbf{j} = c\cdot curl\mathbf{M}$, which, in turn, gives rise to a vector potential

$$\begin{aligned}\mathbf{A}(\mathbf{r},t) &= \tfrac{1}{c}\int d\mathbf{r}'\tfrac{\mathbf{j}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|} = \\ &= \int d\mathbf{r}'\tfrac{curl'\mathbf{M}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|}\ ,\end{aligned} \tag{5.13}$$

or

$$\mathbf{A}(\mathbf{r},t) = \int d\mathbf{r}'\frac{\mathbf{M}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)\times(\mathbf{r}-\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|^3}\ ; \tag{5.14}$$

in the quasi-static limit we may use $\mathbf{M}(\mathbf{r}',t)$; for $r \gg r'$ we may also take approximately

$$\mathbf{A}(\mathbf{r},t) = -v\mathbf{M}\times grad\frac{1}{r}\ , \tag{5.15}$$

where v is the volume of the magnetized body. We can see that it is the surface contribution which gives rise to this vector potential. Since $div\mathbf{A} = v\mathbf{M}curl \cdot grad(1/r) = 0$ we have a vanishing scalar potential $\Phi = 0$, in accordance with the fact that the magnetization current $\mathbf{j}$ has not an associated charge density. Similarly, the electric field $\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}$ can be neglected in the quasi-static limit; we are left with the magnetic field

$$\mathbf{H}_m = curl\mathbf{A} = 4\pi v\mathbf{M}\delta(\mathbf{r}) + v\frac{3\mathbf{r}(\mathbf{Mr}) - \mathbf{M}r^2}{r^5} \ , \tag{5.16}$$

which is a dipolar field. We can see that this field exhibits resonance through the transverse magnetization $\mathbf{M}$ given by equations (5.9) and (5.10).

The magnetic field given by equation (5.16) induces an electromotive force E_{em} in a coil placed in the neighbourhood of the magnetized body, according to Faraday's law

$$curl\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}_m}{\partial t} \ ; \tag{5.17}$$

for the flux of the component $H_{m,y}$ through the area S placed at the distance d we get the electromotive force

$$E_{em} \simeq -\frac{2v}{cd^3}S\frac{\partial M_y}{\partial t} = \frac{vS}{cd^3}\omega_0\omega_s H\frac{\Delta\omega\cos\omega t - \alpha_2\sin\omega t}{(\Delta\omega)^2 + \alpha_2^2} \ , \tag{5.18}$$

where $\Delta\omega = \omega - \omega_0$. It is worth noting the change of the phase $\tan\delta = \alpha_2/\Delta\omega$ on passing through the resonance frequency $\omega = \omega_0$.

5.3 Line width

The damping coefficient α_2 in the resonance formulae gives the resonance line width $\Delta\omega \simeq \alpha_2$. The coefficient α_2 originates mainly in residual interactions. For instance, the dipolar interaction between two magnetic moments μ separated by distance r gives a magnetic field $B_i \sim \mu/r^3$ (actually an internal magnetic field, *i.e.* a magnetic induction). For protons $\mu = 1.4 \times 10^{-23} erg/Gs$; for $r = 2\text{Å}$ we get $B_i \simeq 2Gs$. This field coresponds to a frequency $\alpha_2 = \gamma B_i \simeq$

$5 \times 10^4 Hz$. Comparing it with $\omega_0 = 10 MHz$, we can see that the resonance line is very sharp.

The magnetic moments may feel a field B_i (and a damping coefficient α_2) during a time τ; thereafter, being in motion, a magnetic moment feels a field $-B_i$ during a time $\overline{\tau}$, such that, over iregular successions of time intervals τ and $\overline{\tau}$, the magnetic moment feels a zero average field. Obviously, the effective field B_i and the damping coefficient α_2 are reduced by the factor $\alpha_2\tau$, where τ is the average relaxation time. Indeed, if in a "random walking" the phase is $\delta\Phi = \sum_{i=1}^{n} \delta\varphi_i$, then $\overline{(\delta\Phi)^2} = n(\delta\varphi)^2 = n(\gamma B_i \tau)^2$ and the reduced damping coefficient is $\alpha_2^{'} = \overline{(\delta\Phi)^2}/n\tau = (\gamma B_i)^2\tau = \alpha_2(\alpha_2\tau)$. The reduction of the line width due to the motion of the magnetic moments (the diffusion of the magnetic moments[7]) is known as the motional narrowing.[8] The effect increases with increasing temperature and is more visible in liquids. For instance, the relaxation time of the rotational motion of water molecules is $\simeq 10^{-10}s$; for $\alpha_2 = 10^5 Hz$ we have $\alpha_2^{'} = 1Hz$, which is an appreciable reduction.

The motional narrowing is due to interactions, not to collisions. For instance, a paramagnet has an exchange interaction J between the electron spins of neighbouring atoms; then $\hbar/J$ acts as a "relaxation" time τ, and the damping coefficient α_2 is reduced by the factor $\alpha_2\tau = \alpha_2\hbar/J$. This is known as the exchange narrowing.

5.4 Hyperfine splitting

The electronic energy levels in atoms (ions) are split by the fine interaction originating in relativistic effects. The aditional interaction of the electrons with the nucleus is called hyperfine interaction. It originates in the magnetic field generated by the electron and acting upon the nucleus, and in the electron motion, on one side, and, on the other, in the magnetic field (and electric field) generated by the nucleus and acting upon the electrons. The magnetic field of the electron

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[7] H. C. Torrey, "Bloch equations with diffusion terms", Phys. Rev. **104** 563 (1956).

[8] N. Bloembergen, E. M. Purcell and R. V. Pound, "Relaxation effects in nuclear magnetic resonance absorption", Phys. Rev. **73** 679 (1948).

is produced by the electronic orbital and spin currents. The orbital currents give a weak field, because they are away from the nucleus; but the spin current for zero orbital momentum (s state) is located just on the nucleus; this is the contact hyperfine interaction.

An electron is localized over its Compton length $\lambda = \hbar/mc$ ($3.8 \times 10^{-11} cm$); it produces a magnetic moment $\mu_B = \frac{|e|}{2c} c\lambda = \frac{|e|\hbar}{2mc}$, which is the Bohr magneton. The current is $I = |e|\, c/\lambda$; it produces a magnetic field $H = I/c\lambda = |e|\,/\lambda^2$; the nucleus sees the fraction $|\psi(0)|^2\, \lambda^3$ of the electron, where ψ is the electron wavefunction; the effective magnetic field is $H = |e|\, |\psi(0)|^2\, \lambda \simeq \mu_B\, |\psi(0)|^2$. The corresponding Zeeman energy is $U = -\mu H = -\mu\mu_B\, |\psi(0)|^2$ or, since the magnetic moment of the nucleus is $\mu = \gamma\hbar I$ and the electron field is oriented with respect to the spin S, $U \simeq -\gamma\hbar\mu_B\, |\psi(0)|^2\, \mathbf{IS}$, where $\mathbf{I}$ is the nuclear spin and $\mathbf{S}$ is the electron spin; we can see that $\mu_B\, |\psi(0)|^2$ is a magnetic field, $\gamma\mu_B\, |\psi(0)|^2$ is a frequency and $a = \gamma\hbar\mu_B\, |\psi(0)|^2$ is an energy; the contact hyperfine interaction is written as $U = -a\mathbf{IS}$. For hydrogen, for instance, $a \simeq 500Gs$, corresponding to $\simeq 1420MHz$. This is seen in the radiofrequency line of the interstellar (atomic) hydrogen.

The fine splitting corresponds to $S_z = \pm 1/2$; the hyperfine interaction splits each of the two $S_Z = \pm 1/2$ levels into other I_z levels; for instance, for $I = 1/2$ we have the levels $S_z = 1/2$, $I = \pm 1/2$ and $S_z = -1/2$, $I_z = \pm 1/2$.

A missing negative ion in alkali halides may leave behind a trapped electron; this is a colour center (F center); the electron interacts hyperfinely with the neighbouring ions, leading to many split levels; the corresponding transitions can be seen in magnetic resonance, which, this time, is called paramagnetic resonance (or electron spin resonance).[9] Similarly, a donor atom, like phosphorus in silicon, exhibits a paramagnetic electron, whose spin levels are split by the hyperfine interaction with the surrounding atoms. The transitions can be seen in spin (paramagnetic) resonance (together with motional narrowing).

In metals, the conduction electrons can give rise to a hyperfine interaction $-aI_z\overline{S}_z$, so that, the nuclear momentum sees an energy $-\gamma\hbar H_0 I_z - a\overline{S}_z I_z$, where H_0 is the external field and S_z is the elec-

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[9] E. J. Zavoisky, "Spin magnetic resonance in the decimetre-wave region", J. Phys. U. S. S. R. **10** 197 (1946).

tron spin component oriented along the z-axis; the average value $\overline{S}_z$ is related to the external field by Pauli spin magnetization $M_z = gN\mu_B\overline{S}_z = \chi_s H_0$, where N is the number of electrons; it follows the Zeeman energy $-\gamma\hbar H_0 I_z - a\overline{S}_z I_z = -\gamma\hbar(1 + a\chi_s/g\gamma\hbar N\mu_B)I_z H_0$; we can see that the external field suffers a shift $\Delta H_0/H_0 = a\chi_s/g\gamma\hbar N\mu_B$ due to the hyperfine coupling of the nuclear momentum with the spin of the conduction electrons. This is known as the Knight shift.[10] The interaction of the nuclear spin with induced electron orbital moment gives rise to another frequency shift, known as chemical shift.[11]

5.5 Ferromagnetic resonance

The magnetization of a ferromagnet can be aligned by a static external field and a transverse (usually large) magnetization can be induced by an external radiofrequency (microwaves) field to precess about the aligned magnetization. Very often, magnons are generated before reaching a regular precession. The exchange interaction may narrow appreciably the resonance line; the (de-) magnetization factors should be taken into account, since the magnetization is large.[12]

The exchange interaction between spins should be included in the Bloch equations, especially in thin ferromagnetic films;[13] this interaction acts as a local field which implies the spatial derivatives of the magnetization, so it is convenient to use spatial Fourier transforms; the wavevector is related to the thickness of the film.

Similarly, magnetic resonance can be seen in antiferromagnets,[14] or in other magnetic structures; in all cases the local fields must be carefully

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[10] C. W. Townes, C. Herring and W. D. Knight, "The effect of electronic paramagnetism on nuclear magnetic resonance frequencies in metals", Phys. Rev. **77** 852 (1950).

[11] N. F. Ramsey, "Magnetic shielding of nuclei", Phys. Rev. **78** 699 (1950); "Chemical effects in nuclear magnetic resonance and in diamagnetic susceptibility", Phys. Rev. **86** 243 (1952).

[12] C. Kittel, "Interpretation of anomalous Larmor frequencies in ferromagnetic resonance experiment", Phys. Rev. **71** 270 (1947); "On the theory of ferromagnetic resonance absorption", Phys. Rev. **73** 155 (1948).

[13] C. Kittel, "Excitation of spin waves in a ferromagnet by a uniform rf field", Phys. Rev. **110** 1295 (1958).

[14] C. Kittel, "Theory of antiferromagnetic resonance", Phys. Rev. **82** 565 (1951).

estimated.

5.6 Classical quasi-particles

The magnetic resonance involves classical dynamics of the classical magnetization, although the origin of magnetization resides in the quantum spins and quantum magnetic moments; the magnetic resonance suggests a classical behaviour of the magnetization in condensed matter. The quasi-classsical dynamics is a more general feature in condensed matter.

Consider a piece of classical (normal) condensed matter, consisting of particles (molecules), usually at thermal equilibrium, at least locally. By "classical" (or "normal") we mean that the particles are sufficiently heavy, or we are at a sufficiently high temperature, that the particles trajectories exist and they can be approximated by classical paths; or there are elementary excitations densely distributed in energy. In contrast, the constituents of quantum condensed matter, like superfluids, superconductors, ferromagnetics, have quantum entangled trajectories and are macroscopically condensed on quantum states. The constituents of a classical piece of matter, while moving classically, may still have a quantum internal dynamics, which, approximately, is representable in classical terms.

The interaction between particles in condensed matter leads usually to elementary excitations, either quasi-particles, more or less localized, or extended, delocalized, collective excitations (waves); then, the condensed matter reduces to a collection of such elementary excitations, which we may call also "particles".

Let $\varphi_n(x)$ be the wavefunctions of the stationary states of energy ε_n for such a particle with coordinates (spin included) denoted generically by x. We can represent the wavefunction $\varphi_n(x)$ as $\varphi_n(x) = c_n(x)e^{i\Phi_n(x)}$, using an amplitude c_n and a phase Φ_n. If there exists at least one more measurable quantity A, then we have $A(x)\varphi_n(x) = a_n\varphi_n(x)$, so that we can have the representation $\varphi_n(x) = c_n e^{ia_n x}$ and $A(x) = -i\frac{\partial}{\partial x}$, where c_n is a constant and the phase $\Phi_n(x)$ is $\Phi_n(x) = a_n x$. The notation $a_n x$ means a scalar product if x is a vector and the eigenvalues a_n are also vectors.

Usually, the condensed matter exhibits a relevant behaviour at the macroscopic level, and, consequently, we are interested in a description of the condensed matter at the macroscopic level. A macroscopic-level description means to consider a large number N of particles around any point in matter and to average the physical properties over that number of particles; the resulting average is assigned to that point. Being condensed, the spatial region where all those N points reside is small enough to allow us to consider it as a point. We can see that such a picture may apply to usual solids, liquids, dense gases, etc; for instance, this is the well-known macroscopic-average picture of the classical Electromagnetism (and, in general, of classical Physics) (it may also be termed "coarse graining").

The assembly of N particles is described by the wavefunction

$$\begin{gathered}\psi_{n_1 n_2 ... n_N}(x_1, x_2, ...x_N) = c_{n_1}(x_1)...c_{n_N}(x_{n_N})\cdot \\ \cdot e^{i[\Phi_{n_1}(x_1)+...+\Phi_{n_N}(x_N)]-i(\omega_{n_1}+...\omega_{n_N})t} \ ,\end{gathered} \tag{5.19}$$

where $\omega_{n_i} = \varepsilon_{n_i}/\hbar$, $i = 1, 2, ...N$; if the particles are disentangled, we need not a symmetrization in case the particles are identical; if symmetrized (when entangled), we have a phase $\Phi_{n_1...n_N}(x_1, ...x_N)$, an amplitude $c_{n_1...n_N}(x_1, ...x_N)$ and an energy $E_{n_1...n_N}$, which are not separable (factorizable). For convenience, we use $\Phi_{n_i} = a_{n_i} x_i$ and introduce the notations

$$\begin{gathered}c_{n_1}...c_{n_N} = c_n \ , \ a_{n_1}x_1 + ... + a_{n_N}x_N = a_n x \ , \\ \omega_{n_1} + ...\omega_{n_N} = \omega_n \ ,\end{gathered} \tag{5.20}$$

where $n = (n_1, n_2, ...n_N)$ and $a_n x$ is the notation for the scalar product of the corresponding vectors with N components. The wavefunction given by equation (5.19) can be written as

$$\Psi_n(x, t) = c_n e^{i(a_n x - \omega_n t)} \ . \tag{5.21}$$

The basic observation is that, for large N, there is a multitude of states $n = (n_1, n_2, ...n_N)$, which differ from one another at least by the smallest change in one n_i, which are very close to each other in energy and whose wavefunctions are also very close to each other;

most of them are degenerate; these states from a continuum of states. Under these circumstances, the actual behaviour of the assembly is described by a superposition

$$\Psi(x,t) = \int dnc_n e^{i(a_n x - \omega_n t)} \ , \tag{5.22}$$

where we may use a series expansion in powers of $n-n_0$ around some fixed n_0, because c_n, a_n and ω_n vary slowly; and we may extend the integration over the whole space, since there is a large multitude of such continuum states. As it is well known, this is the standard technique of wavepackets. Therefore, we may use

$$\begin{gathered} c_n = c_0 + nc_1 + n^2 c_2 ... \ , \ a_n = a_0 + na_1 + n^2 a_2 + ... \ , \\ \omega_n = \omega_0 + n\omega_1 + n^2\omega_2 + ... \ , \end{gathered} \tag{5.23}$$

where we have chosen $n_0 = 0$ for convenience; of course, products like nc_1 should be read as the scalar product $n_i c_{1i}$, and products like $n^2 a_2$ are to be read as quadratic forms $n_i n_j a_{2ij}$, $i,j = 1, 2., ...N$. For a general phase $\Phi_n(x)$ we have

$$\Phi_n(x) = \Phi_0(x) + n\Phi_1(x) + n^2\Phi_2(x) + ... \ . \tag{5.24}$$

Therefore, the wavepacket becomes

$$\begin{gathered} \Psi(x,t) = e^{i(a_0 x - \omega_0 t)} \int dn(c_0 + nc_1 + ...) \cdot \\ \cdot e^{i(a_1 x - \omega_1 t)n + i(a_2 x - \omega_2 t)n^2 + ...} \ . \end{gathered} \tag{5.25}$$

The leading contribution to this integral gives $\Psi(x,t) \simeq \delta(a_1 x - \omega_1 t)$. This is a localized wavepacket which goes as a classical "particle" along a classical path given by $a_1 x - \omega_1 t = 0$ (in general, $\Phi_1(x) - \omega_1 t = 0$). The probability of localization given by $|\Psi|^2 \sim \delta^2(a_1 x - \omega_1 t)$ is, in fact, $\sim \Delta n \delta(a_1 x - \omega_1 t)$ since the δ-function is localized over a phase $\Delta(a_1 x - \omega_1 t) \sim 1/\Delta n$, where Δn is the range of the continuum of states n. We can see that indeed the localization is substantial, both in depth and breath, giving a satisfactory classical picture.

The next-to-leading contributions to the integral in equation (5.25) bring additional features. The most interesting one is the contribution of the n^2-term in the exponent, which leads to a gaussian; the coefficients c_n in equation (5.22) may include also possible degeneracies; such factors, along with the gaussian factors, contribute terms which decrease as the time increases. Indeed, we can see from equation (5.25) that the integral decreases as the time increases, due to rapid oscillations of the integrand. We can say that the wavepacket decays in a certain characteristic duration τ of the time, which can be taken as the lifetime of the wavepacket. During this time the assembly of N particles may move, so we have also a mean free path; the assembly of N particles, with a classical dynamics, a finite lifetime and a finite mean free path, defines an elementary excitation, or a (classical) quasi-particle; it is characterized by the label n_0. Being at thermal equilibrium, after death, the n_0-elementary excitation resurrects, in general with another n_0. Of course, the time of establishing the thermal equilibrium (the "lifetime of the fluctuations") should be shorter than the lifetime of the elementary excitations. The thermal equilibrium, the transport and the response to external perturbations in condensed matter proceed by such elementary excitations (quasi-particles). Such elementary excitations are the mechanical modes of motion of complex assemblies like the assembly of N particles considered here. It is worth noting that integrating over quantum states n in the wavepacket and having an arbitrary n_0 amounts to going over from a quantum-mechanical description to a classical one; in addition, the integration over many quantum states amounts to taking into account processes which imply a large amount of mechanical action, *i.e.* many quanta $\hbar$ of action, which means indeed the classical limit $\hbar \to 0$ of the Quantum Mechanics.

The spin of the assembly of N particles, where N is very large, may vary from small values to high values; the small values are beyond our macroscopic scale, the large ones make the spin a classical angular moment. In the absence of other specific interactions the spin of the classical, macroscopic elementary excitations remains undetermined. In case of spatial disentanglement the notion of quantum statistics remains irrelevant for the macroscopic elementary excitations. Usually, the angular momenta are quenched in condensed matter. In case of entanglement, like, for instance, the electrons in condensed matter, which, due to their natural spatial delocalization, behave quantum-mechanically, wavepackets can also be constructed, more or less localized. The essential thing in the classical, macroscopic description of condensed matter is the existence of densely distributed energy levels (and wavefunctions). For quantum condensed matter, where, at low temperature, the particles condense on a single quantum state, such a classical description is not valid.

We can see from the above treatment that the construction of a wavepacket and, implicitly, of a classical dynamics for macroscopic, elementary excitations, is based on the existence of a continuum of states n which allows a continuous and slow variation and an expansion in powers of $n - n_0$ around some n_0. Consider an operator $O(x_1, x_2, ...x_N) = \sum_{i=1}^{N} O_i(x_i)$ pertaining to the assembly of N particles, or its density $N^{-1}\sum_{i=1}^{N} O_i(x_i)$. The equation of motion $\dot{O} = \frac{i}{\hbar}[H, O]$ of such an operator reads

$$\begin{gathered}\dot{O}_{nm} = \tfrac{i}{\hbar}(E_n - E_m)O_{nm} \ , \\ \dot{O}_{nm} = i\omega_{nm}O_{nm} \ , \ \ddot{O}_{nm} + \omega_{nm}^2 O_{nm} = 0 \ , \end{gathered} \tag{5.26}$$

where we can recognize the equation of a harmonic oscillator. We write $m = n + s$ and $\omega_{nm} = -s\omega_{1n} + ...$, where $-s\omega_{1n}$ is the leading term in the expansion in powers of s of $\omega_n - \omega_{n+s} = (E_n - E_{n+s})/\hbar$. The matrix element of the operator O can be written as

$$O_{n,n+s} \simeq c_n^* c_{n+s} \int dx e^{-ia_n x} O(x) e^{ia_{n+s}x} \cdot e^{-is\omega_{1n}t} \ ; \tag{5.27}$$

we can see that $s\omega_{1n}$ is a frequency ω_s, corresponding to (n, s); with the notation

$$O_{n,n+s} = O_s e^{-i\omega_s t} \tag{5.28}$$

the matrix elements of the operator O reduce themselves to the temporal Fourier components of a classical quantity $O(t)$. The quantum behaviour remains embedded in

$$O_s = c_n^* c_{n+s} \int dx e^{-ia_n x} O(x) e^{ia_{n+s}x} \tag{5.29}$$

which has a slow dependence on n. The equations of motion (5.26) become

$$\dot{O}_s = -i\omega_s O_s \ , \ \ddot{O}_s + \omega_s^2 O_s = 0 \ , \tag{5.30}$$

where $O = O(t) = O_s e^{-i\omega_s t}$. We note that O is hermitian, $O^*_{-s} = O_s$, $\omega_{-s} = \omega_s$. For O_s real, the equation $\dot{O}_s = -i\omega_s O_s$ is equivalent with equation $\dot{O}_s = i\omega_s O_s$, such that we have the harmonic-oscillator equation $(\frac{d}{dt} + i\omega_s)(\frac{d}{dt} - i\omega_s)O_s = \ddot{O}_s + \omega_s^2 O_s = 0$. We can also denote $-iO_s = Q_s$ and get $\dot{O}_s = \omega_s Q_s$ and $\dot{Q}_s = -i\dot{O}_s = -\omega_s O_s$, hence $\ddot{O}_s = -\omega_s^2 O_s$. The classical limit described here is made possible by using the leading terms in the expansions in powers of the state labels, which in turn is made possible by the existence of a slowly varying continuum of states. In condensed matter this is practically always possible locally.

5.7 Quasi-classical dynamics

Consider a sample of condensed matter consisting of composite particles (*e.g.* molecules, molecular structures, atomic nuclei, fine grains, etc). In many cases these particles move around fixed positions, as in solids, or move along classical trajectories, as in classical liquids or gases, such that, when identical, their motion is not entangled and we may consider them as being discernable. We assume that the particles are endowed with an internal dynamics, given in terms of generalized coordinates x_i, $i = 1, 2, ...N$ (spin included), a hamiltonian $H = \sum_{i=1}^N h_i(x_i)$ and wavefunctions $\varphi_{n_i}(x_i)$, $h_i\varphi_{n_i}(x_i) = \varepsilon_{n_i}\varphi_{n_i}(x_i)$, where N is the particle number and ε_{n_i} are the particle energies; the coordinates x_i may denote a vector associated to the i-th particle, like for translations, rotations or vibrations in the three-dimensional space, n_i denoting the corrresponding quantum numbers. We assume that each particle has its own internal motion, independent of the motion of other particles, such that the total energy is $E_{\mathbf{n}} = \sum_{i=1}^N \varepsilon_{n_i}$ and the wavefunctions of the assembly of N particles can be written as $\varphi_{\mathbf{n}}(x_1, ...x_N) = \varphi_{\mathbf{n}}(\mathbf{x}) = \prod_{i=1}^N \varphi_{n_i}(x_i)$, where $\mathbf{n} = (n_1, n_2, ...n_N)$ and $\mathbf{x} = (x_1, x_2, ...x_N)$; since the internal coordinates are disentangled from each other, there is no need for symmetrization when particles are identical.

The number N can be the number of particles in the sample, but we can also consider an arbitrary position $\mathbf{r}$ in the sample and $N(\mathbf{r}, t)$ particles around this position at one moment of time t; then, the energy $E_{\mathbf{n}}$, the wavefunctions $\varphi_{\mathbf{n}}$ and the dimension of the vector $\mathbf{n}$ depend on $\mathbf{r}$ and t through $N(\mathbf{r}, t)$. An average over all these particles around any position $\mathbf{r}$ at any moment of time t provides a continuum model of matter; within such a model the physical properties depend on the position $\mathbf{r}$ and the time t. This is one of the basic assumption of all the classical physics, like elasticity, fluids, electromagnetism, statistical physics, etc.

Consider two vectors $\mathbf{n} = (n_1, ...n_i...n_N)$ and $\mathbf{n}^{'} = (n_1, ...n_i^{'}...n_N)$ which differ by two values n_i, $n_i^{'}$ of the quantum number of the i-th particle. For any reasonable difference $n_i^{'} - n_i$ and N very large ($N \gg 1$) the two vectors $\mathbf{n}$ and $\mathbf{n}^{'}$ differ slightly from each other; this holds also for the energies $E_{\mathbf{n}}$, $E_{\mathbf{n}'}$ and for the wavefunctions $\varphi_{\mathbf{n}}$, $\varphi_{\mathbf{n}'}$. For $N \gg 1$ there exists a large number of states $\mathbf{n}$ (which grows exponentialy with N), many of them degenerate, which are densely distributed in energy and wavefunctions. For instance, we can represent the energy as $E_{\mathbf{n}} = \sum_{i=1}^{N} \varepsilon_{n_i} = N\overline{\varepsilon}_{n_i}$ and the energy variation as $\delta E_{\mathbf{n}} = \delta\overline{\varepsilon}_{n_i}$ for some n_i, and we have $\delta E_{\mathbf{n}}/E_{\mathbf{n}} < 1/N \ll 1$ for $N \gg 1$. In quantum processes, the uncertainty $\delta E_{\mathbf{n}}$ in energy and the uncertainty δt in time duration are related through $\delta E_{\mathbf{n}}\delta t \simeq \hbar$, while $\Delta E_{\mathbf{n}} = N\delta E_{\mathbf{n}}$ and $\Delta E_{\mathbf{n}}\delta t \simeq N\hbar \gg 1$, which shows that the averaging process over a macroscopic number of particles leads to a classical dynamics. A similar "classical" uncertainty relation holds also for momentum and coordinate, as a consequence of the coarse graining procedure of macroscopic averaging described here.

Under these circumstances the relevant wavefunctions are superpositions of the type

$$\psi_{\mathbf{n}_0}(\mathbf{x}, t) = \int d\mathbf{n}\varphi_{\mathbf{n}}(\mathbf{x})e^{-\frac{i}{\hbar}E_n t} = \int d\mathbf{n}c_{\mathbf{n}}(\mathbf{x})e^{i[\Phi_{\mathbf{n}}(\mathbf{x}) - \omega_{\mathbf{n}}t]} \quad , \qquad (5.31)$$

where we introduced the modulus $c_n(\mathbf{x})$ and the phase $\Phi_n(\mathbf{x})$ of the wavefunctions $\varphi_{\mathbf{n}}(\mathbf{x})$, and denoted by $\omega_{\mathbf{n}} = E_{\mathbf{n}}/\hbar$ the frequency corresponding to the energy $E_{\mathbf{n}}$; the integration in equation (5.31) extends over a large domain around an arbitrary value $\mathbf{n}_0$ of the quantum numbers. Since the quantities in equation (5.31) are slowly varying functions of $\mathbf{n}$ we may use the series expansions

$$\begin{aligned} c_{\mathbf{n}} &= c^{(0)} + \mathbf{s}\mathbf{c}^{(1)} + s_i s_j c^{(2)} + \ldots \; , \\ \Phi_{\mathbf{n}} &= \Phi^{(0)} + \mathbf{s}\mathbf{\Phi}^{(1)} + s_i s_j \Phi^{(2)}_{ij} + \ldots \; , \\ \omega_{\mathbf{n}} &= \omega^{(0)} + \mathbf{s}\omega^{(1)} + s_i s_j \omega^{(2)}_{ij} + \ldots \; , \end{aligned} \tag{5.32}$$

where $\mathbf{s} = \mathbf{n} - \mathbf{n}_0$. Equation (5.31) becomes

$$\begin{aligned} \psi_{\mathbf{n}_0}(\mathbf{x},t) \simeq e^{i[\Phi^{(0)}(\mathbf{x})-\omega^{(0)}t]} \int d\mathbf{s}[c^{(0)}(\mathbf{x}) + \ldots] \cdot \\ \cdot e^{i\mathbf{s}[\mathbf{\Phi}^{(1)}(\mathbf{x})-\omega^{(1)}t]+is_i s_j[\Phi^{(2)}_{ij}-\omega^{(2)}_{ij}t]} \; , \end{aligned} \tag{5.33}$$

and, in the first approximation, we get

$$\begin{aligned} \psi_{\mathbf{n}_0}(\mathbf{x},t) \simeq c^{(0)}(\mathbf{x}) e^{i[\Phi^{(0)}(\mathbf{x})-\omega^{(0)}t]} \int d\mathbf{s} e^{i\mathbf{s}[\mathbf{\Phi}^{(1)}(\mathbf{x})-\omega^{(1)}t]} \simeq \\ \simeq (2\pi)^N c^{(0)}(\mathbf{x}) e^{i[\Phi^{(0)}(\mathbf{x})-\omega^{(0)}t]} \delta(\mathbf{\Phi}^{(1)}(\mathbf{x}) - \omega^{(1)}t) \; ; \end{aligned} \tag{5.34}$$

we can see that the wavefunction superposition is a localized wavepacket with a classical trajectory given by $\mathbf{\Phi}^{(1)}(\mathbf{x}) - \omega^{(1)}t = grad_{\mathbf{n}}\Phi(\mathbf{x}) - \omega^{(1)}t = 0$. Due to the large number of particles, the local, (free) internal motion in condensed matter is a classical motion. For instance, if the coordinates $\mathbf{x}$ are the angles of free rotations with angular frequency ω, then the phase is $\Phi_{\mathbf{l}} = \mathbf{l}\mathbf{x}$, the energy is $E_{\mathbf{l}} = \frac{1}{2}\hbar\mathbf{l}\omega$, the derivatives in the expansions given by equations (5.32) are taken with repect to the componens of the vector $\mathbf{l} = (\mathbf{l}_1, \mathbf{l}_2, \ldots \mathbf{l}_N)$, where $\mathbf{l}$ is the angular momentum, and the equations of motion are the classical equations $\mathbf{x} = \omega t$ of free rotations. If the internal motion consists of vibrations, then the wavepacket does not propagate, but, instead, it reduces to a local, classical vibration; if the internal motion is rotation of electric dipoles or magnetic moments, it reduces to classical motion of spatial rotators; if the internal motion is that of electric charges and currents in atomic nuclei, then, in condensed matter, it reduced to classical motion of local charges and currents; etc.

As it is well known, the next-order approximation to equation (5.33) involves the quadratic terms in s_i which leads to (imaginary) gaussians with pre-factors proportional to $t^{-N/2}$ at least. With increasing time the gaussians oscillate rapidly and the wavepacket flattens, gets delocalized, and, consequently, has a finite lifetime (and a mean free path if propagating). In this context, we may speak of classical quasi-particles which govern the internal motion in condensed matter; apart from finite lifetimes and mean free paths, the quasi-particles are characterized by arbitrary vectors $\mathbf{n}_0$ around which the wavepackets are constructed. In the first approximation, the wavefunctions of the quantum states which form the quasi-particles can be written as

$$\chi_{\mathbf{n}_0,s}(\mathbf{x},t) \simeq c^{(0)}(\mathbf{x})e^{i[\Phi^{(0)}(\mathbf{x})-\omega^{(0)}t]} \cdot e^{i\mathbf{s}[\mathbf{\Phi}^{(1)}(\mathbf{x})-\omega^{(1)}t]} \tag{5.35}$$

(up to a normalization constant), where $c^{(0)}$, $\Phi^{(0)}$, $\mathbf{\Phi}^{(1)}$, $\omega^{(0)}$ and $\omega^{(1)}$ depend slightly on $\mathbf{n}_0$. A particular situation in this context is offered by the harmonic oscillators whose wavefunctions are real and the frequencies are linear in the quantum numbers. A superposition of such wavefunctions yields an oscillating (vibrating) localized wavepacket; however, it is important to realize that there still exists the continuum of states and energies for a macroscopic set of such N oscillators.

It is easy to see that the above considerations can be extended to interacting internal motions as well as to the external motion of the particles in (normal) condensed matter. Indeed, around any arbitrary position in a condensed matter sample we consider N particles described by a wavefunction $\varphi_{\mathbf{n}}(\mathbf{x}) = \varphi_{n_1 n_2 ... n_N}(x_1, x_2, ...x_N)$ with an energy $E_{\mathbf{n}} = E_{n_1 n_2 ... n_N}$, where the quantum numbers n_1,n_2,...n_N are allowed to take values in a reasonably large range. Under such conditions we have a large multitude of quantum states, most of them degenerate, densely distributed in energy and wavefunctions; such states form quasi-particle wavepackets whose motion, like (limited) free translations and rotations in the case of "external" motion, turns out to be a classical motion. All what is necessary for such a picture to hold is the existence of individual quantum numbers n_1, n_2, ...n_N; it is not necessary to have individual wavefunctions φ_{n_i}, nor energy levels ε_{n_i}, $i = 1, 2, ...N$, and, moreover, the symmetrization of the wavefunction for identical particles does not produce any difficulty. Consequently, the description may apply to both internal and external interacting motion of individual particles with individual quantum numbers.

Usually, the interaction between the internal degrees of freedom or the interaction between particles in their motion relative to one another in condensed matter lead to (quantum) elementary excitations, which are either quasi-particles, like quasi-electrons, polarons, etc, or collective, correlated elementary excitations like phonons, magnons, plasmons, etc. When localized, we may form locally sets of N quasi-particles and apply the above formalism of coarse graining, which leads to a classical dynamics. When delocalized, and labelled by wavevectors $\mathbf{k}$, we can form superpositions of such $\mathbf{k}$-quasi-particles, which again leads to localized wavepackets and a classical dynamics. The colective excitations are usually propagating waves labelled by wavevectors $\mathbf{k}$ (or global vibrations like the volume plasmons); usually, each of these $\mathbf{k}$-wave obeys a harmonic-oscillator dynamics, with quantum numbers $n_{\mathbf{k}}$. We can form sets of such $\mathbf{k}$-waves, say $\mathbf{k}_1, \mathbf{k}_2, ...\mathbf{k}_N$, in the vicinity of some $\mathbf{k}$, and consider harmonic-oscillator states labelled by $n_{\mathbf{k}_1}, n_{\mathbf{k}_2}, ...n_{\mathbf{k}_N}$, which lead again to a classical dynamics; this time, the classical quasi-particles are localized in the $\mathbf{k}$-space (and delocalized in the direct space, *i.e.* they retain, in general, their wavelike character; a more appropriate term for them might be classical "quasi-waves"). The wavepackets for harmonic oscillators are, in general, oscillating (vibrating, not propagating) wavepackets, but what is essential in this picture is the fact that there exist energies $E_{n_{k_1}...n_{k_N}} = \hbar(\omega_{k_1} n_{k_1} + \omega_{k_N} n_{k_N})$ which are densely distributed over the states n_{k_1}, n_{k_N} and, similarly, densely-distributed wavefunctions.

A notable exception from the picture described above is provided by the quantum condensed matter ("condensates"), *i.e.* quantum "liquids" like superfluids, superconductors, ferromagnetics, etc, where the particles condense macroscopically on a single quantum state (or a few), at low temperature. The adjective "normal" is used to differentiate the usual condensed matter from the quantum condensed matter. In normal condensed matter the wavefunctions and energy levels have a limited validity, due, on one side, to the large number of states densely distributed in energy, to the natural uncertainties arising from internal, residual interactions and, on the other side, to the inevitable interaction with the external world, which makes practically impossible the preparation of a pure quantum state. In fact, mixed states described by the density matrix, or thermodynamic states described by the statistical matrix are appropriate for condensed matter, exhibiting, to a large extent, a classical behaviour.

An arbitrary physical quantity $F(\mathbf{x})$ can be defined as a local one-particle operator $F(\mathbf{x}) = \sum_{i=1}^{N} f_i(x_i)$ for the set of N particles discussed above and a density $F(\mathbf{x})/N$ can be employed. Suitable extensions, like two-particle operators, can be introduced similarly. Consider an external field which couples to condensed matter, like, for instance, the coupling of the electromagnetic, electric or magnetic fields to electric charges and currents, electric dipoles, or, respectively, magnetic moments.

An external perturbation $h(x,t)$ changes the unperturbed wavefunctions
$\psi_n(x,t) = g_n\varphi_n(x)e^{-\frac{i}{\hbar}E_n t}$ into perturbed wavefunctions

$$\widetilde{\psi}_n = \widetilde{g}_n\varphi_n(x)e^{-\frac{i}{\hbar}E_n t} + \sum_k{}' c_{kn}\varphi_k e^{-\frac{i}{\hbar}E_k t} \quad , \tag{5.36}$$

where the prime over summation means $k \neq n$; in order to simplify the notation we write simply n instead of bold $\mathbf{n}$ for the state label and, for technical reasons, we introduce the weights g_n, $\sum_n |g_n|^2 = 1$, which help us get the density matrix. Indeed, the mean value

$$\overline{F} = \sum_{nm}(\psi_n, F\psi_m) = \sum_{nm} g_n^* g_m F_{nm} e^{i\omega_{nm}t} \tag{5.37}$$

of an arbitrary physical quantity F, where $\hbar\omega_{nm} = E_n - E_m$, shows that $g_n^* g_m \to \rho_{mn}$ is a representation (of pure states) for the density matrix ρ_{mn}. The statistical matrix $w_n = e^{-\beta E_n}/\sum_n e^{-\beta E_n}$, where $\beta = 1/T$ is the inverse of the temperature T, is diagonal (in the energy representation) and corresponds to $g_n^* g_n \to \rho_{nn} \to w_n$ ($\sum_n e^{-\beta E_n}$ is the free energy). The Schrodinger equation $i\hbar\frac{\partial\widetilde{\psi}}{\partial t} = (H+h)\widetilde{\psi}$ leads to

$$\begin{aligned} i\hbar\dot{\widetilde{g}}_n &= \widetilde{g}_n h_{nn}(t) + \textstyle\sum_k' c_{kn}h_{nk}(t)e^{i\omega_{nk}t} \quad , \\ i\hbar\dot{c}_{kn} &= \widetilde{g}_n h_{kn}e^{i\omega_{kn}t} + \textstyle\sum_{k'}' c_{k'n}h_{kk'}e^{i\omega_{kk'}t} \quad , \end{aligned} \tag{5.38}$$

and, in the first order of the perturbation theory, we have

$$\widetilde{g}_n = g_n e^{-\frac{i}{\hbar}\int^t dt' h_{nn}(t')} \simeq g_n[1 - \frac{i}{\hbar}\int^t dt' h_{nn}(t')] \tag{5.39}$$

and

$$i\hbar\dot{c}_{kn} = g_n e^{i\omega_{kn}t} h_{kn}(t) \ . \tag{5.40}$$

We can see that

$$\begin{gathered}(\widetilde{\psi}_n, \widetilde{\psi}_n) = g_n^2 \ , \\ (\widetilde{\psi}_n, \widetilde{\psi}_m) = \widetilde{g}_n^* c_{nm} + \widetilde{g}_m c_{mn}^* \ , \ n \neq m \ ,\end{gathered} \tag{5.41}$$

which shows that unitarity $\sum_n g_n^2 = 1$ is preserved (the normalization is $\sum_n (\psi_n, \psi_n) = \sum |g_n|^2 = 1)$); we shall see below that the orthogonality $(\widetilde{\psi}_n, \widetilde{\psi}_m) = 0$, for $n \neq m$, is also preserved.

We introduce the perturbation slowly from $t = -\infty$ ("adiabatically") and get the coefficients

$$c_{kn} = -\frac{i}{\hbar} g_n \int_{-\infty}^{t} dt^{'} e^{i\omega_{kn}t^{'} + \alpha t^{'}} h_{kn}(t^{'}) \tag{5.42}$$

(from equation (5.40)), where $\alpha \rightarrow 0^+$; for a periodic perturbation $h(t) = h \cos \omega t$

$$c_{kn} = -\frac{g_n h_{kn}}{2\hbar} \left[\frac{e^{i(\omega_{kn}+\omega)t+\alpha t}}{\omega_{kn} + \omega - i\alpha} + \frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn} - \omega - i\alpha} \right] \ . \tag{5.43}$$

The coefficient c_{kn} gives the probability for the transition $n \rightarrow k$; obviously, for $\omega_{kn} > 0$ the second term in equation (5.43) brings the main contribution ($\omega > 0$); for $\alpha \rightarrow 0$ we get

$$c_{kn} = -\frac{g_n h_{kn}}{2\hbar} \cdot 2\pi i \delta(\omega_{kn} - \omega) \tag{5.44}$$

and the transition probability per unit time (the rate of transition)

$$|c_{kn}|^2 / t = \frac{2\pi}{\hbar} |g_n|^2 |h_{kn}/2|^2 \delta(E_k - E_n - \hbar\omega) \tag{5.45}$$

which is the famous Fermi's "golden rule" ($\delta(\omega = 0) = t/2\pi$). Up to the weights g_n, g_k, an equal rate holds for the transition from the state k to the state n (which is an illustration of the principle of detailed balancing), the net balance depending on the original populations of states,

$$\begin{gathered}\tfrac{\partial|c_{kn}|^2}{\partial t}-\tfrac{\partial|c_{nk}|^2}{\partial t}=\\=\tfrac{2\pi}{\hbar}(|g_n|^2-|g_k|^2)\,|h_{kn}/2|^2\,\delta(E_k-E_n-\hbar\omega)\ .\end{gathered}\tag{5.46}$$

Making use of equation (5.43) we get immediately $w_m c^*_{mn}=-w_n c_{nm}$, *i.e.* the orthogonality equation (5.41) $(\widetilde{\psi}_n,\widetilde{\psi}_m)=0$ for $n\neq m$.

In view of the slow variation with the state labels we may write $\omega_{kn}\simeq \mathbf{s}\omega^{(1)}=\omega_s$ in equation (5.44) and $h_{kn}\simeq h_s$, where $\mathbf{k}=\mathbf{n}+\mathbf{s}$; we may limit ourselves to the lowest ω_s. In order to calculate the matrix elements h_{kn} we may use the wavefunctions given by equation (5.35), such as $h_s=N\overline{h}_s$, $\overline{h}_s$ being an average over the N particles ($h(x)=\sum_{i=1}^N h_i(x_i)$). The coefficient c_{kn} becomes

$$c_{kn}\simeq c_{n;s}=-\frac{i}{\hbar}g_n[2\pi(N\overline{h}_s/2)\delta(\omega_s-\omega)]\ ;\tag{5.47}$$

we can see that the temporal Fourier transform of the external interaction is included in the bracket in equation (5.47), corresponding to the characteristic frequency ω_s. The coefficient c_{kn} governs the response of the condensed matter sample to the external field. Usually, the weigths g_n correspond to the statistical weights $w_n=e^{-\beta E_n}/\sum_n e^{-\beta E_n}$, which, for energies small in comparison with the temperature, can be approximated by $1/N$; making use of equation (5.46), where we retain only the $|g_n|^2$-term, and leaving aside other weights and multiplicities we can write down the energy absorbed per unit time from the external field as

$$\begin{gathered}\tfrac{2\pi}{\hbar}N\left|\overline{h}_s/2\right|^2\omega\delta(\omega_s-\omega)=\\=\tfrac{1}{\hbar}N\left|\overline{h}_s/2\right|^2\tfrac{2\alpha\omega}{(\omega-\omega_s)^2+\alpha^2}\ ,\ \alpha\to 0\ \ ,\end{gathered}\tag{5.48}$$

which is a typical resonance absorption. Equation (5.48) shows that the response of the assembly of N particles to an external field proceeds by the classical motion of harmonic oscillators with frequency ω_s.

For instance, an electric field E coupled to the displacement u of charges q with mass m gives a hamiltonian $\overline{h} = qEu\cos\omega t$; the quantization yields $u = \sqrt{\hbar/2m\omega_s}(a + a^+)$, and we can see that u_s corresponds to transitions $n = 0 \rightarrow n = 1$, where n is the number of quanta; therefore, we have $u_s = \sqrt{\hbar/2m\omega_s}$ ($2m\omega_s u_s^2/\hbar$ is the oscillator strength) and, from equation (5.48), the power absorption

$$P = \frac{q^2E^2}{4m}\frac{\alpha}{(\omega - \omega_s)^2 + \alpha^2} \tag{5.49}$$

per particle. This is indeed the power absorbtion of a classical oscillator with the equation of motion

$$m\ddot{u}_s + m\omega_s^2 u_s + m\gamma\dot{u}_s = qE\cos\omega t \ , \tag{5.50}$$

where

$$u_s = \tfrac{qE}{2m\omega_s}\tfrac{\omega_s - \omega}{(\omega_s - \omega)^2 + \alpha^2}\cos\omega t + \tfrac{qE}{2m\omega_s}\tfrac{\alpha}{(\omega_s - \omega)^2 + \alpha^2}\sin\omega t \ ,; \tag{5.51}$$

where $\alpha = \gamma/2$; from equation (5.50) we get

$$\frac{d}{dt}\left(\frac{1}{2}m\dot{u}_s^2 + \frac{1}{2}m\omega_s^2 u_s^2\right) + m\gamma\dot{u}_s^2 = qE\dot{u}_s\cos\omega t \tag{5.52}$$

and the (average) absorbed power

$$P = m\gamma\overline{\dot{u}_s^2} = \frac{q^2E^2}{4m}\frac{\alpha}{(\omega - \omega_s)^2 + \alpha^2} \ , \tag{5.53}$$

which coincides with equation (5.49). However, for thermal equilibrium it is noteworthy that the approximation g_n, $w_n \simeq 1/N$ (and $g_n = g_k$) is not valid.

The matrix elements of an arbitrary quantity F between perturbed states given by equation (5.36) are

$$\begin{gathered} \widetilde{F}_{nm} = (\widetilde{\psi}_n, F\widetilde{\psi}_m) = \\ == \widetilde{g}_n^*\widetilde{g}_m e^{i\omega_{nm}t}F_{nm} + \\ + \sum\nolimits_k' \left[\widetilde{g}_n^* F_{nk}c_{km}e^{i\omega_{nk}t} + \widetilde{g}_m F_{km}c_{kn}^* e^{i\omega_{km}t}\right] \ , \end{gathered} \tag{5.54}$$

or, by making use of the coefficients given by equation (5.43),

$$\begin{gathered}\widetilde{F}_{nm}=g_n^*g_m\left[1-\tfrac{i}{\hbar}\int^t dt^{'}\left(h_{mm}-h_{nn}\right)\right]e^{i\omega_{nm}t}F_{nm}-\\ -g_n^*g_m\frac{e^{i\omega_{nm}t}}{2\hbar}\sum\nolimits_k'\left[\frac{F_{nk}h_{km}}{\omega_{km}+\omega-i\alpha}+\frac{h_{nk}F_{km}}{\omega_{kn}-\omega+i\alpha}\right]e^{i\omega t}-\\ -g_n^*g_m\frac{e^{i\omega_{nm}t}}{2\hbar}\sum\nolimits_k'\left[\frac{F_{nk}h_{km}}{\omega_{km}-\omega-i\alpha}+\frac{h_{nk}F_{km}}{\omega_{kn}+\omega+i\alpha}\right]e^{-i\omega t}\ ,\end{gathered}\tag{5.55}$$

where

$$1-\frac{i}{\hbar}\int^t dt^{'}\left(h_{mm}-h_{nn}\right)=1-\frac{i}{\hbar\omega}\left(h_{mm}-h_{nn}\right)\sin\omega t\ ;\tag{5.56}$$

we can see the occurrence of the (unperturbed) density matrix $g_n^*g_m\rightarrow\rho_{mn}$.

According to equation (5.55) the evolution of a quantity F associated to two states n and m proceeds by transitions which involve both the states n and m and intermediate states labelled by $k\neq n,m$. For $k=n$ in the ω_{km}-terms and $k=m$ in the ω_{kn}-terms in equation (5.55) we have "direct processes", while all the other k-states (intermediate states) are involved in "indirect processes"; these are also called virtual transitions, because they do not conserve the energy ($\omega_{km}\neq\omega_{nm}$, $\omega_{kn}\neq\omega_{mn}$). In view of the continuum of states in condensed matter the main contribution comes from those k-states lying in the vicinity of the n,m-states ("direct processes"). We write

$$\begin{gathered}\omega_{km}=\omega_{nm}+\omega_{kn}=\omega_{nm}+(\mathbf{k}-\mathbf{n})\omega_{1n}+...\ ,\\ \omega_{kn}=\omega_{mn}+\omega_{km}=-\omega_{nm}+(\mathbf{k}-\mathbf{m})\omega_{1m}+...\end{gathered}\tag{5.57}$$

and leave aside the $\omega_{1n,m}$-terms in equation (5.55); we get

$$\begin{gathered}\widetilde{F}_{nm}\simeq g_n^*g_m\left[1-\tfrac{i}{\hbar\omega}\left(h_{mm}-h_{nn}\right)\sin\omega t\right]e^{i\omega_{nm}t}F_{nm}-\\ -g_n^*g_m\frac{1}{2\hbar}[F,h]_{nm}\left[\frac{e^{i(\omega_{nm}+\omega)t}}{\omega_{nm}+\omega}+\frac{e^{i(\omega_{nm}-\omega)t}}{\omega_{nm}-\omega}\right]\ ,\end{gathered}\tag{5.58}$$

or

$$\begin{gathered}\dot{\tilde{F}}_{nm} \simeq g_n^* g_m \left[1 - \tfrac{i}{\hbar}(h_{mm} - h_{nn})\cos\omega t\right] e^{i\omega_{nm}t} F_{nm} + \\ + g_n^* g_m \left[1 - \tfrac{i}{\hbar\omega}(h_{mm} - h_{nn})\sin\omega t\right] i\omega_{nm} e^{i\omega_{nm}t} F_{nm} + \\ + g_n^* g_m \tfrac{i}{\hbar} e^{i\omega_{nm}t}[h(t), F]_{nm} \ .\end{gathered} \tag{5.59}$$

Leaving aside the weight factors we can write

$$\dot{\tilde{F}}_{nm} \simeq i\omega_{nm} e^{i\omega_{nm}t} F_{nm} + \frac{i}{\hbar} e^{i\omega_{nm}t}[h(t), F]_{nm} \tag{5.60}$$

for the quasi-classical motion of a quantity F in condensed matter subjected to a perturbation h; this equation can be obtained directly from Schrodinger's equation $i\hbar\frac{\partial\psi}{\partial t} = [H + h(t)]\psi$, by taking the matrix elements $(\psi^{'}, F\psi)$ within the approximation used above. Indeed, we get

$$i\hbar\frac{\partial}{\partial t}(\psi^{'}, F\psi) = (\psi^{'}, [F, H + h(t)]\psi) \ , \tag{5.61}$$

or, with $\psi = e^{-\frac{i}{\hbar}Ht}\Phi$,

$$\begin{gathered}\tfrac{\partial}{\partial t}(\Phi^{'}, e^{\frac{i}{\hbar}Ht} F e^{-\frac{i}{\hbar}Ht}\Phi) = \tfrac{i}{\hbar}(\Phi^{'}, e^{\frac{i}{\hbar}Ht}[H, F] e^{-\frac{i}{\hbar}Ht}\Phi) + \\ + \tfrac{i}{\hbar}(\Phi^{'}, e^{\frac{i}{\hbar}Ht}[h(t), F] e^{-\frac{i}{\hbar}Ht}\Phi) \ .\end{gathered} \tag{5.62}$$

Making use of equation (5.36) we get

$$\Phi_n = \varphi_n + {\sum_k}' c_{kn}\varphi_k \tag{5.63}$$

for $g_n = 1$ and

$$\begin{gathered}\tfrac{i}{\hbar}(\Phi_n, e^{\frac{i}{\hbar}Ht}[H, F] e^{-\frac{i}{\hbar}Ht}\Phi_m) = i\omega_{nm} e^{i\omega_{nm}t} F_{nm} - \\ - \tfrac{i}{2\hbar} e^{i\omega_{nm}t} \textstyle\sum_k' \left[\frac{\omega_{nk}F_{nk}h_{km}}{\omega_{km}+\omega-i\alpha} + \frac{\omega_{km}F_{km}h_{nk}}{\omega_{kn}-\omega+i\alpha}\right] e^{i\omega t} - \\ - \tfrac{i}{2\hbar} e^{i\omega_{nm}t} \textstyle\sum_k' \left[\frac{\omega_{nk}F_{nk}h_{km}}{\omega_{km}-\omega-i\alpha} + \frac{\omega_{km}F_{km}h_{nk}}{\omega_{kn}+\omega+i\alpha}\right] e^{-i\omega t} \ ;\end{gathered} \tag{5.64}$$

for k close to n in terms containing ω_{km} and for k close to m in terms containing ω_{km} the quantity given by equation (5.64) in brackets is zero; from equation (5.62) we are left with

$$\begin{gathered}\tfrac{\partial}{\partial t}(\Phi_n, e^{\frac{i}{\hbar}Ht}Fe^{-\frac{i}{\hbar}Ht}\Phi_m) \simeq i\omega_{nm}e^{i\omega_{nm}t}F_{nm}+ \\ +\tfrac{i}{\hbar}(\varphi_n, e^{\frac{i}{\hbar}Ht}[h(t),F]e^{-\frac{i}{\hbar}Ht}\varphi_m) \ ,\end{gathered} \tag{5.65}$$

which is equation (5.60) for $g_n = 1$.

In equation (5.60) we can absorb the exponential factors $e^{i\omega_{nm}t}$ in F_{nm}, which becomes now time-dependent; in addition, we may limit ourselves to states lying close to n or m in the commutator, such that equation (5.60) can be written now as

$$\dot{F}_{nm} \simeq i\omega_{nm}F_{nm} + \frac{i}{\hbar}[h(t),F]_{nm} \ , \tag{5.66}$$

where we recognize the equation of motion $\dot{F} = \frac{i}{\hbar}[H+h(t),F]$. Moreover, since the evolution of a classical quantity is governed by Poisson's bracket $\dot{} = \{H,F\} = \frac{\partial F}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial F}{\partial p}\frac{\partial H}{\partial q}$, where q and p are the canonical coordinate and momentum, respectively, writing $p = -i\hbar\frac{\partial}{\partial q}$, we get

$$\begin{gathered}F = \{H,F\} = \tfrac{\partial H}{\partial p}\tfrac{\partial F}{\partial q} - \tfrac{\partial F}{\partial p}\tfrac{\partial H}{\partial q} = \\ = \tfrac{i}{\hbar}\left[\tfrac{\partial H}{\partial p}(pF) - \tfrac{\partial F}{\partial p}(pH)\right] = \\ = \tfrac{i}{\hbar}[(\Delta H)F - (\Delta F)H] = \\ = \tfrac{i}{\hbar}[HF - FH] = \tfrac{i}{\hbar}[H,F] \ ;\end{gathered} \tag{5.67}$$

therefore, we can write equation (5.66) as

$$\dot{F}_{nm} \simeq i\omega_{nm}F_{nm} + \{h(t),F\} = i\omega_{nm}F_{nm} + \left(\frac{\partial F}{\partial t}\right)_{cl,h} \ , \tag{5.68}$$

which indicates a classical dynamics for F; we can pass now to the classical description, and prefer to use $\omega_{nm} \simeq -\omega_s$; we get

$$\dot{F} \simeq -i\omega_s F + \left(\frac{\partial F}{\partial t}\right)_{cl,h} \ , \ \ddot{F} + \omega_s^2 F = (\partial/\partial t)\left(\frac{\partial F}{\partial t}\right)_{cl,h} \ , \tag{5.69}$$

which is the equation of motion for a harmonic oscillator with the characteristic frequency ω_s, driven by an external (generalized) force generated by the perturbation $h(t)$.

From equation (5.54) we find the mean value

$$\begin{gathered}\overline{F} = \sum\nolimits_{nm}(\widetilde{\psi}_n, F\widetilde{\psi}_m) = \\ = \sum\nolimits_{nm}\left[\widetilde{g}_n^*\widetilde{g}_m + \sum\nolimits_k'(\widetilde{g}_n^* c_{mk} + \widetilde{g}_m c_{nk}^*)\right] e^{i\omega_{nm}t} F_{nm} \ \ ,\end{gathered} \tag{5.70}$$

hence the perturbed density matrix

$$\begin{gathered}\widetilde{\rho}_{mn} = \rho_{mn}\left[1 - \tfrac{i}{\hbar}\int^t dt'(h_{mm} - h_{nn})\right] - \\ -\tfrac{1}{2\hbar}\sum\nolimits_k' \rho_{kn}h_{mk}\left[\tfrac{e^{i(\omega_{mk}+\omega)t}}{\omega_{mk}+\omega-i\alpha} + \tfrac{e^{i(\omega_{mk}-\omega)t}}{\omega_{mk}-\omega-i\alpha}\right] + \\ +\tfrac{1}{2\hbar}\sum\nolimits_k' \rho_{mk}h_{kn}\left[\tfrac{e^{i(\omega_{kn}+\omega)t}}{\omega_{kn}+\omega-i\alpha} + \tfrac{e^{i(\omega_{kn}-\omega)t}}{\omega_{kn}-\omega-i\alpha}\right] \ \ ;\end{gathered} \tag{5.71}$$

indeed, this is the equation of motion $\dot{\widetilde{\rho}} = \frac{i}{\hbar}[\rho, e^{\frac{i}{\hbar}Ht}h(t)e^{-\frac{i}{\hbar}Ht}]$ for the density matrix. For a diagonal unperturbed density matrix we get $\overline{F} = \sum_{nm}\widetilde{\rho}_{mn}F_{nm}$ and

$$\begin{gathered}\widetilde{\rho}_{mn} = \rho_{mm}\delta_{mn} + \\ +\tfrac{1}{2\hbar}(\rho_{mm} - \rho_{nn})h_{mn}\left[\tfrac{e^{i\omega t}}{\omega_{mn}+\omega-i\alpha} + \tfrac{e^{-i\omega t}}{\omega_{mn}-\omega-i\alpha}\right] \ \ .\end{gathered} \tag{5.72}$$

Using the statistical matrix $\rho_{mm} = w_m = e^{-\beta E_m}/\sum_m e^{-\beta E_m}$ we can compute the quasi-classical response

$$\delta\overline{F} = \sum_{ms}\beta\omega_s w_m \frac{\omega_s\cos\omega t + i\omega\sin\omega t}{\omega^2 - \omega_s^2 - 2i\alpha\omega_s}h_s F_s \tag{5.73}$$

of a quantity F due to the external perturbation for densely-distributed states $\mathbf{n} = \mathbf{m} + \mathbf{s}$; since $\omega_{-s} = -\omega_s$ we get

$$\delta\overline{F} = \beta\frac{2(\omega^2 - \omega_s^2)\omega_s^2\cos\omega t - 4\alpha\omega\omega_s^2\sin\omega t}{(\omega^2 - \omega_s^2)^2 + 4\alpha^2\omega_s^2}h_s F_s \ . \tag{5.74}$$

where we must change the sign of α in order to account for damping. Comparing it with equation (5.51), we can see that the response is that of a harmonic oscillator acted by an external periodic perturbation. It is worth emphasizing that all the derivation given above is valid in the hypothesis of a quasi-classical dynamics.

In conclusion, one may say that a coarse graining, *i.e.* a (local) macroscopic average, in (normal) condensed matter leads to a (quasi-) classical description of both internal and external motion. In general, classical quasi-particles are relevant for such a motion, localized either in the direct space (for quantum quasi-particles) or in the **k**-space for collective (wave-like) excitations. The coupling and the response of the normal condensed matter to external fields is described in terms of classical harmonic oscillators, the only remnants of the quantum nature being characteristic frequencies and oscillator strengths. The quasi-classical limit of the transition rate, absorbed power, equation of motion of arbitrary quantities, density and statistical matrices have been derived, all exhibiting typical features of resonant dynamics of harmonic oscillators. This picture is valid for the quanta of mechanical action much smaller than the separation of the energy levels and, in general, for the lowest energy levels.

5.8 Nuclear quadrupole resonance

Consider identical nuclear spins I in condensed matter. Usually, in a symmetric environment, the quantum states are degenerate with respect to the quantum number m of the z-component of the spin; I^2 and one component, say, I_z are usually conserved quantities. Consider a local interaction, generated by the environment, usually an electric one. The charge distribution in the nucleus is affected by such an interaction, according to a multipole expansion. In the ground state the nuclear dipoles are vanishing; the next-order interaction is a quadrupole one. If Φ is the electric potential we have, at the position of the nucleus, an interaction

$$\begin{gathered} V=\sum_a q_a\Phi(\mathbf{r}_a)=\sum_a q_a\Phi+\sum_{ai} q_a x_{ai}\frac{\partial\Phi}{\partial x_{ai}}+ \\ +\frac{1}{2}\sum_{aij} q_a x_{ai}x_{aj}\frac{\partial^2\Phi}{\partial x_{ai}\partial x_{aj}}+\dots\ , \end{gathered} \tag{5.75}$$

where x_{ai} are the coordinates of the position vector $\mathbf{r}_a$ of the (proton) charge q_a. The first term in equation (5.75) is the monopole interaction, the second term is the dipole interaction, the third term is the quadrupole interaction; the quadrupole interaction can also be written as

$$\begin{aligned} V_2 = \tfrac{1}{6}\textstyle\sum_{aij} q_a(3x_{ai}x_{aj} - r_a^2\delta_{ij})\frac{\partial^2\Phi}{\partial x_{ai}\partial x_{aj}} = \\ = -\tfrac{1}{6}\textstyle\sum_{aij} q_a(3x_{ai}x_{aj} - r_a^2\delta_{ij})\frac{\partial E_{ai}}{\partial x_{aj}} \ , \end{aligned} \tag{5.76}$$

where $\mathbf{E}_a$ is the electric field acting upon the a-th proton; the derivatives are taken at the position of the nucleus, which is placed at the origin, so that $V_{ij} = \partial E_{ai}/\partial x_{aj}$ do no depend on a; in equation (5.76) the Laplace equation $\Delta\Phi = 0$ has been used; the symmetric tensor

$$D_{ij} = \sum_a q_a(3x_{ai}x_{aj} - r_a^2\delta_{ij}) \tag{5.77}$$

of rank two and vanishing trace is the quadrupole moment. If we average over the proton coordinates we get

$$D_{ij} \to Q_{ij} = \frac{3Q}{2I(2I-1)}(I_iI_j + I_jI_i - \frac{2}{3}I^2\delta_{ij}) \ , \tag{5.78}$$

where I_i is the spin components; the pre-factor in equation (5.78) is chosen such as

$$Q_{zz} = \frac{Q}{I(2I-1)}(3I_z^2 - I^2) = \frac{Q}{I(2I-1)}[3m^2 - I(I+1)] \tag{5.79}$$

and

$$Q_{zz}(m = I) = Q = \sum_a q_a(3z_a^2 - r_a^2) \ , \tag{5.80}$$

where the summation is performed over all coordinates in the quantum state $m = I$; we can see that the quadrupole moment is zero for spin $I = 0$ and spin $I = 1/2$.

The quadrupole interaction

$$V_2 = \frac{1}{6}\sum_{ij} Q_{ij}V_{ij} \ , \ V_{ij} = \frac{\partial^2\Phi}{\partial x_{ai}\partial x_{aj}} \tag{5.81}$$

removes the degeneracy with respect to the quantum number m, partially or totally. Indeed, making use of $I_\pm = I_x \pm iI_y$ and $I^2 = I_+I_- + I_z^2 - I_z = I_-I_+ + I_z^2 + I_z$ in

$$\begin{gathered} V_2 = \tfrac{Q}{2I(2I-1)}[(I_x^2 - \tfrac{1}{3}I^2)V_{xx}+ \\ +(I_y^2 - \tfrac{1}{3}I^2)V_{yy} + (I_z^2 - \tfrac{1}{3}I^2)V_{zz}+ \\ + + (I_xI_y + I_yI_x)V_{xy}+ \\ +(I_yI_z + I_zI_y)V_{yz} + (I_xI_z + I_zI_x)V_{xz}] \end{gathered} \tag{5.82}$$

we get the diagonal term

$$\overline{V}_2 = \frac{Q}{2I(2I-1)}\left[V_{zz} - \frac{1}{2}(V_{xx} + V_{yy})\right] I_z^2 \tag{5.83}$$

(up to a constant), which leads to energies $\sim m^2$; we denote this interaction by $\overline{V}_2 = -gI_z^2$, where g is the modulus of the pre-factor of I_z^2 in equation (5.83). The energy levels $\overline{E}_2 = -gm^2$ arise in the first order of the perturbation theory. We can see that there is still a degeneracy of the energy levels $\pm m$, which is similar to Kramers' theorem: an electric interaction may remove completely the degeneracy for integer spin I, but it does this only partially, as expressed by m^2, for a half-integer spin I. By a suitable rotation of the spin $\mathbf{I}$ we can diagonalize the matrix V_{ij} and the quadratic form V_2, which becomes $V_2 = v_xI_x^2 + v_yI_y^2 + v_zI_z^2$ (up to a constant). We can see that for axial symmetry $v_x = v_y$ the interaction is proportional to I_z^2.

Making use of this interaction we get the equations of motion $\dot{\mathbf{I}} = \frac{i}{\hbar}[\overline{V}_2, \mathbf{I}]$ in the form

$$\dot{I}_x = \frac{g}{\hbar}(I_yI_z + I_zI_y)\ ,\ \dot{I}_y = -\frac{g}{\hbar}(I_xI_z + I_zI_x)\ ,\ \dot{I}_z = 0\ . \tag{5.84}$$

Consider an external perturbation

$$U = -\gamma\hbar I_xH\cos\omega t\ , \tag{5.85}$$

where H is a magnetic field with frequency ω, oriented along the x-direction and $M_x = \gamma\hbar I_x$ is the magnetization along the same axis, γ

being the gyromagnetic factor. The commutation relations $[I_i, I_j] = i\varepsilon_{ijk}I_k$, where ε_{ijk} is the totally antisymmetric tensor of rank three (without summation over k), lead to the same equation of motion $\dot{\mathbf{I}} = \gamma\mathbf{I} \times \mathbf{H}$ as does the classical dynamics. Therefore, together with equations (5.84), we have

$$\begin{gathered} \tfrac{dI_x}{dt} = \tfrac{g}{\hbar}(I_y I_z + I_z I_y) - \alpha I_x \ , \\ \tfrac{dI_y}{dt} = -\tfrac{g}{\hbar}(I_x I_z + I_z I_x) + \gamma I_z H \cos\omega t - \alpha I_y \ , \\ \dot{I}_z = -\gamma I_y H \cos\omega t - \alpha I_z \ \ , \end{gathered} \tag{5.86}$$

where relaxation terms have been included, with the same damping coefficient α. We introduce the local collection of N spins which obey a classical dynamics. Equations (5.86) are only approximate equations for such a dynamics. In the absence of the external field the spins are in their ground state; or, more likely, they are thermally distributed over all the m-states with energy levels $\overline{E}_2 = -gm^2$. Consequently, the macroscopic, well-defined magnitude $\overline{I}_z$ of the z-component of the spin has various values $\overline{I}_z = m = \delta\overline{E}_2/2g$ (for $\delta m = -1$, $m > 0$; we may take also $\delta\overline{E}_2 = 2g(m - 1/2)$). We can see now that the particular solution for I_x and I_y in equations (5.86) is proportional to the external field H, such that we may neglect the H-contribution to the equation of motion of the I_z (which is a constant of the motion) and replace I_z by its values $\overline{I}_z$ in equations for $I_{x,y}$. In addition, the damping terms should take the form $\dot{I}_z \sim -\alpha_1(I_z - \overline{I}_z)$, $\dot{I}_{x,y} \sim -\alpha_2 I_{x,y}$. We get several frequencies $\omega_0 = \frac{2g}{\hbar}\overline{I}_z = \frac{2g}{\hbar}m = \delta\overline{E}_2/\hbar$ and $\omega_s = \gamma H m$. We write the resulting equations only for one set of frequencies. The final result can be multiplied with the thermal weight $(e^{-\beta\overline{E}_2} - e^{-\beta(\overline{E}_2+\delta\overline{E}_2)})/\sum e^{-\beta\overline{E}_2}$, corresponding to the transitions $\overline{E}_2 \longleftrightarrow \overline{E}_2 + \delta\overline{E}_2$. The equations of motion (5.86) can now be written as

$$\frac{dI_x}{dt} = \omega_0 I_y - \alpha I_x \ , \ \frac{dI_y}{dt} = -\omega_0 I_x + \omega_s \cos\omega t - \alpha I_y \tag{5.87}$$

for the macroscopic classical "spins" (magnetization components). These equations are similar with the equations for magnetic resonance (Bloch equations). The quadrupole interaction $\overline{V}_2$ plays here the same role as the external uniform magnetic field H_0 does in the magnetic resonance. Apart from the decaying solution of the homogeneous equations (that oscillates with the frequency ω_0), we have the induced solution

$$\begin{gathered} I_x = a\cos\omega t + b\sin\omega t \ , \\ I_y = \tfrac{-a\omega+b\alpha}{\omega_0}\sin\omega t + \tfrac{b\omega+a\alpha}{\omega_0}\cos\omega t \ \ , \end{gathered} \tag{5.88}$$

where

$$\begin{gathered} a = -\omega_0\omega_s\tfrac{\omega^2-\omega_0^2-\alpha^2}{(\omega^2-\omega_0^2-\alpha^2)^2+4\omega^2\alpha^2} \ , \\ b = \omega_0\omega_s\tfrac{2\omega\alpha}{(\omega^2-\omega_0^2-\alpha^2)^2+4\omega^2\alpha^2} \ \ , \end{gathered} \tag{5.89}$$

which can be simplified by assuming $\alpha \ll \omega_0$, ω_s and ω close to ω_0 to get

$$I_x \simeq a\cos\omega t + b\sin\omega t \ , \ I_y \simeq -a\sin\omega t + b\cos\omega t \ \ , \tag{5.90}$$

where

$$a \simeq -\tfrac{1}{2}\omega_s\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha^2} \ , \ b \simeq \tfrac{1}{2}\omega_s\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ . \tag{5.91}$$

This solution is identical with the solution for the magnetic resonance; the spins $I_{x,y}$ generate the magnetizations $M_{x,y} = \gamma\hbar I_{x,y}$, which absorb the power

$$P = \overline{H\dot{M}_x\cos\omega t} = \frac{1}{2}\gamma\hbar H b\omega = \frac{1}{4}\gamma^2\hbar H^2\overline{I}_z\frac{\omega\alpha}{(\omega-\omega_0)^2+\alpha^2} \ ; \tag{5.92}$$

all these equations are typical equations for a resonance phenomenon; it is called the nuclear quadrupole resonance (NQR).[15] The oscillating magnetization generates a current, which, in turn, generates an electromagnetic field. The characteristic frequencies ω_0 are in the radiofrequencies range. The above description is a (quasi-) classical

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[15] W. A. Nierenberg, N. F. Ramsey and S. B. Brody, "Measurements of Nuc1ear Quadrupole Moment Interactions", Phys. Rev. **70** 773 (1946); W. A. Nierenberg and N. F. Ramsey, "The radiofrequency spectra of sodium halides", Phys. Rev. **72** 1075 (1947); H.-G. Dehmelt and H. Kruger, "Kernquadrupolfrequenzen in festen dichlorathylen", Naturwiss. **37** 111 (1950); R. V. Pound, "Nuclear electric quadrupole interactions in crystals", Phys. Rev. **79** 685 (1950).

description of the quantum transitions which appear in the nuclear quadrupole resonance in condensed matter. The resonance frequencies correspond to transitions $m \to m \pm 1$, according to the selection rules for angular momenta; there are I frequencies for integer I and $I - 1/2$ frequencies for half-integer I.

An external, uniform magnetic field H_0 can be applied; within the same approximation the energy levels can be written as $-\gamma\hbar H_0 m - gm^2$; we can see that the resonance frequencies are then of the form $\gamma H_0 + \frac{2g}{\hbar}m$, where γH_0 is the main frequency seen in the NMR and $\frac{2g}{\hbar}m$ are NQR frequencies.

The quadrupole interaction can be diagonalized exactly, leading to the energy levels E_{2m}. We consider the motion with a certain frequency $\omega_0 = E_{2m} - E_{2m'}$ allowed by the selection rules; other effects can be included in energy and the corresponding frequency, as, for instance, the off-diagonal terms in V_2 in the second-order of the perturbation theory. Consider an interaction $-\gamma\hbar I_x H \cos\omega t$ and write down the equations of motion of the classical, macroscopic angular momentum

$$\begin{aligned} \dot{I}_x &= -i\omega_0 I_x - \alpha I_x \ , \\ \dot{I}_y &= -i\omega_0 I_y + \gamma I_z H \cos\omega t - \alpha I_y \ , \\ \dot{I}_z &= -i\omega_0 I_z - \gamma I_y H \cos\omega t - \alpha I_z \ . \end{aligned} \tag{5.93}$$

This is a homogeneous system of equations whose solution is

$$\begin{aligned} I_y &= \left[\cos\left(\tfrac{\gamma H}{\omega}\sin\omega t\right) I_y^0 + \sin\left(\tfrac{\gamma H}{\omega}\sin\omega t\right) I_z^0\right] e^{-i\omega_0 t - \alpha t} \ , \\ I_z &= \left[-\sin\left(\tfrac{\gamma H}{\omega}\sin\omega t\right) I_y^0 + \cos\left(\tfrac{\gamma H}{\omega}\sin\omega t\right) I_z^0\right] e^{-i\omega_0 t - \alpha t} \end{aligned} \tag{5.94}$$

and $I_x = I_x^0 e^{-i\omega_0 t - \alpha t}$, where $\mathbf{I}^0$ is the initial value of the angular momentum. These are decaying oscillations, which do not exhibit a resonance phenomenon.

The interaction should have an anisotropy, for instance along the z-axis; it can be created either by the quadrupole interaction in an axial symmetry, or by the presence of an external magnetic field, even a low one, or by an internal anisotropy magnetic field, etc; in this case, one component, say I_z, is a constant of the motion, the ω_0-oscillating part decays and the H-contribution to the equation of motion for I_z may be neglected; we see that I_z is saturated (its damping coefficient should be different from the damping coefficient of the transverse components of the angular momentum)e. We are left with typical resonance equations for I_y, as described above. We can see that the anisotropy axis may differ from the z-axis; the magnitude of the resonance oscillations depends then on the orientation of the sample; this effect can be seen easily in crystals. In powders the resonance is diminished; in some cases, with spherical symmetry, as in liquids, it is vanishing.

On the other hand, within the quasi-classical approximation the I_z and I_y in the interaction contributions to equations (5.93) should be replaced by c-numbers, in order the interaction hamiltonian to commute with the main hamiltonian; we get (for the real part of I_y)

$$\ddot{I}_y + \omega_0^2 I_y + \alpha \dot{I}_y = -\gamma (I_z) \omega H \sin \omega t \tag{5.95}$$

and a similar equation for I_z (with (I_y)), which lead to the typical harmonic-oscillator resonance; the c-number parameters (I_z) and (I_y) are determined by comparing the absorbed power of the resonant oscillator with the absorbed power of the quantum jumps (the result depends on the spin orientation).

5.9 Quantum transitions

For energy levels $\overline{E}_2 = -gm^2$ of axial symmetry the $\pm m$-states are degenerate. An external interaction $-\gamma\hbar I_x H \cos \omega t$ induces transitions from m to $m-1$ and from $-m$ to $-(m-1)$, according to the matrix elements

$$\begin{gathered} I_+ \left| m \right\rangle = [(I-m)(I+m+1)]^{1/2} \left| m+1 \right\rangle \ , \\ I_- = [(I+m)(I-m+1)]^{1/2} \left| m-1 \right\rangle \ , \end{gathered} \tag{5.96}$$

and

$$I_x\left|m\right\rangle=\tfrac{1}{2}[(I-m)(I+m+1)]^{1/2}\left|m+1\right\rangle+$$
$$+\tfrac{1}{2}[(I+m)(I-m+1)]^{1/2}\left|m-1\right\rangle\ ,$$
$$I_y\left|m\right\rangle=-\tfrac{i}{2}[(I-m)(I+m+1)]^{1/2}\left|m+1\right\rangle+$$
$$+\tfrac{i}{2}[(I+m)(I-m+1)]^{1/2}\left|m-1\right\rangle\ ; \tag{5.97}$$

the transition energy is $\hbar\omega_0=-g(m-1)^2+gm^2=g(2m-1)$ for $m>0$; we have

$$(I_x)_{\pm(m-1),\pm m}=\frac{1}{2}[(I+m)(I-m+1)]^{1/2}\ ; \tag{5.98}$$

this corresponds to the coefficient $c=c_{kn}$ given by equation (5.43) for $\omega_{kn}>0$ (and $\omega>0$):

$$c=\frac{1}{4}\gamma H[(I+m)(I-m+1)]^{1/2}\frac{e^{i(\omega_0-\omega)t+\alpha t}}{\omega_0-\omega-i\alpha}\ ; \tag{5.99}$$

we get the transition probability $\left|c\right|^2$, the rate of transition probability $\partial\left|c\right|^2/\partial t$ and the absorbed power

$$P=\hbar\omega\frac{\partial}{\partial t}\left|c\right|^2=\frac{1}{8}\hbar\gamma^2H^2(I+m)(I-m+1)\frac{\omega\alpha}{(\omega_0-\omega)^2+\alpha^2} \tag{5.100}$$

(which should be multiplied by the statistical weight of the state $\pm m$); comparing this equation with equation (5.92) we get

$$\overline{I}_z=\frac{1}{4}(I+m)(I-m+1)\ . \tag{5.101}$$

Initially, the spin is in the state $\varphi_1=a_1\left|m\right\rangle+a_2\left|-m\right\rangle$, the final state being $\varphi_2=b_1\left|m-1\right\rangle+b_2\left|-m+1\right\rangle$, where $a_{1,2}$, $b_{1,2}$ are mixing coefficients. The perturbed state is $\psi=\varphi_1e^{-\frac{i}{\hbar}E_1t}+c\varphi_2e^{-\frac{i}{\hbar}E_2t}$; the mean value of I_x in the perturbed state is

$$\overline{I}_x=(I_x)_{12}ce^{-i\omega_0t}+(I_x)_{21}c^*e^{i\omega_0t}\ ; \tag{5.102}$$

we get

$$\overline{I}_x = \frac{1}{4}\left|a_1 b_1^* + a_2 b_2^*\right| \gamma H (I+m)(I-m+1)\cdot$$
$$\cdot\left[\tfrac{\omega_0-\omega}{(\omega_0-\omega)^2+\alpha^2}\cos(\omega t+\delta)+\tfrac{\alpha}{(\omega_0-\omega)^2+\alpha^2}\sin(\omega t+\delta)\right] \quad , \tag{5.103}$$

where δ is the phase of $a_1 b_1^* + a_2 b_2^*$. We can see that equation (5.100) has the same form as equation (5.90).

5.10 Quasi-quantum mechanical dynamics

Consider a sample of condensed matter with the hamiltonian H_0 at thermal equilibirum. It has a continuum of quantum states, densely distributed in energy and wavefunctions, usually with a great degeneracy, such that only wavepackets are relevant, which suggest classical quasi-particles; the wavefunctions and the energy levels are affected by important uncertainties. The sample is characterized by average values $\overline{F} = \sum_n w_n F_{nn}$ of physical quantities F, where w_n is the statistical matrix, diagonal in the energy representation, and F_{nn} are mean values of (time-independent) F over quantum states with energy E_n; additional degeneracy weights should be included in such average values. The time evolution of the physical quantities $O_{n,n+s} \simeq O_s$ is a classical one, $\dot{O}_s = -i\omega_s O_s$, of harmonic-oscillator type, where $\omega_s \simeq (E_{n+s} - E_n)/\hbar$; due to the dense distribution of states the matrix elements and the energy differences depend, mainly, only on the difference in the state labels. For degenerate states $\omega_s = 0$ and O_s is constant in time. The (stationary) wavefunctions depend on the time through exponential factors like $e^{-\frac{i}{\hbar}E_n t}$, but the averages $\overline{F}$ do not depend on the time.

The above picture can be generalized to samples prepared in such a way as to be described by a density matrix ρ_{mn} instead of the statistical matrix w_n, in general non-diagonal and dependent on the time. The quasi-classical character of the dynamics of the condensed matter samples is preserved.

We apply an interaction to such a sample of condensed matter. It can be an external interaction, or an internal one, or both. For instance, we apply a constant, uniform magnetic field H_0 directed along the z-axis, with the hamiltonian $H_1 = -M_z H_0$, where M_z is the z-component of the magnetization (we recall that the magnetization is the magnetic moment of the unit volume, and the magnetic moment $\mathbf{m}$ is related to the angular momentum $\mathbf{I}$ through $\mathbf{m} = \gamma\hbar\mathbf{I}$, where γ is a gyromagnetic factor). We may consider also an internal quadrupole interaction V_2, which can also be expressed in terms of the angular momentum (the angular momentum of the atomic nuclei). We apply also a time-dependent magnetic field $H\cos\omega t$, usually along the x-axis, with the hamiltonian $h(t) = h\cos\omega t$, where $h = -\gamma\hbar I_x H$ (or $h = -M_x H$). We want to know what are the (observable) changes produced by these interactions. Since the sample is characterized by quantities F, we focus on such quantities, especially those which can be affected by the interaction; in particular, we focus on the angular momentum $\mathbf{I}$ or the magnetization $\mathbf{M}$). Usually, the states of the condensed matter sample are degenerate with respect to the quantum number m of the component I_z (and the number I of the square angular momentum $\mathbf{I}^2 = I(I+1)$), while the interactions H_1, V_2 and $h(t)$ remove, totally or partially, this degeneracy. Therefore, we focus upon m-states of the total momentum $I = const$.

There are two ways of treating this problem. First, we consider H_1, V_2 and $h(t)$ as external perturbations. The states m, n are then quantum states of the (unperturbed) hamiltonian H_0; they are degenerate. According to the discussion in the previous sections the dynamics of any relevant quantity F is a classical one; in particular, the unperturbed equation of motion $\dot{O}_s = -i\omega_s O_s$ is now $\dot{O}_s = 0$, and we are left with classical equations of motion generated by H_1, V_2 and $h(t)$. This procedure is applied to H_1 and $h(t)$ for the magnetic resonance (equations (5.3)) and to an approximation of V_2 (the diagonal $\overline{V}_2$) and $h(t)$ for the nuclear quadrupole resonance (equations (5.86)). In particular, constant interactions like H_1 and V_2 ($\overline{V}_2$) remove the degeneracy and preserve the classical dynamics. It is worth emphasizing that, while this procedure is entirely a classical one for the magnetic resonance, where both H_1 and $h(t)$ include magnetic fields, which give (classical) torques acting upon magnetization, it is not entirely a classical one for the nuclear quadrupole resonance, where V_2 is bilinear in angular momenta, and we have not classical equations of motion for the angular momenta; we have to assume a linearization of this interaction, by introducing a fictitious magnetic field, and to determine this magnetic field by self-consistency, if possible.

There is another way of treating the problem, by including the interactions H_1 or V_2, alongside H_0, in the hamiltonian of the condensed matter sample. Now, the states m, n are the states of the hamiltonians H_0+H_1 or H_0+V_2, and we focus on the change brought about by the external perturbation $h(t)$ upon an arbitrary quantity F, whose average value is given by equation (5.72); we get

$$\begin{gathered}\overline{F}=\sum_{mn}\widetilde{\rho}_{mn}F_{nm}\rightarrow\\ \rightarrow\sum_n w_n\{F_{nn}+\tfrac{1}{2\hbar}\sum_m[h_{nm}F_{mn}\cdot\\ \cdot\left(\tfrac{e^{i\omega t}}{\omega_{nm}+\omega-i\alpha}+\tfrac{e^{-i\omega t}}{\omega_{nm}-\omega-i\alpha}\right)+c.c.]\}\ ;\end{gathered}\tag{5.104}$$

we can see that the perturbation brings about a change

$$\begin{gathered}\delta F_{nn}=\tfrac{1}{2\hbar}\sum_m[h_{nm}F_{mn}\cdot\\ \cdot\left(\tfrac{e^{i\omega t}}{\omega_{nm}+\omega-i\alpha}+\tfrac{e^{-i\omega t}}{\omega_{nm}-\omega-i\alpha}\right)+c.c]\end{gathered}\tag{5.105}$$

(in the first order of the perturbation theory) in the mean values F_{nn} of the quantity F, which depends on the time. In principle, the sample is taken away from the statistical equilibrium, though, usually, the perturbation varies sufficiently slow to preserve the equilibrium, *i.e.* the perturbing period ω^{-1} is much longer than the very short thermal time necessary for ensuring the thermal equilibrium (adiabatic perturbation). The change δF_{nn} in the mean value F_{nn} proceeds by quantum transitions which imply off-diagonal matrix elements h_{nm} and F_{mn} of both the perturbation h and the quantity F (virtual states). For fixed $\omega>0$ there may exist a resonant term in equation (5.105); for instance, for $\omega_{mn}=\omega_0>0$ we get

$$\delta F_{nn}=-\frac{1}{2\hbar}\sum_{m'}h_{nm'}F_{m'n}\left(\frac{e^{i\omega t}}{\omega_0-\omega+i\alpha}+c.c\right)\ ,\tag{5.106}$$

where m' denotes all the degenerate states of the energy level E_m (this

δF_{nn} is actually a δF_{nm}). We get

$$\delta F_{nn} = -\tfrac{1}{\hbar}\left|\textstyle\sum_{m'} h_{nm'}F_{m'n}\right| \cdot \\ \cdot \tfrac{(\omega_0-\omega)\cos(\omega t+\delta)+\alpha\sin(\omega t+\delta)}{(\omega_0-\omega)^2+\alpha^2} \quad , \tag{5.107}$$

where δ is the phase of $\sum_{m'} h_{nm'}F_{m'n}$. This is a typical resonance for a harmonic oscillator, where the sign of α should be changed in order to account properly for the damping; δF_{nn} satisfies the equation of motion

$$\tfrac{d^2}{dt^2}\delta F_{nn} + \omega_0^2\delta F_{nn} + \alpha\tfrac{d}{dt}\delta F_{nn} = \\ = \tfrac{1}{\hbar}\left|\textstyle\sum_{m'} h_{nm'}F_{m'n}\right|\omega_0\cos(\omega t+\delta) \ . \tag{5.108}$$

We can compute now the change $\delta\mathbf{I}$ in the angular momentum, the change $\delta\mathbf{M}$ in the magnetization and the absorbed power $\overline{\dot{\mathbf{M}}\mathbf{H}}$ for an external perturbing magnetic field $H\cos\omega t$ oriented along one axis, say, the x-axis. Such a classical dynamics originates in virtual quantum transitions; this is why we can call it a quasi-quantum mechanical dynamics. It is worth noting that both the quasi-classical dynamics expressed by the equation of motion $\dot{F} \simeq -i\omega_s F + \left(\frac{\partial F}{\partial t}\right)_{cl,h}$ (equation (5.69)) and the quasi-quantum dynamics expressed by the equation of motion (5.108) originate in quantum transitions, direct or, respectively, indirect, which resonate with the external perturbation $h(t)$. The difference consists in the fact that the former refers to off-diagonal matrix elements F_s (F_{nm}), with $\omega_s = (E_m - E_n)/\hbar$, while the latter refers to diagonal matrix elements F_{nn}. In this respect, both procedures are equivalent.

5.11 A parametrization for the NQR

It is convenient to write the quadrupole interaction

$$V_2 = \frac{1}{6}\cdot\frac{3Q}{2I(2I-1)}\sum_{ij} V_{ij}(I_iI_j + I_jI_i - \frac{2}{3}I^2\delta_{ij}) \tag{5.109}$$

given by equation (5.81) as

$$V_2 = \sum_{ij} V_{ij}I_iI_j \quad , \tag{5.110}$$

where $\sum_i V_{ii} = 0$, V_{ij} is symmetric, and we absorbed the Q-pre-factor in the new interaction parameters V_{ij}. In an NQR experiment we get information about the interaction parameters V_{ij} which characterize the local environment of the spin $\mathbf{I}$. The spin states are usually degenerate with respect to I^2 and a spin component, say I_z; the quadrupole interaction can remove this degeneracy, partially or totally. The interaction V_2 can be diagonalized for any spin $\mathbf{I}$, yielding energy levels E_m and corresponding eigenfunctions; the label m takes $2I+1$ values, but it is not, in general, the quantum number of the component I_z of the spin (which, in general, is not conserved). Sometimes, an external uniform and constant magnetic field $\mathbf{H}_0$ is applied, giving rise to an additional interaction $V_{ext} = -\mathbf{m}\mathbf{H}_0$, where $\mathbf{m} = \gamma\hbar\mathbf{I}$ is the magnetic moment; in this case, the diagonalization is done for $V_{ext} + V_2$ (the magnitude m of the magnetic moment should not be mistaken for the quantum number m). An external magnetic field $\mathbf{H}\cos\omega t$ is applied, giving rise to a time-dependent interaction $h(t) = -\mathbf{m}\mathbf{H}\cos\omega t = -h\cos\omega t$; transition rates between various pairs of states m, m' are estimated and the absorbed power is computed according to equation (5.100). The comparison with experimental spectra gives information about the interaction parameters V_{ij}, and, implicitly, about the local environment of the spin $\mathbf{I}$. The resonance curve for the spectral power provides two parameters - the height of the curve (the amplitude) and its position; in order to get five interaction parameters we need at least three spectral lines, *i.e.* we need at least the spin $I = 1$, as expected.

It is easy to see that such information depends on the reference frame; the information gained about the interaction parameters is relevant for the actual atomic environment only for an oriented, perfect crystal. Usually, the crystal is not oriented, or the sample is an amorphous solid, or it is impurified, or it is a powder, etc. In such cases, the interaction parameters are only averages over various, unknown parameters (like, for instance, the orientation of the sample).

The interaction matrix V_{ij} can be diagonalized, such as the quadrupole interaction can be written as $V_2 = v_x I_x^2 + v_y I_y^2 + v_z I_z^2$; this is a quadratic form (or a tensor of rank two) brought to its principal axes. We can view it as the scalar product of the vectors $(v_x I_x,\, v_y I_y,\, v_z I_z)$ and $(I_x,\, I_y,\, I_z)$. The reference frame can be rotated such as the z-axis be directed along one of these vectors, which would simplify the problem, but the orientation of the principal axes depends on the unknown parameters V_{ij}.

The energy levels generated by the interaction V_2 can, in principle, be determined by the equations of motion of the spin operators, which imply the commutators of these operators with the interaction V_2; unfortunately, these equations of motion are non-linear (they are quadratic in spin operators), and an approximate, linearization procedure is needed. We describe here such a linearization procedure which is adequate for the quasi-classical dynamics of the spin operators with quadrupolar interaction.

The commutator of the spin $\mathbf{I}$ with the interaction V_2 is

$$[\mathbf{I}, V_2] = i(\mathbf{V} \times \mathbf{I} - \mathbf{I} \times \mathbf{V}) \ , \tag{5.111}$$

where $\mathbf{V}$ is the vector with the components $V_i = \sum_j V_{ij} I_j = \sum_j V_{ji} I_j$; the interaction V_2 can be written as $V_2 = \mathbf{IV} = \mathbf{VI}$. The commutator given by equation (5.111) is similar with the commutator $[\mathbf{I}, \mathbf{AI}] = i\mathbf{A} \times \mathbf{I}$, where $\mathbf{A}$ is a vector which commutes with $\mathbf{I}$. We introduce the local set of N spins, $N \gg 1$, and define the spin as the sum $\mathbf{I} = \sum_{a=1}^{N} \mathbf{I}_a$ of tensorial products, acting upon tensorial products of wavefunctions corresponding to each spin $\mathbf{I}_a$. The spin $\mathbf{I}$ can be viewed as block-diagonal, each block corresponding to a spin $\mathbf{I}_a$. We know that the set of N spins (particles) has a quasi-classical dynamics; it is easy to see, for instance, that the commutator of two such operators $A = \sum_{a=1}^{N} A_a$, $B = \sum_{a=1}^{N} B_a$,

$$[A, B] = \sum_a [A_a, B_a] \tag{5.112}$$

is vanishing in the first approximation, since A, $B \sim N$, AB, $BA \sim N^2$ and $\sum_a [A_a, B_a] \sim N$; therefore, the leading N^2-terms in the products AB and BA cancel each other, such as the two operators A and B commute in the first approximation; therefore, they may be viewed as classical quantities. It follows that we may write equation (5.111) approximately as

$$[\mathbf{I}, V_2] = 2i\mathbf{V} \times \mathbf{I} \tag{5.113}$$

and view **I** and **V** as classical quantities; for convenience we can use local averages of the type $\mathbf{I} = \frac{1}{N}\sum_{a=1}^{N}\mathbf{I}_a$, in order to have the correspondence $\mathbf{I} \longleftrightarrow \mathbf{I}_a$. We introduce now the magnetic moment $\mathbf{m} = \gamma\hbar\mathbf{I}$ and the ("fictitious") magnetic field $\mathbf{H}_0 = -(2/\gamma\hbar)\mathbf{V}$, viewed as independent (commuting) quantities and write the quadrupole interaction as $V_2 = -\mathbf{m}\mathbf{H}_0$; the commutator

$$[\mathbf{I}, V_2] = -\sum_i [\mathbf{I}, m_i] H_{0i} = i\mathbf{m} \times \mathbf{H}_0 = -2i\mathbf{I} \times \mathbf{V} \tag{5.114}$$

reproduces the commutator given by equation (5.113) and the equation of motion

$$\dot{\mathbf{I}} = \frac{i}{\hbar}[V_2, \mathbf{I}] = \frac{1}{\hbar}\mathbf{m} \times \mathbf{H}_0 \tag{5.115}$$

reproduces the classical equation

$$\dot{\mathbf{m}} = \gamma\hbar\dot{\mathbf{I}} = \gamma\mathbf{m} \times \mathbf{H}_0 \tag{5.116}$$

for the motion of the magnetic moment **m** in the magnetic field $\mathbf{H}_0$. We have thereby replaced the five independent interaction parameters V_{ij} by three components of the vector $\mathbf{H}_0$ and two components of the vector **m**, the latter having a fixed magnitude m $(= \gamma\hbar\sqrt{I(I+1)})$. The original spin degrees of freedom are lost in passing from $V_2 = \sum V_{ij} I_i I_j$ to $V_2 = -\mathbf{m}\mathbf{H}_0$ (the linearization process), such that we should view **m** and $\mathbf{H}_0$ as depending on the label m, corresponding to each spectral line.

We can see easily that the average magnetic moment is oriented along $\mathbf{H}_0$; at thermal equilibrium it is given by the Curie-Langevin equation $m_0 = \frac{1}{3}\beta m^2 H_0$, where $m = \gamma\hbar\sqrt{I(I+1)}$ is the magnitude of the magnetic moment and $\beta = 1/T$ is the inverse of the temperature T.

Consider now a time-dependent magnetic field $H\cos\omega t$ oriented along the x-axis. Let $\mathbf{H}_0 = H_0(\cos\theta,\, \sin\theta\sin\varphi,\, \sin\theta\cos\varphi)$ be the magnetic field $\mathbf{H}_0$, where θ and φ are unknown angles. The average magnetic moment has the same orientation $\mathbf{m}_0 = m_0(\cos\theta,\, \sin\theta\sin\varphi,\, \sin\theta\cos\varphi)$. We rotate the reference frame, first, by angle $-\varphi$ about the x-axis, thereafter we perform a rotation of angle $\alpha = \theta - \pi/2$ about the y-axis. This way, we brought the vectors $\mathbf{H}_0$ and $\mathbf{m}_0$ along the z-axis, while the time-dependent magnetic field becomes $(H\cos\alpha,\, 0,\, H\sin\alpha)\cos\omega t$

$= (H\sin\theta,\, 0,\, -H\cos\theta)\cos\omega t$. The total magnetic field becomes

$$(H\cos\alpha\cos\omega t,\, 0,\, H_0 - H\sin\alpha\cos\omega t) \tag{5.117}$$

and the equations of motion of the magnetic moment are

$$\begin{aligned}\dot{m}_x &= \omega_0 m_y + \gamma H m_y \sin\alpha\cos\omega t - \alpha_2 m_x \ , \\ \dot{m}_y &= -\omega_0 m_x - \gamma H m_x \sin\alpha\cos\omega t + \\ &\quad + \gamma H m_z \cos\alpha\cos\omega t - \alpha_2 m_y \ , \\ \dot{m}_z &= -\gamma H m_y \cos\alpha\cos\omega t - \alpha_1(m_z - m_0) \ ,\end{aligned} \tag{5.118}$$

where $\omega_0 = \gamma H_0$. We can see that $m_z \simeq m_0$ is a constant of the motion in the first approximation in H, so we may limit ourselves to the equations

$$\begin{aligned}\dot{m}_x &= \omega_0 m_y - \alpha_2 m_x \ , \\ \dot{m}_y &= -\omega_0 m_x + \omega_s H\cos\alpha\cos\omega t - \alpha_2 m_y \ ,\end{aligned} \tag{5.119}$$

where $\omega_s = \gamma m_0$; these are Bloch's equations with solutions

$$\begin{aligned}m_x &= a\cos\omega t + b\sin\omega t \ , \\ m_y &= \tfrac{-a\omega + b\alpha_2}{\omega_0}\sin\omega t + \tfrac{b\omega + a\alpha_2}{\omega_0}\cos\omega t \ ,\end{aligned} \tag{5.120}$$

where

$$\begin{aligned}a &= -\omega_0\omega_s H\cos\alpha\tfrac{\omega^2-\omega_0^2-\alpha_2^2}{(\omega^2-\omega_0^2-\alpha_2^2)^2+4\omega^2\alpha_2^2} \ , \\ b &= \omega_0\omega_s H\cos\alpha\tfrac{2\omega\alpha_2}{(\omega^2-\omega_0^2-\alpha_2^2)^2+4\omega^2\alpha_2^2} \ .\end{aligned} \tag{5.121}$$

We can simplify these solutions by assuming $\alpha_2 \ll \omega_0$, ω_s and ω close to ω_0. We get

$$m_x \simeq a\cos\omega t + b\sin\omega t \ , \ m_y \simeq -a\sin\omega t + b\cos\omega t \ , \tag{5.122}$$

where

$$\begin{aligned}a &\simeq -\tfrac{1}{2}\omega_s H\cos\alpha\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha_2^2} \ , \\ b &\simeq \tfrac{1}{2}\omega_s H\cos\alpha\tfrac{\alpha_2}{(\omega-\omega_0)^2+\alpha_2^2} \ .\end{aligned} \tag{5.123}$$

Equations (5.119) are equivalent with equations of motion for harmonic oscillators. The power absorbed from the field and dissipated by the motion of the transverse magnetic moment can be obtained from these equations of motion of the harmonic oscillators through

$$\begin{gathered}\frac{d}{dt}\left(\tfrac{1}{2}\dot{m}_x^2+\tfrac{1}{2}\omega_0^2m_x^2\right)+\alpha_2\dot{m}_x^2=\omega_0\omega_sH\dot{m}_x\cos\alpha\cos\omega t\ ,\\ \frac{d}{dt}\left(\tfrac{1}{2}\dot{m}_y^2+\tfrac{1}{2}\omega_0^2m_y^2\right)+\alpha_2\dot{m}_y^2=-\omega\omega_sH\dot{m}_y\cos\alpha\sin\omega t\ .\end{gathered}\tag{5.124}$$

We get

$$\begin{gathered}P=\overline{H\dot{m}_x\cos\alpha\cos\omega t}=\\ =\tfrac{1}{2}Hb\omega\cos\alpha=\tfrac{1}{4}\omega_sH^2\cos^2\alpha\frac{\omega\alpha_2}{(\omega-\omega_0)^2+\alpha_2^2}\ .\end{gathered}\tag{5.125}$$

First, we note that the power depends on the orientation of $\mathbf{m}_0$ (and $\mathbf{H}_0$), through the angle α, and there are orientations ($\alpha=\pi/2$) for which the effect disappears. The average power is obtained for $\overline{\cos^2\alpha}=\frac{1}{2}$. If the random distribution occurs at the atomic level, as for instance for liquids, the average should be performed over the orientations of the field $\mathbf{H}_0$, and we can see that the NQR effect does not exist, since $\overline{\mathbf{H}}_0=0$.

Next, we note that equation (5.125) is valid for each spectral line, in the sense that the parameters H_0 ($\omega_0=\gamma H_0$) and α (orientation of $\mathbf{H}_0$) depend on the spectral lines. The parametrization introduced here includes three componens of the magnetic field $\mathbf{H}_0$, given by H_0, $\theta=\alpha+\frac{\pi}{2}$ and φ, and two components m_x and m_y of the magnetic moment. The approximation used here is valid for m_x and m_y sufficiently small ($m_{x,y}\ll m_0$), such as the parameters $m_{x,y}$ become irrelevant, while the results do not depend on the angle φ. It follows that for each spectral line we are able to determine only one "interaction" parameter, specifically the angle α (θ), or two parameters if we count also the position of the line (ω_0), which gives the magnitude of the magnetic field H_0. This would be equivalent with the original parametrization in terms of the interaction parameters V_{ij}, though the connection between the original V_{ij} and H_0 and α is lost.

Since $H_{0i}=-\frac{2}{(\gamma\hbar)^2}\sum_jV_{ij}m_j$ and $\mathbf{H}_0$ is parallel with $\mathbf{m}_0$, we have

$$H_{0i}=-\frac{2}{(\gamma\hbar)^2}\sum_jV_{ij}m_j=\lambda m_i\ \ ,\tag{5.126}$$

where λ are proportional to the eigenvalues of the matrix V_{ij}. In the rotated reference frame we have only the z-components of these vectors, such that we can write

$$H_0 = -\frac{2}{(\gamma\hbar)^2}\widetilde{V}_{zz}m_0 = \lambda m_0 = \lambda\frac{1}{3}\beta(\gamma\hbar)^2 I(I+1)H_0 \ ; \tag{5.127}$$

we can see that the approximation scheme used here gives only one eigenvalue of the matrix V_2, corresponding to

$$\lambda = -\frac{2}{(\gamma\hbar)^2}\widetilde{V}_{zz} = \frac{3}{\beta(\gamma\hbar)^2 I(I+1)} \tag{5.128}$$

and the interaction

$$\widetilde{V}_{zz} = -\frac{3T}{2I(I+1)} \ . \tag{5.129}$$

The interaction parameters V_{ij} can be derived as functions of the parameter $\widetilde{V}_{zz}$ by using the rotations of angle $-\alpha$ about the y-axis and angle φ about the x-axis. For a vector $\mathbf{A} = (0,\, 0,\, A)$ the first rotation gives $(-A\sin\alpha,\, 0,\, A\cos\alpha)$, while the second rotation gives $(-A\sin\alpha,\, A\cos\alpha\sin\varphi,\, A\cos\alpha\cos\varphi)$; therefore, the tensor V_{ij} is given by

$$\begin{gathered}
V_{xx} = \widetilde{V}_{zz}\sin^2\alpha = \widetilde{V}_{zz}\cos^2\theta \ , \\
V_{xy} = -\widetilde{V}_{zz}\sin\alpha\cos\alpha\sin\varphi = \widetilde{V}_{zz}\cos\theta\sin\theta\sin\varphi \ , \\
V_{xz} = -\widetilde{V}_{zz}\sin\alpha\cos\alpha\cos\varphi = \widetilde{V}_{zz}\cos\theta\sin\theta\cos\varphi \ , \\
V_{yy} = \widetilde{V}_{zz}\cos^2\alpha\sin^2\varphi = \widetilde{V}_{zz}\sin^2\theta\sin^2\varphi \ , \\
V_{yz} = \widetilde{V}_{zz}\cos^2\alpha\sin\varphi\cos\varphi = \widetilde{V}_{zz}\sin^2\theta\sin\varphi\cos\varphi \ , \\
V_{zz} = \widetilde{V}_{zz}\cos^2\alpha\cos^2\varphi = \widetilde{V}_{zz}\sin^2\theta\cos^2\varphi \ .
\end{gathered} \tag{5.130}$$

Indeed, from $H_{0i} = -\frac{2}{(\gamma\hbar)^2}\sum_j V_{ij}m_j$ (equation (5.126)) and $\mathbf{H}_0 = H_0(\cos\theta,\, \sin\theta\sin\varphi,\, \sin\theta\cos\varphi)$, $\mathbf{m} = m_0(\cos\theta,\, \sin\theta\sin\varphi,\, \sin\theta\cos\varphi)$

we get the eigenvalues equations

$$\begin{gathered}
[V_{xx}+\tfrac{1}{2m_0}(\gamma\hbar)^2H_0]\cos\theta+\\
+V_{xy}\sin\theta\sin\varphi+V_{xz}\sin\theta\cos\varphi=0\ ,\\
V_{xy}\cos\theta+[V_{yy}+\tfrac{1}{2m_0}(\gamma\hbar)^2H_0]\sin\theta\sin\varphi+\\
+V_{yz}\sin\theta\cos\varphi=0\ ,\\
V_{xz}\cos\theta+V_{yz}\sin\theta\sin\varphi+\\
+[V_{zz}+\tfrac{1}{2m_0}(\gamma\hbar)^2H_0]\sin\theta\cos\varphi=0\ ;
\end{gathered}\tag{5.131}$$

making use of V_{ij} given by equations (5.130) we get one eigenvalue $H_0=-\frac{2}{(\gamma\hbar)^2}\widetilde{V}_{zz}m_0$ (equation (5.127)) for the system of equations (5.131). We can see that only two parameters ($\widetilde{V}_{zz}$ and α) are determined for five independent interaction parameters; in addition, $\widetilde{V}_{zz}$ does not depend on the interaction and the angle α depends, in principle, on the spectral line. This is why the approximate interaction V_{ij} given by the present scheme of approximation can be called an effective interaction.

6 Electric Dipolar Resonance

6.1 Quasi-classical dynamics

Let O be a dynamical variable of a quantum-mechanical motion governed by a hamiltonian H (independent of time); its equation of motion is $\dot{O} = (i/\hbar)[H, O]$, or $\dot{O}_{mn} = (i/\hbar)(E_m - E_n)O_{mn}$, where O_{mn} are the matrix elements for the states m, n with energies E_m, E_n. We assume $O_{mn} \neq 0$ for $m \neq n$ (if $O_{mn} = 0$ for $m \neq n$, then $\dot{O}_{mn} = 0$ and all its time derivatives vanish for $m \neq n$). For large values of the energy levels E_m and the quantum number m the energy levels are "dense" (densely distributed), in the sense that $\Delta E_m/E_m = (E_m - E_n)/E_m \ll 1$ for any finite difference $\Delta E_m = E_m - E_n$; according to Bohr's correspondence principle we are approaching the (quasi-) classical limit in this case. Moreover, under the same conditions, the matrix elements O_{mn} depend weakly on m and fall abruptly to zero with increasing $|m - n|$ (due to the rapid oscillations of the wavefunctions with large quantum numbers); according to the equation of motion, the matrix elements O_{mn} are approximated by the Fourier components O_{n-m} of the classical quantity O(t). We write $n = m + s$, $\omega_n = E_n/\hbar = \omega_{m+s} = \omega_m + s(\partial\omega_m/\partial m) + ...$ and $O_{mn} = O_{m,m+s} \simeq O_s$ for small values of s (in comparison with m, $s \ll m$). For a superposition $\psi = \sum_m c_m \varphi_m e^{-i\omega_m t}$ of wavefunctions $\varphi_m e^{-i\omega_m t}$, the mean value of the variable O is

$$\begin{gathered}\overline{O} = \sum_{mn} c_m^* c_n O_{mn} e^{i(\omega_m - \omega_n)t} \simeq \\ \simeq \sum_{ms} c_m^* c_m O_s e^{-is(\partial\omega_m/\partial m)t} \simeq \sum_s O_s e^{-i\omega_s t} \quad ,\end{gathered} \tag{6.1}$$

which is the Fourier transform of the classical quantity $O(t)$ with frequencies $\omega_s = s(\partial\omega_m/\partial m)$. The equation of motion for one component reads

$$\dot{O}_s = -i\omega_s O_s \quad , \tag{6.2}$$

for a fixed m.

The nature and meaning of this equation require a few clarifications. First, we note the approximate character of the equation (6.2), as a result of the approximations involved in deriving equation (6.1). Equation (6.2) is an approximation for the classical equation of motion of the classical quantity O. Indeed, on one hand it retains partially the quantum-mechanical character of the motion through $\omega_s = (E_{m+s} - E_m)/\hbar$ and the presence of m in O_s (not written explicitly); on the other hand, it refers to a motion which changes the energy, while the classical motion proceeds with the conservation of the energy. For such reasons, we call equation (6.2) the quasi-classical equation of motion. For instance, writing $O_s = O_s^{(1)} + iO_s^{(2)}$, we have $\dot{O}_s^{(1)} = \omega_s O_s^{(2)}$, $\dot{O}_s^{(2)} = -\omega_s O^{(1)}$ and $\ddot{O}_s^{(1)} = -\omega_s^2 O_s^{(1)}$, $\ddot{O}_s^{(2)} = -\omega_s^2 O_s^{(2)}$; the classical quantity is either $O_s^{(1)}$ or $O_s^{(2)}$; the classical equations of motion can be represented as $\dot{O}_s^{(1)} = \partial H/\partial P$, $\dot{P} = -\partial H/\partial O_s^{(1)}$, $\ddot{O}_s^{(1)} = (\partial/\partial t)(\partial H/\partial P)$, where P is a generalized momentum and $(\partial/\partial t)(\partial H/\partial P)$ acts as a generalized force (and similar equations for $O_s^{(2)}$); in general, the generalized force $(\partial/\partial t)(\partial H/\partial P)$ differs from the harmonic-oscillator force $-\omega_s^2 O_s^{(1)}$. For the particular case of a harmonic oscillator with eigenfrequency ω_0 the quasi-classical equation of motion is formally the same as the classical equation of motion, but the former assumes in addition $\hbar\omega_0 = E_{m+1} - E_m$, *i.e.* the quantum-mechanical condition for the quantization of the energy. The quantum-mechanical motion governed by the commutator with the hamiltonian is equivalent in the (quasi-) classical limit $\hbar \rightarrow 0$ with the classical motion governed by the Poisson brackets, though the quasi-classical motion is associated with the quantum jumps (change of energy), while the classical motion refers to a given orbit (which implies the energy conservation). In the classical limit $\hbar \rightarrow 0$ the quantum jumps disappear and we are left with a classical motion; but the classical equation of motion is not necessarily the equation of motion of a harmonic oscillator. It is a remarkable property of the Quantum Mechanics that the quantum-mechanical motion of any dynamical variable can be approximated by a harmonic-oscillator motion in the quasi-classical limit, as indicated by equation (6.2).

The quasi-classical equation of motion (6.2) implies that the motion is governed by a harmonic-oscillator effective hamiltonian

$$H_{eff} = \frac{1}{2M} P_s^2 + \frac{1}{2} M \omega_s^2 O_s^2 \ , \tag{6.3}$$

where P_s is the canonical-conjugate momentum for the "coordinate" O_s and M is a "mass" parameter.

In the presence of a time-dependent, external interaction given by a hamiltonian $H_{int}(t) = h \cos \omega t$, the change in time of the quantity O_s acquires a new contribution, which we write as $\dot{O}^{cl}$; equation (6.2) becomes

$$\dot{O}_s = -i\omega_s O_s + \dot{O}^{cl} \ ; \tag{6.4}$$

the new term $\dot{O}^{cl}$ denotes that part of the time derivative of the classical quantity O, denoted O^{cl}, which arises from the external interaction. At this moment, we may drop out the suffix s in equation (6.4) and denote $\omega_0 = \omega_s$. With $O = O^{(1)} + iO^{(2)}$ we get from equation (6.4) $\dot{O}^{(1)} = \omega_0 O^{(2)} + \dot{O}^{cl}$, $\dot{O}^{(2)} = -\omega_0 O^{(1)}$ and

$$\ddot{O}^{(1)} + \omega_0^2 O^{(1)} = [(\partial/\partial t)\dot{O}^{cl}]_{int} \tag{6.5}$$

(since the classical quantity O^{cl} is a real quantity); the suffix *int* in equation (6.5) indicates that we retain only the contribution of the external interaction. Equation (6.5) is the equation of motion of a harmonic oscillator under the action of a generalized force $[(\partial/\partial t)\dot{O}^{cl}]_{int}$; a similar equation is obtained for $O^{(2)}$; we may drop out the labels (1), (2) and write simply

$$\ddot{O} + \omega_0^2 O = [(\partial/\partial t)\dot{O}^{cl}]_{int} \ . \tag{6.6}$$

We are interested in the particular solution of equation (6.6), which is generated by the interaction. Within the quasi-classical dynamics, the interaction produces small effects, so that we may denote δO the particular solution of equation (6.6); it is the variation of the quantity O for small changes $s \ll m$ in the quantum numbers m; equation (6.6) becomes

$$\delta\ddot{O} + \omega_0^2 \delta O = [(\partial/\partial t)\dot{O}^{cl}]_{int} \ ; \tag{6.7}$$

if present in the *rhs* of this equation, δO should be neglected there, in order to preserve the perturbation character of the interaction. A damping term can be introduced in equation (6.7), which becomes

$$\delta\ddot{O} + \omega_0^2 \delta O + 2\alpha \delta\dot{O} = (\partial/\partial t)(\dot{O}^{cl})_{int} \ ; \tag{6.8}$$

multiplying by $\delta\dot{O}$ we get a conservation law,

$$\frac{d}{dt}\left(\frac{1}{2}(\delta\dot{O})^2+\frac{1}{2}\omega_0^2(\delta O)^2\right)+2\alpha(\delta\dot{O})^2=\delta\dot{O}[(\partial/\partial t)\dot{O}^{cl}]_{int}\ \ , \tag{6.9}$$

which is related to the energy conservation. We can see that the quasi-classical approximation to the quantum-mechanical motion of the dynamical variables is equivalent with the motion of harmonic oscillators.

The calculation of the generalized force $[(\partial/\partial t)\dot{O}^{cl}]_{int}$ is carried out by means of the Poisson brackets. For the classical dynamics of the variable O we have $\dot{O}=\{O,H_{eff}\}+\{O,H_{int}\}$ and

$$\begin{gathered}(\partial/\partial t)\dot{O}=\{\{O,H_{eff}\},H_{eff}\}+\{\{O,H_{eff}\},H_{int}\}+\\ +\{\{O,H_{int}\},H_{eff}\}+\{\{O,H_{int}\},H_{int}\}\ ;\end{gathered} \tag{6.10}$$

the first term in the *rhs* of equation (6.10) must be left aside since it does not contain the interaction; similarly, the last term in equation (6.10) must be left aside, since we limit ourselves to the first order of the perturbation theory in H_{int}; therefore, we get

$$(\partial/\partial t)(\dot{O}^{cl})_{int}=\{\{O,H_{eff}\},H_{int}\}+\{\{O,H_{int}\},H_{eff}\} \tag{6.11}$$

for the generalized force appearing in equation (6.7). We note that the effective hamiltonian H_{eff} is used in equation (6.11), and not the classical counterpart of the original hamiltionian H, in order to preserve the consistency of the quasi-classical approximation. For special forms of the interaction hamiltonian the generalized force given by equation (6.11) may contain O and P generated by H_{eff} (or expressions containing such O and P); let us denote them by O_0 and P_0. The classical behaviour of these quantities implies undetermined constants (arising from initial conditions), besides a time dependence. If the external interaction proceeds at a slower time scale than the motion of these quantities, we may average the classical O_0 and P_0 over the time. In condensed matter at thermal equilibrium O_0 and P_0 can be determined by their thermal averages. We may also take approximately for O_0 and P_0 the mean values for the quantum state m. All these procedures introduce an additional approximate character in the solution of the quasi-classical equation (6.8). It is also worth stressing upon the fact that there might be cases (like the motion of the magnetization in condensed matter) where we have equations of motion but not necessarily a (classical) hamiltonian formalism; in that case the time derivative $\partial/\partial t$ in equation (6.7) retains its basic meaning of a derivative with respect to the time.

Assuming that h depends only on O in $H_{int}(t) = h\cos\omega t$ and using the hamiltonian given by equation (6.3) we get
$\dot{O}^{cl} = P/M$ and

$$\begin{aligned}[(\partial/\partial t)\dot{O}^{cl}]_{int} = (\dot{P}/M)_{int} = -(\partial H_{int}/\partial O)/M = \\ = -(1/M)(\partial h/\partial O)\cos\omega t\ ;\end{aligned} \tag{6.12}$$

equation (6.8) becomes

$$\delta\ddot{O} + \omega_0^2\delta O + 2\alpha\delta\dot{O} = -(1/M)(\partial h/\partial O)\cos\omega t \tag{6.13}$$

with the solution

$$\delta O = a\cos\omega t + b\sin\omega t\ \ , \tag{6.14}$$

where

$$\begin{aligned} a = (1/M)(\partial h/\partial O)\tfrac{\omega^2-\omega_0^2}{(\omega^2-\omega_0^2)^2+4\omega^2\alpha^2} \simeq \\ \simeq \tfrac{(\partial h/\partial O)}{2M\omega_0}\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha^2}\ , \\ b = -(1/M)(\partial h/\partial O)\tfrac{2\omega\alpha}{(\omega^2-\omega_0^2)^2+4\omega^2\alpha^2} \simeq \\ \simeq -\tfrac{(\partial h/\partial O)}{2M\omega_0}\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2}\ \ , \end{aligned} \tag{6.15}$$

for ω near ω_0. The mean power dissipated (absorbed) by the oscillator is

$$\begin{aligned}\delta P_{osc} = M\overline{\delta\dot{O}[(\partial/\partial t)\dot{O}^{cl}]_{int}} = \\ = M\overline{(-a\omega\sin\omega t + b\omega\cos\omega t)}\cdot \\ \cdot\overline{[-(1/M)(\partial h/\partial O)\cos\omega t)]} = \\ = -\tfrac{1}{2}b\omega(\partial h/\partial O) = \tfrac{(\partial h/\partial O)^2}{4M}\cdot\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \rightarrow \\ \rightarrow \tfrac{\pi(\partial h/\partial O)^2}{4M}\delta(\omega_0-\omega)\end{aligned} \tag{6.16}$$

(for $\alpha \rightarrow 0$).

It is worth comparing this result with the quantum-mechanical theory of perturbation. Let

$$\psi = \varphi_n e^{-\frac{i}{\hbar}E_n t} + {\sum_k}' c_{kn}\varphi_k e^{-\frac{i}{\hbar}E_k t} \tag{6.17}$$

be the wavefunction produced to the first order of the perturbation theory by the interaction $H_{int}(t) = h\cos\omega t$; from the Schrodinger equation $i\hbar\partial\psi/\partial t = (H + H_{int})\psi$ we get

$$i\hbar\dot{c}_{kn} = \frac{1}{2}h_{kn}\left[e^{i(\omega_{kn}+\omega)t+\alpha t} + e^{i(\omega_{kn}-\omega)t+\alpha t}\right] \ , \tag{6.18}$$

where the interaction is introduced adiabatically ($\alpha \rightarrow 0^+$); hence,

$$c_{kn} = -\frac{h_{kn}}{2\hbar}\left[\frac{e^{i(\omega_{kn}+\omega)t+\alpha t}}{\omega_{kn}+\omega-i\alpha} + \frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha}\right] \ . \tag{6.19}$$

The transition from the state n to the state k with the absorption of the quanta of energy $\hbar\omega_{kn} = E_k - E_n$ corresponds to the coefficient

$$c_{kn} \simeq -\frac{h_{kn}}{2\hbar}\cdot\frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha} \ ; \tag{6.20}$$

it produces

$$\begin{aligned}R = \tfrac{\partial|c_{kn}|^2}{\partial t} = \tfrac{|h_{kn}|^2}{2\hbar^2}\cdot\tfrac{\alpha}{(\omega_{kn}-\omega)^2+\alpha^2} \rightarrow \\ \rightarrow \tfrac{\pi|h_{kn}|^2}{2\hbar^2}\delta(\omega_{kn}-\omega)\end{aligned} \tag{6.21}$$

transitions per unit time and absorbs (dissipates) a power

$$P_q = \frac{|h_{kn}|^2}{2\hbar}\omega_{kn}\frac{\alpha}{(\omega_{kn}-\omega)^2+\alpha^2} \rightarrow \frac{\pi\,|h_{kn}|^2}{2\hbar}\omega_{kn}\delta(\omega_{kn}-\omega) \quad (6.22)$$

(the suffix q stands for "quantum"). We set $n \rightarrow m$ and $k \rightarrow m+s$ and get

$$P_q = \frac{|h_s|^2}{2\hbar}\omega_0\frac{\alpha}{(\omega_0-\omega)^2+\alpha^2} \rightarrow \frac{\pi\,|h_s|^2}{2\hbar}\omega_0\delta(\omega_0-\omega)\ . \quad (6.23)$$

We compare δP_q given by equation (6.23) with δP_{osc} given by equation (6.16); in order for these two quantities be equal we should have

$$\delta\left(\frac{|h_s|^2}{2\hbar}\omega_0\right) = \frac{(\partial h/\partial O)^2}{4M}\ ; \quad (6.24)$$

such an equality is not fulfilled in general; it gives the deviation of the quasi-classical approximation (based on harmonic oscillators) from the quantum-mechanical dynamics. Equation (6.24) is satisfied for a harmonic oscillator, as expected; indeed, we have

$$\delta\left(\frac{|h_s|^2}{2\hbar}\omega_0\right) = \frac{h_s\delta h_s}{\hbar}\omega_0 = \frac{h_s(\partial h_s/\partial O)\delta O}{\hbar}\omega_0 = \frac{(\partial h/\partial O)^2}{4M}\ , \quad (6.25)$$

or

$$h\delta O = \frac{\hbar}{4M\omega_0}(\partial h/\partial O)\ , \quad (6.26)$$

where we dropped out the suffix s and assumed a constant ω_0. Equation (6.26) can also be written as

$$h\delta O = \frac{\hbar}{4M\omega_0 s}\cdot\frac{\partial h}{\partial O}\delta n\ ; \quad (6.27)$$

for $h = f_r O^r$ we get $O = \sqrt{(\hbar r/2M\omega_0 s)n}$, which, for $r = s = 1$, is the matrix element of the displacement operator for a harmonic oscillator with mass M and frequency ω_0. For $h = fO$, we get $\delta P_{osc} = (\pi f^2/4M)\delta(\omega_0-\omega)$ from equation (6.16) and $P_{osc} = (\pi f^2/4M)n\delta(\omega_0-\omega)$, which coincides with equation (6.23) for large

n. In general, for interactions of the form $h = fO$, we get from equation (6.24) $\delta(O^2\omega_0) = \hbar/2M$, or $\delta(O\dot{O}) = \hbar/2M$, $\delta(OP) = \hbar/2$, which corresponds to the uncertainty relations $\delta P \delta O \simeq \hbar/2$. For usual cases the difference between δP_q and δP_{osc} is only a numerical factor of the order of the unity.

Similarly, the mean value of an operator O for the wavefunction ψ given by equation (6.17) is

$$\overline{O} = O_{nn} + \sum_k{}' \left(c_{kn} O^*_{kn} e^{-i\omega_{kn}t} + c^*_{kn} O_{kn} e^{i\omega_{kn}t} \right) \ ; \tag{6.28}$$

hence, we may see that the change brought about by the interaction in the (quasi-) classical matrix elements of an operator is included in

$$\frac{h}{2\hbar} O \left(\frac{e^{-i\omega t}}{\Delta\omega + i\alpha} + c.c. \right) = \frac{h}{\hbar} O \frac{\Delta\omega \cdot \cos\omega t - \alpha \sin\omega t}{(\Delta\omega)^2 + \alpha^2} \ , \tag{6.29}$$

where $\Delta\omega = \omega_0 - \omega$, the interaction has been removed adiabatically from t to $t \to \infty$ (in accordance with the relaxation term in the harmonic-oscillator equation) and irrelevant phase factors have been left aside. Now we compare the variation of this change with the classical solution given by equation (6.14),

$$2\frac{h}{\hbar}\delta O = \frac{(\partial h/\partial O)}{2M\omega_0} \ , \tag{6.30}$$

which is identical with equation (6.26) (the factor 2 in the *lhs* of equation (6.30) comes from the fact that the final state k is both $n+s$ and $n-s$).

The quasi-classical approximation described above can be extended to condensed matter. In condensed matter the energy levels have a limited meaning, as a consequence of the interaction between the atomic constituents. A coarse graining is meaningful in this case, which consists in taking a number N of atomic constituents, labelled by $i = 1, 2, ...N$, around each point in the sample, such that $N \gg 1$, but still N may be much smaller than the total number of atomic constituents in the sample. The coarse graining implies averages of the type $O = (1/N)\sum_{i=1}^{N} O_i$ for any physical quantity O, so that any change δO is of the order $\delta O \sim \delta O_i/N$ (for an incoherent motion, like in "normal" condensed matter), or $\delta O/\delta O_i \sim 1/N \ll 1$, such that the levels are dense and the quasi-classical approximation can be applied. Moreover, the quantum-mechanical states for each atomic constituent i are usually limited in number (like magnetic-moment states, for instance), so that the comparison between the quasi-classical approximation and the quantum-mechanical computations involves small quantum numbers; in this case δO is practically O, and δP_{osc} is practically P_q, up to numerical factors of the order of the unity. Usually, the (normal) condensed matter is at finite temperatures, which implies both direct and reverse quantum transitions (jumps). Making use of equation (6.22), the temperature-dependent power can be written as

$$\begin{gathered}P_{q,th} = \tfrac{\pi}{2\hbar}\omega_0\left(\textstyle\sum_n'\right)\times\\ \times\{\textstyle\sum_{m(n)}\left|h_{n+s,n}(m)\right|^2 e^{-\beta E_n} -\\ -\textstyle\sum_{m(n+s)}\left|h_{n,n+s}(m)\right|^2 e^{-\beta E_{n+s}}\}\cdot\\ \cdot\delta(\omega_0-\omega)/Z\ \ ,\end{gathered} \tag{6.31}$$

where $(\sum_n')$ stands for the summation over those states n which are separated by the same frequency ω_0 from states $n+s$; $\sum_{m(n)}$ indicates a summation over possible degenerate states labelled by $m(n)$ for n (and $m(n+s)$ for $n+s$), which may affect the matrix elements of the interaction hamiltonian h; $\beta = 1/T$ is the reciprocal of the temperature; and

$$Z = \sum_n \sum_{m(n)} e^{-\beta E_n} \tag{6.32}$$

is the partition function. In the quasi-classical approximation equation (6.31) can be written approximately as

$$\begin{aligned}P_{q,th} &= \left(\textstyle\sum_n'\right)\tfrac{\pi|h_s|^2}{2\hbar}\omega_0(\beta\hbar\omega_0)f(n)e^{-\beta E_n}\delta(\omega_0-\omega)/Z =\\ &= \left(\textstyle\sum_n'\right)P_q(n)(\beta\hbar\omega_0)f(n)e^{-\beta E_n}/Z\ \ ,\end{aligned} \tag{6.33}$$

where $|h_s|^2 f(n)$ is the approximate result of the summation $\sum_{m(n)}\left|h_{n+s,n}(m)\right|^2$ and $\beta\hbar\omega_0$ was assumed to be much smaller than unity. In equation (6.33) P_{osc} may be used approximately for $P_q(n)$, according to the discussion above. For the particular case of a harmonic oscillator there is no degeneracy and summation in equation (6.33) extends over all the states ($P_q(n) \sim n$). The partition function is $Z = \sum_{n=o} e^{-\beta\hbar\omega_0 n} \simeq 1/\beta\hbar\omega_0$ and $\sum_{n=0} ne^{-\beta\hbar\omega_0 n} = 1/(\beta\hbar\omega_0)^2$, so that $P_{q,th}$ does not depend on temperature.

6.2 Vibration resonance

Molecules vibrate; the ionic crystals exhibit optical phonons; amorphous solids may exhibit local vibrations of the electric charges; complex matter (*e.g.* granular matter) may exhibit local vibrations of electric charges; complex molecules may exhibit internal vibrations (vibrons) of electric charges. All these vibrations couple electric dipoles to an external electric field of the form $\mathbf{E}(t) = \mathbf{E}\cos\omega t$. The frequency of these vibrations lies in the range $\nu_0 = 10^{13} - 10^{14}s^{-1}$ (infrared radiation), which corresponds to $10 - 100meV$ ($1eV = 1.6 \times 10^{12}erg$, Planck's constant $\hbar \simeq 10^{-27}erg$), or $10^2 - 10^3K$ (Boltzmann constant $1K = 1.38 \times 10^{-16}erg$, $1eV = 1.1 \times 10^4K$); the room temperature is $300K \simeq 40meV$ ($\simeq 10^{13}s^{-1}$).

For one degree of freedom the equation of motion for dipolar vibration reads

$$\ddot{d} + \omega_0^2 d + \gamma\dot{d} = \frac{q^2}{m}E\cos\omega t \ , \tag{6.34}$$

where d is the dipole moment, ω_0 is the eigenfrequency, γ ($\ll \omega_0$) is a damping coefficient, q and m is a charge parameter and a mass parameter, respectively. The solution of this equation (the induced dipole) is

$$\begin{gathered} d = a\cos\omega t + b\sin\omega t \ , \\ a = -\tfrac{q^2}{m}E\tfrac{\omega^2-\omega_0^2}{(\omega^2-\omega_0^2)^2+\gamma^2\omega^2} \ , \ b = \tfrac{q^2}{m}E\tfrac{\gamma\omega}{(\omega^2-\omega_0^2)^2+\alpha^2\omega^2} \ , \end{gathered} \tag{6.35}$$

or

$$\begin{gathered} a = -\tfrac{q^2}{2m\omega_0}E\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2/4} \ , \\ b = \tfrac{q^2}{2m\omega_0}E\tfrac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \end{gathered} \tag{6.36}$$

for $\omega \simeq \omega_0$. Since

$$\frac{d}{dt}(\frac{1}{2}\dot{d}^2 + \frac{1}{2}\omega_0^2 d^2) + \gamma\dot{d}^2 = \frac{q^2}{m}E\dot{d}\cos\omega t \tag{6.37}$$

from equation (6.34), we get the absorbed power

$$\delta P_{osc} = \overline{E\dot{d}\cos\omega t} = \frac{1}{2}Eb\omega = \frac{q^2}{4m\omega_0}E^2\frac{\omega\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \ ; \tag{6.38}$$

this is the dipolar vibration resonance (infrared spectroscopy). The polarization (dipole moment per unit volume) is $n\dot{d}$, where n is the concentration (density) of dipoles; the frequency parameter $\omega_p = \sqrt{4\pi nq^2/m}$ which enters the equations given above is a plasma frequency; for a typical solid $n \simeq 10^{22}cm^{-3}$; for $q = 4.8 \times 10^{-10}esu$ (electron charge; electron mass $\simeq 10^{-27}g$) we get $\omega_p \simeq 10^{15}s^{-1}$.

The free vibrations of the dipoles are those of harmonic oscillators with frequency ω_0; the energy $\hbar\omega_0$ in the range $10 - 100meV$ is comparable with the room temperature; under these conditions, these eigen-oscillations are quantum-mechanical, and a few energy levels of the oscillators are excited. For an electric field $E = 10^3V/m$ (rather high; $1V/m = \frac{1}{3} \times 10^{-4}statvolt/cm$) and $d = 4.8 \times 10^{-10} \cdot 10^{-8} = 4.8\times10^{-18}esu$ we get an energy $dE \simeq 10^{-7}eV \simeq 10^{-3}K$; in view of this very small interaction energy, the low-energy vibrations of the dipoles in condensed matter (coarse graining included) under the action of the external field are a (quasi-) classical motion. It is worth noting that the free vibrations of the dipoles imply the matrix elements of the form d_s which oscillate with frequency $\omega_s = \omega_0$, $\dot{d}_s = -i\omega_s d_s$, or $\ddot{d} = -\omega_0^2 d$, according to equation (6.34).

The absorbed power given by equation (6.38) should be compared with the power absorbed in quantum transitions. An interaction $H_{int}(t) = h\cos\omega t$ (introduced adiabatically) leads to a mixture of states $\psi_n e^{-\frac{i}{\hbar}E_n t} + \sum_k' c_{kn}\psi_k e^{-\frac{i}{\hbar}E_k t}$ $(k \neq n)$, where, in the first order of the perturbation theory, $\dot{c}_{kn} = -\frac{i}{\hbar}(H_{int})_{kn}e^{i\omega_{kn}t}$ and

$$c_{kn} = -\frac{1}{2\hbar}h_{kn}\left(\frac{e^{i(\omega_{kn}+\omega)t+\alpha t}}{\omega_{kn}+\omega-i\alpha} + \frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha}\right) \ ; \tag{6.39}$$

the transition rate is given by

$$\frac{\partial\left|c_{kn}\right|^2}{\partial t} = \frac{\pi}{2\hbar^2}\left|h_{kn}\right|^2\delta(\omega_{kn}-\omega) \tag{6.40}$$

and the absorbed power is

$$P_q = \frac{\pi}{2\hbar} \left| h_{kn} \right|^2 \omega_{kn} \delta(\omega_{kn} - \omega) \ . \tag{6.41}$$

We apply this equation to the transition $n \rightarrow n+1$ $(n = 0, 1, ...)$ for $h = -dE$, where $d_{n+1,n} = q\sqrt{\frac{\hbar}{2m\omega_0}}\sqrt{n+1}$ and get

$$P_q = \frac{\pi q^2}{4m} E^2 (n+1) \delta(\omega_0 - \omega) \tag{6.42}$$

and

$$\delta P_q = \frac{\pi q^2}{4m} E^2 \delta(\omega_0 - \omega) \tag{6.43}$$

which coincides with equation (6.38), as expected. Similarly, δP_{osc} is a good approximation (up to numerical factors of the order of the unity) to P_q for small quantum numbers n (in which case δP_{osc} may be written simply P_{osc}). At thermal equilibrium the net absorbed energy is given by

$$\begin{gathered} P_{q,th} = \tfrac{\pi q^2}{4m} E^2 [\textstyle\sum_{n=0} (n+1) e^{-\beta\hbar\omega_0 n} - \sum_{n=1} n e^{-\beta\hbar\omega_0 n}] \cdot \\ \cdot \delta(\omega_0 - \omega) / \textstyle\sum_{n=0} e^{-\beta\hbar\omega_0 n} \quad , \end{gathered} \tag{6.44}$$

where $\beta = 1/T$ is the inverse of the temperature T; we get

$$P_{q,th} = \frac{\pi q^2}{4m} E^2 \delta(\omega_0 - \omega) \ . \tag{6.45}$$

The probability of the classical harmonic oscillator to have the energy in the range $(\mathcal{E}, \mathcal{E} + d\mathcal{E})$ is $Ce^{-\beta\mathcal{E}} d\mathcal{E}$, where C is determined from $C \int e^{-\beta\mathcal{E}} d\mathcal{E} = 1$. The power given by equation (6.38) must be multiplied by this probability and the result summed over all energy values; the result is 1, as in equation (6.45).

6.3 Quasi-classical dynamics

Let H be the hamiltonian and $h(t)$ an external perturbation; the Schrodinger equation $i\hbar\frac{\partial\psi}{\partial t} = (H+h)\psi$ can also be written as $i\hbar\frac{\partial\overline{\psi}}{\partial t} =$

$\widetilde{h}\overline{\psi}$, where $\psi = e^{-\frac{i}{\hbar}Ht}\overline{\psi}$ and $\widetilde{h} = e^{\frac{i}{\hbar}Ht}he^{-\frac{i}{\hbar}Ht}$; the time derivative of a matrix element of an operator O is

$$\begin{gathered}\frac{\partial}{\partial t}(\varphi, O\psi) = \frac{\partial}{\partial t}(\overline{\varphi}, e^{\frac{i}{\hbar}Ht}Oe^{-\frac{i}{\hbar}Ht}\overline{\psi}) = \\ = (\overline{\varphi}, \frac{i}{\hbar}[H, \widetilde{O}]\overline{\psi}) + (\overline{\varphi}, \frac{i}{\hbar}[\widetilde{h}, \widetilde{O}]\overline{\psi}) \ .\end{gathered} \tag{6.46}$$

We assume that h is sufficiently small, such that its effects imply very small amounts of mechanical action; in this limit $\hbar \to 0$ and

$$\begin{gathered}\frac{i}{\hbar}[\widetilde{h}, \widetilde{O}] = \frac{i}{\hbar}e^{\frac{i}{\hbar}Ht}[h, O]e^{-\frac{i}{\hbar}Ht} \simeq \\ \simeq e^{\frac{i}{\hbar}Ht}\{h, O\}e^{-\frac{i}{\hbar}Ht} = \{h, O\} = \left(\frac{\partial O}{\partial t}\right)_{cl,h} \ ,\end{gathered} \tag{6.47}$$

where $\{h, O\}$ is the Poisson bracket of h with O and $(\partial O/\partial t)_{cl,h}$ is the classical rate of change in time of the quantity O as produced by the perturbation h; in addition, h and O are classical variables. This is the (quasi-) classical limit. Under these circumstances, the solution of the equation $i\hbar\frac{\partial\overline{\psi}}{\partial t} = \widetilde{h}\overline{\psi}$ can be represented as $\overline{\psi} = e^{-\frac{i}{\hbar}\int^t dt'\widetilde{h}(t')}\overline{\psi}_0$, where $\overline{\psi}_0$ does not depend on the time; inserting this solution in equation (6.46) we get

$$\begin{gathered}\frac{\partial}{\partial t}(\overline{\varphi}, e^{\frac{i}{\hbar}Ht}Oe^{-\frac{i}{\hbar}Ht}\overline{\psi}) = \frac{\partial}{\partial t}(\overline{\varphi}_0, e^{\frac{i}{\hbar}Ht}Oe^{-\frac{i}{\hbar}Ht}\overline{\psi}_0) = \\ = (\overline{\varphi}_0, \frac{i}{\hbar}[H, \widetilde{O}]\overline{\psi}_0) + (\overline{\varphi}_0, \frac{i}{\hbar}[\widetilde{h}, \widetilde{O}]\overline{\psi}_0) \ ,\end{gathered} \tag{6.48}$$

or

$$\frac{\partial\widetilde{O}}{\partial t} = \frac{i}{\hbar}[H, \widetilde{O}] + \left(\frac{\partial O}{\partial t}\right)_{cl,h} \ , \ \frac{\partial\widetilde{O}}{\partial t} = \frac{i}{\hbar}[H, \widetilde{O}] + \left(\frac{\partial\widetilde{O}}{\partial t}\right)_{cl,h} \ , \tag{6.49}$$

since h commutes with the hamiltonian H. We can give up the tilde upon O (Heisenberg representation) and write

$$\frac{\partial O}{\partial t} = \frac{i}{\hbar}[H, O] + \left(\frac{\partial O}{\partial t}\right)_{cl,h} \ ; \tag{6.50}$$

this is the quasi-classical equation of motion of the quantity O.

In the energy representation equation (6.50) becomes

$$\frac{\partial O_{nm}}{\partial t} = i\omega_{nm} O_{nm} + \left(\frac{\partial O}{\partial t}\right)_{cl,h} \ , \tag{6.51}$$

where $\omega_{nm} = (E_n - E_m)/\hbar$, $E_{n,m}$ being the energy of the states labelled by n and m, respectively; $O_{nm} = O_{n,n+s}$ is the s-th Fourier component O_s of the quasi-classical quantity O; therefore, equation (6.51) can be written as

$$\dot{O}_s = -i\omega_s O_s + (\dot{O})_{cl,h} \ , \tag{6.52}$$

or, with $O_s^{(1)} = Re(O_s)$, $O_s^{(2)} = Im(O_s)$,

$$\dot{O}_s^{(1)} = \omega_s O^{(2)} + (\dot{O})_{cl,h} \ , \ \dot{O}_s^{(2)} = -\omega_s O_s^{1)} \ ; \tag{6.53}$$

hence,

$$\ddot{O}_s^{(1)} + \omega_s^2 O^{(1)} = (\partial/\partial t)(\dot{O})_{cl,h} \ , \tag{6.54}$$

where we may give up the label $^{(1)}$:

$$\ddot{O}_s + \omega_s^2 O_s = (\partial/\partial t)(\dot{O})_{cl,h} \ . \tag{6.55}$$

It is worth noting that $(\partial/\partial t)(\dot{O})_{cl,h}$ is a generalized classical force acting upon O on behalf of the external perturbation $h(t)$. In addition, the unperturbed part of the hamiltonian which governs the dynamics of the quantity O_s is the harmonic-oscillator hamiltonian $H = \frac{1}{2}P^2 + \frac{1}{2}\omega_s^2 O_s^2$. Within the quasi-classical dynamics the perturbation $h(t)$ should commute with H, so that all the dynamical variables which may occur in $h(t)$ and make it non-commuting with H (for instance, $h(t) \sim O_s$) must be replaced by c-numbers.

6.4 Rotation resonance. Planar rotator

Free molecules, like those in gases, may vibrate and rotate. Inter- and intra-molecular vibrations are encountered in solids. In addition, molecules in solids may rotate, either freely or with constraints.[1]

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[1] L. Pauling, "The rotational motion of molecules in crystals", Phys. Rev. **36** 430 (1930); T. E. Stern, "The symmetrical spherical oscillator, and the rotational motion of homopolar molecules in crystals", Proc. Roy. Soc. **A130** 551 (1931).

Consider a dipole $\mathbf{d}$, consisting of a charge q with mass m, which can rotate freely in plane at a distance l form its axis (planar rotator); since $\mathbf{l} = l(\cos\varphi, \sin\varphi)$ and $\dot{\mathbf{l}} = l\dot{\varphi}(-\sin\varphi, \cos\varphi)$, we get the hamiltonian

$$H = \frac{1}{2}ml^2\dot{\varphi}^2 = \frac{1}{2ml^2}L^2 \ , \tag{6.56}$$

where $L = ml^2\dot{\varphi}$ is the angular moment and $I = ml^2$ is the moment of inertia. Since $L = -i\hbar\frac{\partial}{\partial\varphi}$, we get the wavefunctions $\psi_l = \frac{1}{\sqrt{2\pi}}e^{il\varphi}$ and the energy levels $E_l = \hbar^2 l^2/2I$, $l = 0, 1, 2, ...$ (l denotes here both the quantum number and the dipole length); the matrix elements of the dipole moment $\mathbf{d}$ involve only states l and $l \pm 1$, with the frequency $\omega_{l\pm1,l} = (E_{l\pm1} - E_l)/\hbar{=}\frac{\hbar}{I}(\pm l + \frac{1}{2})$; for $I = (10^4 - 10^5) \times 10^{-27} \cdot 10^{-16} g \cdot cm^2 = 10^{-39} - 10^{-38} g \cdot cm^2$ we get $\omega_{l+1,l} \simeq (10^{11} - 10^{12}) \times l\, s^{-1}$, which are typical rotation frequencies (infrared region); we have $10^{11} - 10^{12} s^{-1} \simeq 0.1 - 1meV \simeq 1 - 10K$, which shows that at room temperature we have several (many) excited rotation levels.

From the commutation relation $[L, \varphi] = -i\hbar$ we get $(l - l^{'})\varphi_{ll'} = -i\delta_{ll'}$, and $\varphi_{ll'} = 0$ for $l \neq l^{'}$, while φ_{ll} is undetermined. This result can be verified directly on the matrix elements

$$\begin{gathered}\varphi_{ll'} = \tfrac{1}{2\pi}\int d\varphi \cdot \varphi e^{i(l^{'}-l)\varphi} = \\ = \tfrac{\partial}{\partial[i(l'-l)]}\tfrac{1}{2\pi}\int d\varphi e^{i(l^{'}-l)\varphi} = 0 \ , \ l \neq l^{'} \ ;\end{gathered} \tag{6.57}$$

similarly, $\dot{\varphi} = (i/\hbar)[H, \varphi] = L/I$, $\dot{\varphi}_{ll'} = (i/\hbar)(E_l - E_{l'})\varphi_{ll'} = (\hbar l/I)\delta_{ll'}$ and $\dot{\varphi}_{ll'} = 0$ for $l \neq l^{'}$; the classical motion proceeds with $\dot{\varphi} = L/I = const$ and $\varphi = (L/I)t$, and the equation of motion would imply $(i/\hbar)[H, t] = 1$, which is not admissible; the time t is a parameter and so is the angle φ (and $\dot{t} = 1 + (i/\hbar)[H, t] = 1$, $[H, t] = 0$). This is a typical situation for free motion.[2]

Since φ is a multi-valued function of motion, it is not a dynamical variable, so it is not suitable for a quasi-classical dynamics.

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[2] The direct calculation by parts of the integral in equation (6.57) requires the dismissal of the "surface" term, according to the rules of the Quantum Mechanics regarding orthogonal sets of eigenfunctions (see, for instance, E. Schrodinger, *Colected Papers on Wave Mechanics*, Am. Math. Soc. Chelsea Publishing, Providence, Rhode Island (1982).

The projection of the dipole on an axis can play the role of a dynamical variable. Such an axis can be provided by an external electric field $\mathbf{E}(t) = \mathbf{E}\cos\omega t$. The orientation of the rotator is given by the direction of its angular momentum $\mathbf{L}$. In a local reference frame we may take $\mathbf{L}$ directed along the z axis; then, the electric field has the components $\mathbf{E} = E(\sin\theta, 0, \cos\theta)$ and the dipole can be written as $\mathbf{d} = d(\cos\varphi, \sin\varphi, 0)$. The interaction hamiltonian reads

$$H_{int}(t) = -\mathbf{dE}\cos\omega t = -dE\sin\theta\cos\varphi\cos\omega t \ ; \tag{6.58}$$

we take

$$x = l\cos\varphi \tag{6.59}$$

as a dynamical variable and write the interaction hamiltonian as $H_{int}(t) = -(dE/l)x\sin\theta\cdot\cos\omega t = -qEx\sin\theta\cos\omega t$. We can see that the matrix elements $x_{ll'}$ are non-vanishing for $l^{'} = l \pm 1$; therefore we can write $\ddot{x}_s + \omega_s^2 x_s = 0$, where $s = 1$ and $\omega_s = (\hbar/I)(l+1/2) \simeq (\hbar/I)l$ for $l \gg 1$ (indeed, we need $\hbar\omega_s/E_l = 2l + 1 \gg 1$, in order to have dense energy levels). It is worth noting that $\omega_s = (\hbar/I)l = L/I$ is the classical frequency in $x = l\cos(Lt/I)$ and, indeed, $\ddot{x} + (L/I)^2 x = 0$. We drop out the label s in x_s and denote $\omega_0 = (\hbar/I)l$ with a fixed l; therefore, the corresponding quasi-classical equation of motion reads $\ddot{x} + \omega_0^2 x = 0$. The force acting upon this harmonic oscillator is $(dE/l)\sin\theta\cos\omega t$, so that we have the quasi-classical equation of motion

$$\ddot{x} + \omega_0^2 x = \frac{qE}{m}\sin\theta\cos\omega t \tag{6.60}$$

(where we write simply x instead of δx). Including the damping factor, we get the solution

$$x = a\cos\omega t + b\sin\omega t \ , \tag{6.61}$$

where

$$\begin{aligned} a &= -\tfrac{qE\sin\theta}{2m\omega_0}\cdot\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2/4} \ , \\ b &= \tfrac{qE\sin\theta}{2m\omega_0}\tfrac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \ ; \end{aligned} \tag{6.62}$$

the absorbed power is

$$\begin{aligned} \delta P_{osc} &= \overline{qE\dot{x}\sin\theta\cos\omega t} = \tfrac{1}{2}qEb\omega\sin\theta = \\ &= \tfrac{q^2E^2\sin^2\theta}{4m\omega_0}\tfrac{\omega\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \ . \end{aligned} \tag{6.63}$$

According to equation (6.41) the power absorbed by quantum rotation jumps is given by

$$P_q = \frac{\pi d^2 E^2 \sin^2\theta}{8\hbar}\omega_0 \delta(\omega_0 - \omega) \ ; \tag{6.64}$$

since $\omega_0 = (\hbar/I)l$ we can see that $\delta P_q = (\pi q^2 E^2 \sin^2\theta/8m)\delta(\omega_0 - \omega)$, which differs from δP_{0sc} given by equation (6.63) by a factor 1/2. Such a discrepancy reflects the deviation of the quasi-classical approximation, based on harmonic oscillators, from the original dynamics. We note also that the transition rate given by equation (6.40)

$$R = \frac{d^2 E^2 \sin^2\theta}{4\hbar^2\gamma} \tag{6.65}$$

at resonance is, usually, much smaller than the frequency $\hbar^2 l^2/2I$, such that the perturbation calculation is valid.

We can attempt to use the hamiltonian $H = I\dot{\varphi}^2/2$ given by equation (6.56), written in terms of the new coordinate $x = l\cos\varphi$. Since $\dot{x} = -\dot{\varphi}\sqrt{l^2 - x^2}$, we get $H = I\dot{x}^2/2(l^2 - x^2)$, or $H = (l^2 - x^2)P^2/2I$, and

$$(\partial/\partial t)\dot{x}^{cl} = \frac{qE}{I}(l^2 - x^2)\sin\theta\cos\omega t \tag{6.66}$$

(where P is the conjugate momentum for the coordinate x). In this equation we must replace x by x_0; we may choose to take for x_0^2 the average $\overline{x_0^2} = l^2\overline{\cos^2(L/I)t} = l^2/2$ (we may also take the average $(1/2l)\int dx{\cdot}x^2 = l^2/3$; at thermal equilibrium $\overline{x_0^2} = l^2/4$); the equation of motion becomes

$$\ddot{x} + \omega_0^2 x = \frac{qE}{2m}\sin\theta\cos\omega t \ , \tag{6.67}$$

with solution

$$x = a\cos\omega t + b\sin\omega t \ , \tag{6.68}$$

where

$$\begin{aligned} a &= -\tfrac{qE\sin\theta}{4m\omega_0}\cdot\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2/4} \ , \\ b &= \tfrac{qE\sin\theta}{4m\omega_0}\tfrac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \ . \end{aligned} \tag{6.69}$$

The absorbed power is

$$\delta P_{osc} = \overline{qE\dot{x}\sin\theta\cos\omega t} = \tfrac{1}{2}qEb\omega\sin\theta = \\ = \tfrac{q^2E^2\sin^2\theta}{8m\omega_0}\tfrac{\omega\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \ , \tag{6.70}$$

which coincides with δP_q; we must stress upon the fact that this equality is accidental.

At finite temperature the absorption power reads

$$P_{q,th} = \tfrac{\pi d^2E^2\omega_0}{8\hbar}\times \\ \times[\int d\varphi d\theta\sin\theta\cdot\sin^2\theta\left(e^{-\beta\hbar^2l^2/2I} - e^{-\beta\hbar^2(l+1)^2/2I}\right)]\cdot \\ \cdot\delta(\omega_0-\omega)/Z \ , \tag{6.71}$$

where

$$Z = \int d\varphi d\theta\sin\theta\int_0 dl\cdot e^{-\beta\hbar^2l^2/2I} \ ; \tag{6.72}$$

in equation (6.71) we may take approximately

$$e^{-\beta\hbar^2l^2/2I} - e^{-\beta\hbar^2(l+1)^2/2I} \simeq \frac{\beta\hbar^2}{I}(l+1/2)e^{-\beta\hbar^2l^2/2I} \ . \tag{6.73}$$

We can see that $P_{q,th} = \overline{P}_q(\beta\hbar^2/I)^2l$, where $\overline{P}_q$ includes the average $\overline{\sin^2\theta}$ in P_q given by equation (6.64).

For large l we are in the classical limit, with the hamiltonian $L^2/2I - dE\sin\theta\cos\varphi\cos\omega t$; the equation of motion reads

$$\ddot{\varphi} = -\frac{dE}{I}\sin\theta\sin\varphi\cos\omega t \ ; \tag{6.74}$$

we solve this equation by perturbation theory, with a series $\varphi = \varphi_0 + \lambda\varphi_1 + ...$, where $\lambda = dE\sin\theta/I \ll 1$. With proper initial conditions we get

$$\varphi = \omega_0 t + \tfrac{\lambda}{2}\{\tfrac{\sin(\omega_0+\omega)t-(\omega_0+\omega)t}{(\omega_0+\omega)^2} + \\ + \tfrac{\sin(\omega_0-\omega)t-(\omega_0-\omega)t}{(\omega_0-\omega)^2}\} + ... \ , \tag{6.75}$$

which indicates a rotation with small oscillations. As expected, this classical solution is fundamentally different from the quantum -mechanical jumps and from the quasi-classical approximation. A friction term can be included in φ_0 (with the coefficient γ such as $\gamma\lambda \ll 1$), with a similar conclusion.

6.5 Rotation resonance. Spherical pendulum

A spherical pendulum (spatial, rigid rotator, spherical top) consists of a point of mass M which rotates freely in space at the end of a radius $\mathbf{l} = l(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, as described by the hamiltonian

$$H = \frac{1}{2}M\dot{\mathbf{l}}^2 = \frac{1}{2}Ml^2(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) \; ; \tag{6.76}$$

if the point has a charge q, it is a dipole $\mathbf{d} = q\mathbf{l}$ which can couple to an external electric field $\mathbf{E}\cos\omega t$, with an interaction hamiltonian $H_{int}(t) = -dE\cos\theta\cos\omega t$. We take the electric field directed along the z-axis.

The angular momentum $\mathbf{L} = M\mathbf{l} \times \dot{\mathbf{l}}$ has the components
$L_x = Ml^2(-\dot{\theta}\sin\varphi - \dot{\varphi}\sin\theta\cos\theta\cos\varphi)$,
$L_y = Ml^2(\dot{\theta}\cos\varphi - \dot{\varphi}\sin\theta\cos\theta\sin\varphi)$, $L_z = Ml^2\dot{\varphi}\sin^2\theta$, so that the hamiltonian can be written as

$$H = \frac{1}{2I}L^2 \;\; , \tag{6.77}$$

where $I = Ml^2$ is the moment of inertia. The quantum-mechanical expression for L^2 is

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \;\; , \tag{6.78}$$

with the eigenfunctions Y_{lm} (spherical harmonics) and the eigenvalues $\hbar^2 l(l+1)$, $l = 0, 1, ...$ The z-component of the angular momentum is $L_z = -i\hbar\frac{\partial}{\partial\varphi}$, with the same eigenfunctions Y_{lm}, $L_z Y_{lm} = \hbar m Y_{lm}$, $m = -l, -l+1, ...l$. Therefore, the energy levels of the spherical pendulum are $E_l = \frac{\hbar^2}{2I}l(l+1)$; they are degenerate with respect to the quantum number m which takes $2l+1$ values (l denotes here both the length of the dipole and the quantum number of the angular momentum).

We write the quasi-classical equation of motion as

$$\dot{O}_s = -i\omega_s O_s + \dot{O}^{cl} \ , \tag{6.79}$$

where the suffix s indicates the matrix elements between the states $n+s$ and n, $\omega_s = (E_{n+s} - E_n)/\hbar \simeq s(\partial E_n/\partial n)/\hbar$ and $\dot{O}^{cl}$ is the time derivative of the classical quantity generated by interaction (the dependence of O_s and ω_s on n is weak). With $O_s^{(1)} = Re(O_s)$ and $O_s^{(2)} = Im(O_s)$ we have

$$\dot{O}_s^{(1)} = \omega_s O_s^{(2)} + \dot{O}^{cl} \ , \ \dot{O}_s^{(2)} = -\omega_s O_s^{(1)} \ , \tag{6.80}$$

or

$$\ddot{O}_s^{(1)} + \omega_s^2 O_s^{(1)} = [(\partial/\partial t)\dot{O}^{cl}]_{int} \ , \tag{6.81}$$

where the suffix *int* indicates that part of the time derivatives of the classical quantity O generated by interaction.

Before going to analyze the quasi-classical motion, it is worth investigating the classical dynamics. First we consider the free motion governed by the equations

$$\ddot{\theta} = \dot{\varphi}^2 \sin\theta\cos\theta \ , \ I\frac{d}{dt}(\dot{\varphi}\sin^2\theta) = 0 \ ; \tag{6.82}$$

from the second equation we get $\dot{\varphi} = L_z/I\sin^2\theta$, which indicates the conservation of the component L_z of the angular momentum. Moreover, making use of the equations of motion (6.82), we check easily the conservation of the other two components L_x and L_y of the angular momentum given above; indeed, the angular momentum $\mathbf{L}$ is conserved in the free motion of the spherical pendulum. The hamiltonian given by equation (6.76) can be written as

$$H = \frac{1}{2}I\dot{\theta}^2 + \frac{L_z^2}{2I\sin^2\theta} \ ; \tag{6.83}$$

the effective potential function $L_z^2/2I\sin^2\theta$ has a minimum for $\theta = \pi/2$; the motion may be limited to small oscillations about the equatorial plane $\theta = \pi/2$. Indeed, introducing $\delta\vartheta = \theta - \pi/2$ we get

$$\frac{L_z^2}{2I\sin^2\theta} = \frac{L_z^2}{2I} + \frac{L_z^2}{2I}\delta\theta^2 + ... \tag{6.84}$$

and

$$H \simeq \frac{1}{2}I\delta\dot{\theta}^2 + \frac{L_z^2}{2I}\delta\theta^2 + \frac{L_z^2}{2I} \ , \tag{6.85}$$

$$\begin{gathered} L_x = I(-\delta\dot{\theta}\sin\varphi + \dot{\varphi}\delta\theta\cos\varphi) \ , \\ L_y = I(\delta\dot{\theta}\cos\varphi + \dot{\varphi}\delta\theta\sin\varphi) \ , \ \dot{\varphi} = L_z/I = \Omega \ , \end{gathered} \tag{6.86}$$

where we have introduced the frequency $\Omega = L_z/I$. We can see that there is a precession $\varphi = \Omega t$ about the z-axis and an oscillation $\delta\theta = A\cos(\Omega t + \delta)$, where A is an undetermined amplitude and δ is an undetermined phase, according to the small oscillations governed by the hamiltonian given by equation (6.85). We can check easily that the angular momentum given by equations (6.86) is conserved ($\dot{\mathbf{L}} = 0$); in fact, $L_x = IA\Omega\cos\delta$ and $L_y = IA\Omega\sin\delta$ (and $L_z = I\Omega$). We can rotate the equatorial plane $\theta = \pi/2$ by an angle given by $\sin\alpha = IA\Omega/\sqrt{I^2\Omega^2 + I^2A^2\Omega^2} \simeq A$, such that the motion will be an in-plane motion.

In the presence of the interaction the classical equations of motion are

$$\begin{gathered} \ddot{\theta} = \dot{\varphi}^2\sin\theta\cos\theta - \tfrac{dE}{I}\sin\theta\cos\omega t \ , \\ I\tfrac{d}{dt}(\dot{\varphi}\sin^2\theta) = 0 \ ; \end{gathered} \tag{6.87}$$

we can see that the component $L_z = I\dot{\varphi}\sin^2\theta$ of the angular momentum is conserved, which leads to an effective potential function $U_{eff} = \frac{L_z^2}{2I\sin^2\theta}$ in the hamiltonian given by equation (6.76); it follows that for low energies the angle θ oscillates around the minimum point $\theta = \pi/2$ of this potential function, and only for high energy values it may execute complete rotations. At usual temperatures and for usual electric fields the energies are low and l may acquire large values. In the classical limit, the spherical pendulum rotates as a quasi-planar rotator, with small oscillations around the equilibrium value $\theta = \pi/2$.[3] We limit ourselves to such small oscillations $\delta\theta$ around $\theta = \pi/2$, whose dynamics is governed by the harmonic-oscillator equation

$$\delta\ddot{\theta} + \Omega^2 \delta\theta = -\frac{dE}{I}\cos\omega t \ , \tag{6.88}$$

where $\Omega = L_z/I = \hbar m/I$; we include a damping term $\gamma\delta\dot{\theta}$ and get the solution

$$\delta\theta = a\cos\omega t + b\sin\omega t \ , \tag{6.89}$$

where

$$a = \tfrac{dE}{I}\tfrac{\omega^2-\Omega^2}{(\omega^2-\Omega^2)^2+\gamma^2\omega^2} \ , \ b = -\tfrac{dE}{I}\tfrac{\gamma\omega}{(\omega^2-\Omega^2)^2+\gamma^2\omega^2} \ ; \tag{6.90}$$

we can see that the classical dynamics yields a resonance for $\omega = \Omega$, where $\Omega = L_z/I$; the azimuthal angle $\varphi = \Omega t$ rotates freely. This approximation corresponds to $L_z \simeq L$ ($m \simeq l$, $L_x^2 + L_y^2 \ll L_z^2 \simeq L^2$). The transition rate of quantum jumps for $\omega_0 = (E_{l+1} - E_l)/\hbar = (\hbar/I)(l+1)$ is

$$\frac{\partial \left|c_{lm}\right|^2}{\partial t} = \frac{\pi d^2 E^2}{2\hbar^2}\left|(\cos\theta)_{lm}\right|^2 \delta(\omega_0 - \omega) \ , \tag{6.91}$$

where

$$(\cos\theta)_{lm} = (\cos\theta)_{l+1,m;l,m} = -i\sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}} \ ; \tag{6.92}$$

the absorbed power is

$$\begin{gathered} P_q = \hbar\omega_0 \textstyle\sum_{m=-l}^{l} \frac{\partial|c_{lm}|^2}{\partial t} = \\ = \tfrac{\pi d^2 E^2}{2\hbar}\omega_0 \textstyle\sum_{m=-l}^{l} \left|(\cos\theta)_{lm}\right|^2 \delta(\omega_0 - \omega) = \\ = \tfrac{d^2E^2}{6\hbar}\omega_0(l+1)\tfrac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} = \\ = \tfrac{d^2E^2}{6I}(l+1)^2\tfrac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \ , \end{gathered} \tag{6.93}$$

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[3] This is also the reason why we may leave aside the coupling between vibrations and rotations (the smallness of the electric fields).

and the net absorbed power at finite temperatures is given by

$$P_{q,th} = \tfrac{\pi d^2 E^2}{2\hbar}\omega_0 \times$$

$$\times \textstyle\sum_{m=-l}^{l} \left|(\cos\theta)_{lm}\right|^2 \left\{e^{-\beta\hbar^2 l(l+1)/2I} - e^{-\beta\hbar^2 (l+1)(l+2)/2I}\right\}. \tag{6.94}$$

$$\cdot\delta(\omega_0 - \omega)/Z \ ,$$

where

$$Z = \sum_{l=0}(2l+1)e^{-\beta\hbar^2 l(l+1)/2I} = \frac{2I}{\beta\hbar^2} \ ; \tag{6.95}$$

we get

$$\begin{aligned} P_{q,th} &= \tfrac{\pi d^2 E^2}{12I}(l+1)^3\left(\tfrac{\beta\hbar^2}{I}\right)^2 e^{-\beta\hbar^2 l(l+1)/2I}\delta(\omega_0-\omega) = \\ &= \tfrac{1}{2}P_q(l+1)\left(\tfrac{\beta\hbar^2}{I}\right)^2 e^{-\beta\hbar^2 l(l+1)/2I} \ . \end{aligned} \tag{6.96}$$

The angles φ and θ do no admit a quasi-classical approximation, in the sense discussed here for dynamical variables (this is a typical situation for the free motion). The matrix elements $\varphi_{lm,lm'}$ are vanishing for $m \neq m^{'}$, while the matrix elements $\theta_{l,m;l+s,m}$ do not fall off rapidly with increasing s.[4]

We can take $z = l\cos\theta$ as a quasi-classical variable with $s = 1$, corresponding to transitions from l to $l+1$; the generalized force is

$$(\partial/\partial t)(\dot{z}^{cl}) = \frac{qE}{M}\cos\omega t \tag{6.97}$$

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[4] In general, the quasi-classical approximation discussed here is more than the standard quasi-classical case. The latter requires a short wavelength which should not vary much over distances of interest. This amounts practically to large quantum numbers. The quasi-classical approximation discussed here requires in addition the approximation of the physical quantities by harmonic oscillators over finite regions of the spectrum. For instance, the spherical pendulum may be in the quasi-classical case for large l even for the quantum-mechanical state $m = 0$, in the sense that the Legendre polynomial P_l oscillates rapidly for large l. Similarly, P_{ll} $(m = l)$ is highly localized on the equatorial plane for large l, which indicates the classical limit.

and the equation of motion reads

$$\ddot{z}+\omega_0^2 z=\frac{qE}{M}\cos\omega t\ ; \tag{6.98}$$

its solution is

$$z=a\cos\omega t+b\sin\omega t\ \ , \tag{6.99}$$

where

$$a=-\tfrac{qE}{2M\omega_0}\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2/4}\ ,\ b=\tfrac{qE}{2M\omega_0}\tfrac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4}\ ; \tag{6.100}$$

the absorbed power is

$$\delta P_{osc}=\frac{1}{2}qEb\omega_0=\frac{q^2E^2}{4M}\frac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4}\ ; \tag{6.101}$$

the total power is obtained by multiplying by the number $2l+1$ ($\simeq 2l$) of degenerate (φ-) states; we get

$$\delta P_{osc}=\frac{q^2E^2}{2M}l\frac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4}\ \ , \tag{6.102}$$

which differs from δP_q given by equation (6.93) by a factor 3/2; this difference indicates the deviation of the quasi-classical approximation based on harmonic oscillators from the actual motion.

We may consider the classical limit of the motion, corresponding to large values of $m\simeq l\gg 1$; in this case the φ-motion is in the classical limit (for large m and $\hbar\to 0$ the component L_z remains finite) and the associated Legendre polynomials P_{lm} in the spherical harmonics Y_{lm} are localized near the equator; indeed, $P_{ll}\sim\sin^l\theta$. For small variations $\delta\theta$ around $\pi/2$ we have $\delta\theta\simeq\sin\delta\theta=\cos(\pi/2-\delta\theta)=\cos\theta$, so we have to take the matrix elements of $\cos\theta$, which are different from zero for $l^{'}=l\pm 1$. Consequently, we take $\delta\vartheta$ for O in equation (6.81), $s=1$ and $\omega_0=(E_{l+1}-E_l)/\hbar\simeq(\hbar/I)l$, for a fixed $l\gg 1$; in addition, $\cos\theta$ in the interaction hamiltonian may be approximated by $\delta\theta$, where $\delta\theta$ is the new quasi-classical variable θ_s; the equation of quasi-classical motion is

$$\ddot{\theta}_s+\omega_0^2\theta_s=-\frac{dE}{I}\cos\omega t\ \ , \tag{6.103}$$

which coincides with the equation (6.88) of the classical motion for $m = l$. The absorbed power is given by

$$P = -dE\overline{\dot{\theta}_s \cos\omega t} = -\tfrac{1}{2}dEb\omega \simeq \tfrac{d^2E^2}{4I}\tfrac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \ , \tag{6.104}$$

which coincides with equation (6.101) and the $m = l$-component of P_q in equation (6.93), as expected.

Consider now an additional constant, uniform electric field E_0 applied along the x-axis alongside the time-dependent field $E\cos\omega t$ directed along the z-axis; the hamiltonian reads

$$H = \frac{1}{2}I(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) - dE_0\sin\theta\cos\varphi - dE\cos\theta\cos\omega t \tag{6.105}$$

(it is more convenient to take the z-axis along the static field E_0); the classical equations of motion are

$$\begin{gathered}\ddot{\theta} - \dot{\varphi}^2\sin\theta\cos\theta = \tfrac{dE_0}{I}\cos\theta\cos\varphi - \tfrac{dE}{I}\sin\theta\cos\omega t \ , \\ \tfrac{d}{dt}(\dot{\varphi}\sin^2\theta) = -\tfrac{dE_0}{I}\sin\theta\sin\varphi \ .\end{gathered} \tag{6.106}$$

Usually, the interaction energy associated with the electric fields E_0 and E is extremely small in comparison with the energy scale of the free motion (rotation); in the first order of the perturbation theory we have $\dot{\varphi} = L_z/I\sin^2\theta$ and an effective potential energy $U_{eff} = \frac{1}{2}I\dot{\varphi}^2\sin^2\theta = (L_z^2/2I\sin^2\theta)$, which has a minimum value for $\theta = \pi/2$. Expanding in powers of $\delta\theta$ for $\theta = \pi/2 + \delta\theta$ the hamiltonian becomes

$$H \simeq \frac{1}{2}I\delta\dot{\theta}^2 + \frac{L_z^2}{2I}(1+\delta\theta^2) - dE_0\cos\Omega t + dE\delta\theta\cos\omega t \ ; \tag{6.107}$$

the equation of motion for $\delta\theta$ is

$$\delta\ddot{\theta} + \Omega^2\delta\theta = -\frac{dE}{I}\cos\omega t \ ; \tag{6.108}$$

we can see that the field E_0 does not change the equation of motion (6.88), its sole effect being a time-dependent energy $-dE_0\cos\Omega t$ ($\Omega = L_z/I$). The quasi-classical equation of motion (6.103) remains unchanged. The same conclusion is valid for a field E_0 directed along the z-axis; in that case the effective potential $U_{eff} = (L_z^2/2I\sin^2\theta) - dE_0\cos\theta$ has a minimum value for $\theta = \pi/2 - dE_0/I\Omega^2$. It is worth emphasizing that such a perturbation-theoretical treatment practically views the spherical pendulum as a free one, except for the fixed axis along the static field $\mathbf{E}_0$ which reduces the conservation of the angular momentum $\mathbf{L}$ to only one of its components.

6.6 Rotation resonance. Quenched dipoles

Although many molecules, even in their ground state, possess an electric dipole moment d, usually the dipole-dipole interaction is neglected in rarefied condensed matter, since the distance between the dipoles is large. In these conditions, at finite temperatures, the electric dipoles are randomly distributed; they get slightly aligned in the presence of a static external electric field $\mathbf{E}_0$, which provides a small interaction energy, leading to an induced orientational polarization $\overline{d} = \beta d^2 E_0/3$, known as the Curie-Langevin-Debye law; $\beta = 1/T$ is the inverse of the temperature T.[5]

Typical values of the dipole moment are $d = 10^{-18}esu$; two dipoles separated by distance $a = 10^{-8}cm$ (1Å) interact with an energy $\simeq d^2/a^3 = 10^{-12}erg \simeq 10^3K$ ($1eV = 1.6 \times 10^{-12}erg$, $1K = 1.38 \times 10^{-16}erg$, $1eV = 1.1 \times 10^4K$). This is not a small energy, and, apart from special circumstances, the electric dipole-dipole interaction cannot be neglected in condensed matter.

The interaction energy of two dipoles $\mathbf{d}_1$ and $\mathbf{d}_2$ separated by distance $\mathbf{a}$ (much longer than the dimension of the dipoles) is given by

$$U = -\frac{3(\mathbf{d}_1\mathbf{d}_2)a^2 - (\mathbf{d}_1\mathbf{a})(\mathbf{d}_2\mathbf{a})}{a^5} \ . \tag{6.109}$$

We introduce the angles (θ_1, φ_1) and (θ_2, φ_2) for the direction of the two dipoles with respect to the axis $\mathbf{a}$ and the interaction energy

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[5] P. Curie, "Lois experimentales du magnetisme. Proprietes magnetiques des corps a diverses temperatures", Ann. Chim. Phys. **5** 289 (1895); P. Langevin, "Sur la theorie du magnetisme", J. Physique **4** 678 (1905); P. Langevin, "Magnetism et theorie des electrons", Ann. Chim. Phys. **5** 70 (1905); P. Debye, "Einige Resultate einer kinetischen Theorie der Isolatoren", Phys. Z. **13** 97 (1912).

becomes

$$U = -\frac{d_1 d_2}{a^3}[2\cos\theta_1\cos\theta_2 + 3\sin\theta_1\sin\theta_2\cos(\varphi_1 - \varphi_2)] \; ; \qquad (6.110)$$

this energy has four extrema for $\theta_1 = \theta_2 = 0$, $\theta_1 = \theta_2 = \pi/2$ and $\varphi_1 - \varphi_2 = 0, \pi$; only for $\theta_1 = \theta_2 = \pi/2$, $\varphi_1 - \varphi_2 = 0$ the interaction energy has a local minimum; in the neighbourhood of this minimum value the interaction energy behaves like

$$\begin{aligned} U = \tfrac{d_1 d_2}{a^3}[-3 + \tfrac{3}{2}(\delta\theta_1^2 + \delta\theta_2^2) - 2\delta\theta_1\delta\theta_2 + \\ + \tfrac{3}{2}(\delta\varphi_1 - \delta\varphi_2)^2] = \\ = \tfrac{d_1 d_2}{a^3}[-3 + \tfrac{1}{4}(\delta\theta_1 + \delta\theta_2)^2 + \\ + \tfrac{5}{4}(\delta\theta_1 - \delta\theta_2)^2 + \tfrac{3}{2}(\delta\varphi_1 - \delta\varphi_2)^2] \; , \end{aligned} \qquad (6.111)$$

where $\delta\theta_{1,2} = \theta_{1,2} - \pi/2$ are small deviations of the angles $\theta_{1,2}$ from the polarization axis $\pi/2$. Therefore, the electric dipoles are quenched in equilibrium positions, such that they are parallel to each other and perpendicular to the distance between them. For the other three extrema the interaction energy has either a saddle point (for $\theta_1 = \theta_2 = 0$, $\varphi_1 - \varphi_2 = 0, \pi$) or a maximum (for $\theta_1 = \theta_2 = \pi/2$, $\varphi_1 - \varphi_2 = \pi$). It is likely that the structural environment is distorted such as the dipoles take advantage of the energy minimum. For instance, a structural elongation along the direction $\theta_1 = \theta_2 = 0$ decreases appreciably the dipolar interaction (which goes like $1/a^3$!), such that the corresponding contribution to the energy may be neglected. Under such circumstances, we may say that the dipoles are (spontaneously) polarized along an arbitrary axis.

Substances that have a permanent electric polarization are called pyroelectrics (or electrets); if the polarization is singular just below a critical temperature and vanishes above, those substances are called ferroelectrics (in the state above the critical temperature they are also called paraelectrics); they exhibit a second-order phase transition; all these substances are piezoelectric. There are structural modifications associated with finite discontinuities in polarization (first-order phase transitions), a typical example being barium titanate ($BaTiO_3$);[6] the dimension of the elementary cell in the crystal of $BaTiO_3$ is $a \simeq 4 \times 10^{-8} cm$ (4Å); the dipole of a cell is $d \simeq 5 \times 10^{-18} esu$; if Ba^{2+} and Ti^{4+} are displaced with respect to O^{2-}, then the dipole moment d is achieved for a slight displacement $\delta = 0.1$Å; we can see that the distance a between the dipoles is much longer than the dimension δ of the dipoles. In addition, $BaTiO_3$ exhibits several structural modifications (from cubic to tetragonal to monoclinic to rhombohedral with decreasing temperature), in all polarized phases the structure being elongated along the direction of the polarization.

In a continuum model of polarized substance the dipolar interaction given by equation (6.111) (with identical dipoles d) gives the interaction hamiltonian

$$H_{int} = \frac{1}{a^3} \int d\mathbf{r} \{ \frac{d^2}{a^3} \delta\theta^2 + \frac{5d^2}{4a} (grad\delta\theta)^2 + \\ + \frac{3d^2}{2a} (grad\delta\varphi)^2 \} \ , \tag{6.112}$$

which, together with the kinetic part, leads to the full hamiltonian

$$H = \frac{1}{a^3} \int d\mathbf{r} [\frac{1}{2} I \dot{\delta\theta}^2 + \frac{1}{2} I \dot{\delta\varphi}^2 + \frac{1}{2} I \omega_0^2 \delta\theta^2 + \\ + \frac{1}{2} I v_\theta^2 (grad\delta\theta)^2 + \frac{1}{2} I v_\varphi^2 (grad\delta\varphi)^2 \ , \tag{6.113}$$

where I is the moment of inertia of the dipoles and $\omega_0^2 = 2d^2/Ia^3$, $v_\theta^2 = 5d^2/2Ia = 5\omega_0^2 a^2/4$, $v_\varphi^2 = 3d^2/Ia = 3\omega_0^2 a^2/2$. We can see that the dipolar interaction may generate dipolar waves (waves of orientational polarizability), governed by the wave equations

$$\ddot{\delta\theta} + \omega_0^2 \delta\theta - v_\theta^2 \Delta\delta\theta = 0 \ , \ \ddot{\delta\varphi} - v_\varphi^2 \Delta\delta\varphi = 0 \ ; \tag{6.114}$$

the spectrum of these dipolar waves is given by $\omega_\theta^2 = \omega_0^2 + v_\theta^2 k^2$ and $\omega_\varphi^2 = v_\varphi^2 k^2$; for typical values $d = 10^{-18} esu$, $a = 10^{-8} cm$ and $I = 10^{-38} g \cdot cm^2$ (10^5 electronic mass for the molecular mass, $10^{-8} cm$ for the dipole length) we get the frequency $\omega_0 \simeq 10^{13} s^{-1}$ (infrared) and the wave velocities $v_{\theta,\varphi} \simeq 10^5 cm/s$ (the wavelengths are $\lambda_{\theta,\varphi} \simeq$

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[6] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 8, *Electrodynamics of Continuous Media*, Elsevier (1984).

$\pi\sqrt{5}a$, $\pi\sqrt{6}a$). It is worth noting that the coordinates $\delta\theta$, $\delta\varphi$ are the tilting angles of the polarization with respect to its equilibrium direction. The polar-matter elementary excitations described above can be called "dipolons". They contribute to the anomalous heat-capacity curve *vs* temperature.

The dipolar waves can couple to an external time-dependent electric field. Let $\mathbf{E}(\mathbf{r},t)=\mathbf{E}\cos(\omega t-\mathbf{kr})$ be a radiation electric field (plane wave) which makes an angle α with the polarization direction; the interaction hamiltonian is

$$H^{'}=-\frac{1}{a^3}\int d\mathbf{r}\mathbf{d}\mathbf{E}\cos(\omega t-\mathbf{kr})\ , \tag{6.115}$$

where $\mathbf{E}=E(\sin\alpha\cos\varphi^{'},\, \sin\alpha\sin\varphi^{'},\, \cos\alpha)$ and $\mathbf{d}=d(\sin\delta\theta\cos\varphi,\, \sin\delta\theta\sin\varphi,\, \cos\delta\theta)$; we may limit ourselves to $\varphi=\varphi^{'}$, and get

$$H^{'}=-\frac{1}{a^3}\int d\mathbf{r}dE(\delta\theta\sin\alpha-\frac{1}{2}\delta\theta^2\cos\alpha)\cos(\omega t-\mathbf{kr}) \tag{6.116}$$

(up to irrelevant terms); we can see that the φ-waves do not couple to the external electric field. Moreover, since the wavelength of the radiation field is much longer than the wavelength of the dipolar interaction ($v_{\theta,\varphi}\ll c$, where c is the speed of light), we may drop out the spatial dependence both in equation (6.114) and in the interaction hamiltonian $H^{'}$; we are left with the equation of motion of a harmonic oscillator under the action of an external force,

$$\ddot{\delta\theta}+\omega_0^2\delta\theta+\gamma\dot{\delta\theta}=\frac{dE}{I}\sin\alpha\cos\omega t-\frac{dE}{I}\cos\alpha\delta\theta\cos\omega t\ \ , \tag{6.117}$$

where a damping term has been introduced. The first interaction term gives

$$\ddot{\delta\theta}_1+\omega_0^2\delta\theta_1+\gamma\dot{\delta\theta}_1=\frac{dE}{I}\sin\alpha\cos\omega t\ \ , \tag{6.118}$$

which is the equation of motion of a harmonic oscillator under the action of a harmonic force; the (particular) solution is

$$\delta\theta_1=a\cos\omega t+b\sin\omega t\ \ , \tag{6.119}$$

where

$$\begin{aligned} a &= -\tfrac{dE}{2I\omega_0}\sin\alpha\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2/4}\ , \\ b &= \tfrac{dE}{2I\omega_0}\sin\alpha\tfrac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4} \end{aligned} \tag{6.120}$$

for ω near ω_0; we get a resonance for $\omega=\omega_0$; the absorbed mean power is

$$\begin{aligned} P &= dE\sin\alpha\overline{\cos\omega t\dot{\delta\theta}_1} = \tfrac{1}{2}dE\sin\alpha\cdot b\omega_0 = \\ &= \tfrac{\pi d^2E^2\sin^2\alpha}{4I}\delta(\omega_0-\omega)\ . \end{aligned} \tag{6.121}$$

The second interaction term in equation (6.117) gives the Mathieu's equation

$$\ddot{\delta\theta}_2+\omega_0^2(1+h\cos\omega t)\delta\theta_2=0\ , \tag{6.122}$$

where $h=(dE/I\omega_0^2)\cos\alpha$ (a damping term can be included). As it is well known,[7] the Mathieu's equation has both periodic solutions and aperiodic solutions, which may increase indefinitely; the latter give the parametric resonances occurring at $\omega=2\omega_0/n$, $n=1,2,3,....$ The parameter h acquires, usually, very small values (it dictates the rate of the increase in time of the resonant solutions).

The spontaneous polarization caused by the dipolar interaction as described above may appear in polarization domains, randomly distributed in polar matter (pyroelectrics, ferroelectrics), or in granular matter, where charges may accumulate at the interfaces.[8] This is known as the Maxwell-Wagner-Sillars effect (an average over the angle α should then be taken in the absorbed power). In the latter case the distance between the dipoles is much larger than the atomic

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[7] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, Cambridge (1996).

[8] J. C. Maxwell, *Lehrbuch der Elektrizitat und der Magnetismus*, vol. 1, Art. 328-330, Berlin (1983); K. W. Wagner, "Erklarung der dielektrischen Nachwirkungsvorgange auf Grund Maxwellscher Vorstellungen", Electr. Eng. (Archiv fur Elektrotechnik) **2** 371 (1914); K. W. Wagner, *Die Isolierstoffe der Elektrotechnik*, H. Schering ed., Springer, Berlin (1924); R. W. Sillars, "The properties of a dielectric containing semiconducting particles of various shapes", J. Inst. Electr. Engrs. (London) **80** 378 (1937); see also A. von Hippel, *Dielectrics and Waves*, Wiley, NY (1954) and D. E. Aspnes, Am. J. Phys. **50** 704 (1982).

distances and, consequently, the characteristic frequency ω_0 is much lower; for instance, for a distance $a = 1\mu m$ (10^4Å) we get a frequency $\omega_0 \simeq 10MHz$.

6.7 Parametric resonance

Consider a constant, uniform electric field $\mathbf{E}_0 = E_0(0,0,1)$ oriented along the z-axis; consider also a time-dependent, uniform electric field $\mathbf{E} = E(\sin\alpha, 0, \cos\alpha)\cos\omega t$ which makes an angle α with $\mathbf{E}_0$; consider an assembly of electric dipoles at thermal equilibrium, $\mathbf{d}_i = d(\sin(\theta_i+\theta)\cos(\varphi_i+\varphi), \sin(\theta_i+\theta)\sin(\varphi_i+\varphi), \cos(\theta_i+\theta))$, where θ_i, φ_i are subjected to the thermal agitation, while θ and φ are variables associated with an overall motion; we assume that this motion is much slower than the thermal motion, such that the thermal equilibrium is preserved during the motion (adiabatic motion). The potential energy of a dipole in these fields is

$$\begin{gathered} U_i = -dE_0\cos(\theta_i+\theta) - \\ -dE\cos\omega t[\sin\alpha\sin(\theta_i+\theta)\cos(\varphi_i+\varphi) + \\ +\cos\alpha\cos(\theta_i+\theta)]\ ; \end{gathered} \tag{6.123}$$

we average this potential energy with the statistical weight $\sim e^{\beta dE_0\cos\theta_i}$, where $\beta = 1/T$ is the inverse of the temperature T; since $\beta dE_0 \ll 1$, we get $\overline{\cos\theta_i} = \frac{1}{3}\beta dE_0$ (the Curie-Langevin-Debye law[9]) and $\overline{\sin\theta_i} = \pi/4$; the average energy is

$$\begin{gathered} U = \overline{U_i} = -dE_0C\cos\theta + dE_0S\sin\theta - \\ -dEC\cos\alpha\cos\omega t\cos\theta + dES\cos\alpha\cos\omega t\sin\theta\ \ , \end{gathered} \tag{6.124}$$

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[9] P. Curie, "Lois experimentales du magnetisme. Proprietes magnetiques des corps a diverses temperatures", Ann. Chim. Phys. **5** 289 (1895); P. Langevin, "Sur la theorie du magnetisme", J. Physique **4** 678 (1905); P. Langevin, "Magnetism et theorie des electrons", Ann. Chim. Phys. **5** 70 (1905); P. Debye, "Einige Resultate einer kinetischen Theorie der Isolatoren", Phys. Z. **13** 97 (1912).

where $C = \overline{\cos\theta_i}$ and $S = \overline{\sin\theta_i}$. For small values of θ we get

$$\begin{gathered} U = -dE_0C(1+\tfrac{S^2}{2C^2}) - dEC\cos\alpha\cos\omega t(1+\tfrac{S^2}{2C^2})+ \\ +\tfrac{1}{2}dE_0C(1+\tfrac{E}{E_0}\cos\alpha\cos\omega t)(\theta+\tfrac{S}{C})^2 \ ; \end{gathered} \tag{6.125}$$

with $\theta \to \theta + S/C$ (and leaving aside the precession) the relevant hamiltonian is

$$H = \frac{1}{2}I\dot{\theta}^2 + \frac{1}{2}I\omega_0^2(1+h\cos\omega t)\theta^2 \tag{6.126}$$

with the equation of motion

$$\ddot{\theta} + \omega_0^2(1+h\cos\omega t)\theta = 0 \ , \tag{6.127}$$

where

$$\omega_0^2 = \frac{\beta d^2E_0^2}{3I} \ , \ h = \frac{E}{E_0}\cos\alpha \ , \tag{6.128}$$

I being the moment of inertia of the dipole; $\sqrt{dE_0/I}$ is known as the Rabi frequency.[10] For $I = 10^{-39} - 10^{-38}g \cdot cm^2$, $d = 10^{-18}esu$, $E_0 = 10^3V/m$ $(= \frac{1}{30}statvolt/cm)$ and $T = 300K \simeq 4 \times 10^{-14}erg$ the frequency is $\omega_0 \simeq 10^5 - 10^6 s^{-1}$.

Equation (6.127) is the equation of parametric resonance of the harmonic oscillator, also known as Mathieu's equation.[11]

Unfortunately, the above description is inconsistent, because θ_i fluctuates much more rapidly than θ moves, so the θ-motion is meaningless.

6.8 Parametric resonance. Quenched dipoles

6.8.1 Strong field

Consider a constant, uniform electric field $\mathbf{E}_0 = E_0(0,0,1)$ oriented along the z-axis; the potential energy of an electric dipole

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[10] I. I. Rabi, "On the process of space quantization", Phys. Rev. **49** 324 (1936); I. I. Rabi, "Space quantization in a gyrating magnetic field", Phys. Rev. **51** 652 (1937).

[11] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, Cambridge (1996).

$\mathbf{d} = d(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ of arbitrary orientation θ, φ is $U = -dE_0\cos\theta$. The hamiltonian of rotation in this field is given by[12]

$$H = \frac{1}{2}I(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) - dE_0\cos\theta \ , \tag{6.129}$$

where I is the moment of inertia of the dipole, considered as a sherical pendulum (spherical top). The equation of motion

$$I\frac{d}{dt}(\dot{\varphi}\sin^2\theta) = 0 \tag{6.130}$$

indicates that the component L_z of the angular momentum is conserved, $\dot{\varphi}\sin^2\theta = L_z/I$; consequently, an effective potential function

$$U_{eff} = \frac{L_z^2}{2I\sin^2\theta} - dE_0\cos\theta \tag{6.131}$$

occurs in the hamiltonian. We assume that the dipole energy dE_0 is much greater than the rotation energy L_z^2/I, which is of the order of the temperature T. For typical value $d = 10^{-18}esu$ and temperature $T = 300K \simeq 4\times10^{-14}erg$ this condition requires an electric field $E_0 \gg T/d = 4\times10^4 statvolt/cm \simeq 1.2\times10^9 V/m$. This is a strong electric field; it may appear as an internal field in polar condensed matter. For comparison, the electric field created by an electron charge at distance $1\text{Å} = 10^{-8}cm$ is $4.8\times10^{-10}/10^{-16} = 4.8\times10^6 stavolt/cm$ (atomic fields). At lower temperatures, the field E_0 is lower, with values attainable in the laboratory; at lower temperatures the molecular rotations may be hindered, and the dipoles are quenched; averaging over their small motions (small vibrations and rotations) they may

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[12] In general, since the molecules have various orientations, it is convenient to work with the hamiltonian of rotations with respect to the frame fixed on each molecule. For instance, the general hamiltonian of rotations for an asymmetrical top is $L_\xi^2/2I_1 + L_\eta^2/2I_2 + L_\zeta^2/2I_3$, where ξ, η, ζ are local coordinates, $L_{\xi,\eta,\zeta}$ are the corresponding components of the angular momentum and $I_{1,2,3}$ are the corresponding moments of inertia. In the laboratory frame the coordinates are x, y, z, and the wavefunctions are the rotation matrices. The energy levels depend on the angular momentum L and its component M in the laboratory frame and on particular quantum numbers associated with the moments of inertia. In the particular case of a spherical top, due to its symmetry, there is no need to introduce the coordinates of the fixed axes (though the degeneracy of the states is $(2L+1)^2$).

provide a strong local static electric field. Similarly, a high static electric field may appear near polar impurities with high moments of inertia, embedded in polar matter. The occurrence of such an electric field is very similar with the potential $U_0(1-\cos 2\theta)$ which may act upon rotating molecules in crystals, driving the transition from rotations to vibrations (quenched rotations) which is seen in the curve of the heat capacity *vs* temperature.[13] Under such conditions the effective potential given by equation (6.131) has a minimum value for $\theta_0 \simeq (L_z^2/IdE_0)^{1/4} \simeq (T/dE_0)^{1/4} \ll 1$; it can be expanded in powers of $\delta\theta = \theta - \theta_0$ around this minimum value as

$$U_{eff} \simeq -dE_0 + 2dE_0\delta\theta^2 \ ; \tag{6.132}$$

the hamiltonian given by equation (6.129) becomes

$$H \simeq \frac{1}{2}I\delta\dot{\theta}^2 + \frac{1}{2}I\omega_0^2\delta\theta^2 - dE_0 \ , \tag{6.133}$$

where $\omega_0 = 2\sqrt{dE_0/I}$ is sometimes known as Rabi's frequency;[14] according to our condition of strong field, we have $\omega_0 \gg 10^{12}s^{-1}$. Therefore, the dipoles are quenched in the static electric field E_0, where they execute small oscillations and rotations. The angle φ rotates freely with the frequency $\dot{\varphi} \simeq L_z/I\sin^2\theta_0 = \frac{1}{2}\omega_0$ ($\varphi = \frac{1}{2}\omega_0 t$). It is worth noting that this frequency is given by the static field E_0. Consider an external time-dependent field $\mathbf{E}(t) = E(t)(\sin\alpha, 0, \cos\alpha)$, $E(t) = E\cos\omega t$, which makes an angle α with the z-axis; its interaction with the dipole is

$$H_{int} = -dE(t)(\sin\alpha\sin\theta\cos\varphi + \cos\alpha\cos\theta) \ , \tag{6.134}$$

which provides two relevant interaction hamiltonians:

$$\begin{gathered} H_{1int} = -\tfrac{1}{2}dE\sin\alpha\left[\cos(\omega+\tfrac{1}{2}\omega_0)t + \cos(\omega-\tfrac{1}{2}\omega_0)t\right]\delta\theta \ , \\ H_{2int} = \tfrac{1}{2}dE\cos\alpha\cos\omega t\cdot\delta\theta^2 \ . \end{gathered} \tag{6.135}$$

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[13] L. Pauling, "The rotational motion of molecules in crystals", Phys. Rev. **36** 430 (1930); T. E. Stern, "The symmetrical spherical oscillator, and the rotational motion of homopolar molecules in crystals", Proc. Roy. Soc. **A130** 551 (1931).

[14] I. I. Rabi, "On the process of space quantization", Phys. Rev. **49** 324 (1936); I. I. Rabi, "Space quantization in a gyrating magnetic field", Phys. Rev. **51** 652 (1937).

The interaction hamiltonian H_{1int} produces transitions between the harmonic-oscillator states n and $n+1$ with the resonance frequency $\Omega=\frac{1}{2}\omega_0$, $\frac{3}{2}\omega_0$. In general, for an interaction $H_{int}=h\cos\omega t$, the rate of transition between two states n and $n+s$, with energies E_n, E_{n+s} is

$$\frac{\partial\left|c_{n+s,n}\right|^2}{\partial t}=\frac{\pi}{2\hbar^2}\left|h_{n+s,n}\right|^2\delta(\omega_{n;s}-\omega) \tag{6.136}$$

in the first order of the perturbation theory, where $\omega_{n;s}=(E_{n+s}-E_n)/\hbar$. For H_{1int} we get

$$\frac{\partial\left|c_{n+1,n}\right|^2}{\partial t}=\frac{\pi}{16\hbar I\omega_0}d^2E^2(n+1)\sin^2\alpha\delta(\omega-\Omega) \tag{6.137}$$

and the absorbed power

$$\begin{aligned}P_q=\hbar\Omega\tfrac{\partial\left|c_{n+1,n}\right|^2}{\partial t}=\tfrac{\pi}{16I\omega_0}d^2E^2\Omega(n+1)\sin^2\alpha\delta(\omega-\Omega)=\\ =\tfrac{1}{16I\omega_0}d^2E^2\Omega(n+1)\sin^2\alpha\tfrac{\gamma}{(\omega-\Omega)^2+\gamma^2}\ ,\ \gamma\rightarrow 0^+\ \ ,\end{aligned} \tag{6.138}$$

which is a typical resonance curve. In order to compute the mean power the thermal weigths $e^{-\beta\hbar\omega_0 n}/\sum e^{-\beta\hbar\omega_0 n}$ should be inserted, where $\beta=1/T$ is the inverse of the temperature T; in addition, the reverse transitions must be taken into account. Since $\beta\hbar\omega_0\gg 1$, only the lowest states n are excited by interaction. The temperature dependence is given by

$$\begin{gathered}P_{q,th}=\tfrac{\pi}{16I\omega_0}d^2E^2\Omega\sum\nolimits_{n=0}(n+1)\cdot\\ \cdot\left[e^{-\beta\hbar\omega_0 n}-e^{-\beta\hbar\omega_0(n+1)}\right]\times\\ \times\sin^2\alpha\delta(\omega-\Omega)/\sum\nolimits_{n=0}e^{-\beta\hbar\omega_0 n}\ \ ,\end{gathered} \tag{6.139}$$

where the summation over n is, in principle, limited.

We must limit ourselevs to the lowest states of the harmonic oscillator, since the oscillation amplitude $\delta\theta$ must be much smaller than the angle θ_0. The matrix element $(\delta\theta)_{n+1,n}=\sqrt{\hbar/2I\omega_0}\sqrt{n+1}$ for the harmonic oscillator should be much smaller than $\theta_0\simeq(L_z^2/IdE_0)^{1/4}$, which implies $\hbar(n+1)\ll 4L_z\simeq 4\sqrt{IT}$ (corrections to precession are called nutations); for typical values $I = 10^{-39} - 10^{-38} g \cdot cm^2$ ($10^4 - 10^5$ electronic mass for the molecular mass, $10^{-8} cm$ for the dipole length) we get $n \ll 20 - 80$ for $T = 300K$ (and $n \ll 2 - 8$ for $T = 3K$). For $\beta\hbar\omega_0 \gg 1$ we may extend the summation in equation (6.139) to $n = \infty$; we get $P_{q,th}$ independent of temperature. Making use of the expressions $L_x = I(-\dot{\theta}\sin\varphi - \dot{\varphi}\sin\theta\cos\theta\cos\varphi)$, $L_y = I(\dot{\theta}\cos\varphi - \dot{\varphi}\sin\theta\cos\theta\sin\varphi)$, we get $L_x \simeq -(1/2)I\omega_0\theta_0\cos\omega_o t/2$ and $L_y \simeq -(1/2)I\omega_0\theta_0\sin\omega_o t/2$ for the transverse components of the angular momentum, which show that the high-field approximation corresponds to $L_x^2 + L_y^2 \simeq L^2 \gg L_z^2$.

The quasi-classical approximation can be used for the hamiltonian given by equation (6.133) with the interaction H_{1int} given by equations (6.135) (possibly with a coarse-graining average in condensed matter); it is the quasi-classical approximation for harmonic oscillators subjected to an external field with frequencies $\omega \pm \omega_0/2$.

Under the same conditions, the harmonic-oscillator hamiltonian given by equation (6.133) and the interaction hamiltonian H_{2int} given by equation (6.135),

$$H^{'} = H + H_{2int} = \frac{1}{2}I\delta\dot{\theta}^2 + \frac{1}{2}I\omega_0^2(1 + h\cos\omega t)\delta\theta^2 \ , \qquad (6.140)$$

where $h = \frac{E}{2E_0}\cos\alpha$, leads to the classical equation of motion

$$\delta\ddot{\theta} + \omega_0^2(1 + h\cos\omega t)\delta\theta = 0 \ , \qquad (6.141)$$

which is the well-known equation of parametric resonance (Mathieu's equation). As it is well known, besides periodic solutions, the classical equation (6.141) has also aperiodic solutions, which may grow indefinitely with increasing time; these are (parametrically) resonant solutions, which occur for ω in the neighbourhood of $2\omega_0/n$, $n = 1, 2, 3....$ As we can see immediately, the solutions of equation (6.141) are determined by the initial conditions $\delta\theta(t = 0)$ and $\delta\dot{\theta}(t = 0)$ (as for any homogeneous equation). Since fluctuations generate vanishing initial conditions, the classical solutions of equation (6.141) are vanishing.

The quantum-mechanical dynamics is different. The interaction hamiltonian H_{2int} produces transitions between the oscillator states n and $n+2$ (due to the matrix elements of $\delta\theta^2$; this is an example of a double-quanta process). These transitions have frequency $2\omega_0$, in accordance with the classical dynamics. The transition rate is

$$\frac{\partial \left| c_{n+2,n} \right|^2}{\partial t} = \frac{\pi h^2}{128} \omega_0^2 (n+1)(n+2) \delta(2\omega_0 - \omega) \tag{6.142}$$

and the absorbed power

$$\begin{aligned} P_q = 2\hbar\omega_0 \tfrac{\partial |c_{n+2,n}|^2}{\partial t} = \tfrac{\pi h^2}{64} \hbar\omega_0^3 (n+1)(n+2)\delta(2\omega_0 - \omega) = \\ = \tfrac{h^2}{64} \hbar\omega_0^3 (n+1)(n+2) \tfrac{\gamma}{(2\omega_0 - \omega)^2 + \gamma^2} \ , \ \gamma \rightarrow 0^+ \ , \end{aligned} \tag{6.143}$$

where we may restrict to the lowest states. The intensity given by equation (6.143) is small, because, especially, of the factor $(E/E_0)^2$. The temperature dependence is given by

$$\begin{aligned} P_{q,th} = \tfrac{\pi h^2}{64} \hbar\omega_0^3 \textstyle\sum_{n=0} (n+1)(n+2) \times \\ \times \left[e^{-\beta\hbar\omega_0(2n+1)} - e^{-\beta\hbar\omega_0(2n+3)} \right] \cdot \\ \cdot \delta(2\omega_0 - \omega) / \left[\textstyle\sum_{n=0} e^{-\beta\hbar\omega_0 n} \right]^2 \ , \end{aligned} \tag{6.144}$$

in accordance with the direct transitions $n \rightarrow n+1$, $n+1 \rightarrow n+2$ and the corresponding reverse transitions; $P_{q,th}$ is also diminished by the thermal factor $e^{-\beta\hbar\omega_0}$ for $\beta\hbar\omega_0 \gg 1$.

The parametric resonance disappears for $\alpha = \frac{\pi}{2}$, *i.e.* for the applied field $\mathbf{E}$ at right angle with the quenching field $\mathbf{E}_0$. The quenching field may ocurr, very likely, in (polar) solids; the effect of the parametric resonance depends on the orientation of the crystal; in amorphous samples the absorption is averaged over angles α ($\overline{\cos^2 \alpha} = \frac{1}{3}$). The parameter γ in equation (6.143), which gives the width of the absorption line, is a damping parameter; in solids it originates, very likely, in the dipolar interaction. Since the dipolar interaction may be taken mainly in the quenching effect, we may expect a small damping, and, consequently, rather sharp resonance lines. In liquids, besides the random distribution of the dipoles (and the average over angle α), we may expect the usual motional narrowing of the line. In gases the quenching field is weak, and the parametric resonance is not likely to occur.

6.8.2 Weak field

Consider now the opposite case, when the field E_0 is weak, such that $dE_0 \ll L_z^2/I$. The effective potential U_{eff} given by equation (6.131) has a minimum value for $\theta \simeq \frac{\pi}{2}$ and the hamiltonian given by equation (6.129) reduces to

$$H \simeq \frac{1}{2} I \dot{\widetilde{\theta}}^2 + \frac{1}{2} I \omega_0^2 \widetilde{\theta}^2 \ , \tag{6.145}$$

where $\widetilde{\theta} = \theta - \frac{\pi}{2}$ and $\omega_0 = L_z/I$; the field E_0 brings only a small correction to the $\pi/2$-shift in θ, while its contribution to the hamiltonian is a second-order effect. The angle φ moves freely with angular velocity $\dot{\varphi} = \omega_0$. In contrast with the strong-field case, where the frequency $\dot{\varphi}$ is fixed by the static field E_0, in the weak-field case we may quantize the φ-motion, according to $L_z = \hbar m$, m any integer, such that $\omega_0 = \frac{\hbar}{I} m$; the lowest value of this frequency is $\hbar/I \simeq 10^{11} - 10^{12} s^{-1}$ for typical values $I = 10^{-39} - 10^{-38} g \cdot cm^2$ ($10^4 - 10^5$ electronic mass for the molecular mass, $10^{-8} cm$ for the molecular diameter). We can see that the molecular rotations are described by a set of harmonic oscillators with frequencies $\omega_0 = \frac{\hbar}{I} m$, beside the φ-precession (which has the same frequencies ω_0). The energy quanta are $\hbar \omega_0 = \frac{\hbar^2}{I} m$, with the lowest value $\frac{\hbar^2}{I} = 1K - 10K$. The approximation described above is valid for $\widetilde{\theta}_{n+1,n} = \sqrt{\hbar/2I\omega_0}\sqrt{n+1} \ll 1$, which leads to $\hbar(n+1) \ll 2L_z$, or $n \ll m$. Similarly, the transverse components of the angular momentum are very small, $L_x^2 + L_y^2 \ll L^2 \simeq L_z^2$ ($m \simeq l$). At room temperature m may acquire as high values as $m = 30 - 300$.

The interaction hamiltonian given by equation (6.134) leads to two relevant interactions

$$\begin{gathered} H_{1int} = dE \cos\alpha \cos\omega t \cdot \widetilde{\theta} \ , \\ H_{2int} = \tfrac{1}{4} dE \sin\alpha \left[\cos(\omega + \omega_0)t + \cos(\omega - \omega_0)t\right] \cdot \widetilde{\theta}^2 \ . \end{gathered} \tag{6.146}$$

The interaction H_{1int} produces transitions between the harmonic-oscillator states n and $n+1$, with an absorbed power

$$P_q = \frac{\pi}{4I} d^2 E^2 (n+1) \cos^2\alpha \delta(\omega_0 - \omega) \ . \tag{6.147}$$

For low values of m, due to the validity condition of this approximation ($n \ll m$), only a few states contribute to the absorbed power, such that we restrict ourselves to small values of n in equation (6.147) and sum over a few values of m in $\delta(\omega_0 - \omega) = \delta(\hbar m/I - \omega)$ with the statistical weight $e^{-\beta\hbar^2 m^2/2I}$. As long as $\hbar/I \gg \gamma$, where γ is the resonance width, the spectrum exhibits a few, distinct absorption lines at frequencies $\omega_0 = \hbar m/I$ ($\hbar/I \simeq 10^{11} - 10^{12}s^{-1}$) (a band of absorption). The temperature dependence is given by

$$\begin{gathered} P_{q,th} = \tfrac{\pi}{4I} d^2 E^2 \cos^2\alpha \cdot C \textstyle\sum_{m>0} e^{-\beta\hbar^2 m^2/2I} \times \\ \times \{\textstyle\sum_{n=0}(n+1)\left[e^{-\beta\hbar\omega_0 n} - e^{-\beta\hbar\omega_0(n+1)}\right] / \\ / \textstyle\sum_{n=0} e^{-\beta\hbar\omega_0 n}\}\delta(\omega_0 - \omega)\ , \end{gathered} \tag{6.148}$$

where $\omega_0 = \hbar m/I$ and $C\sum_{m>0} e^{-\beta\hbar^2 m^2/2I} = 1$. At room temperature the envelope of this function is

$$P_{q,th} = \frac{\pi}{4} d^2 E^2 \cos^2\alpha \sqrt{\frac{2\pi\beta}{I}} e^{-\beta I\omega^2/2}\ . \tag{6.149}$$

The interaction hamiltonian H_{2int} given by equation (6.146) produces transitions between states n and $n+2$ (separated by frequency $2\omega_0$) for external frequencies $\omega = \Omega = \omega_0$, $3\omega_0$. The absorbed power is

$$P_q = \frac{\pi\hbar\Omega}{128 I^2\omega_0^2} d^2 E^2 (n+1)(n+2)\sin^2\alpha\delta(\Omega - \omega)\ . \tag{6.150}$$

These parametric resonances occurring at frequencies $\Omega = \omega_0$, $3\omega_0$ are superposed over the transitions produced by H_{1int}. The temperature dependence is given by

$$\begin{gathered} P_{q,th} = \tfrac{\pi\hbar}{128 I^2} d^2 E^2 \sin^2\alpha \cdot C \textstyle\sum_{m>0} \tfrac{\Omega}{\omega_0^2} e^{-\beta\hbar^2 m^2/2I} \times \\ \times \textstyle\sum_{n=0}(n+1)(n+2)\left[e^{-\beta\hbar\omega_0(2n+1)} - e^{-\beta\hbar\omega_0(2n+3)}\right] / \\ / \left[\textstyle\sum_{n=0} e^{-\beta\hbar\omega_0 n}\right]^2 \delta(\Omega - \omega)\ ; \end{gathered} \tag{6.151}$$

summation over n gives

$$P_{q,th} = \tfrac{\pi\hbar}{64I^2} d^2E^2 \sin^2\alpha \cdot C \sum\nolimits_{m>0} \tfrac{\Omega}{\omega_0^2} e^{-\beta\hbar^2 m^2/2I} \cdot \\ \cdot \tfrac{e^{-\beta\hbar\omega_0}}{(1+e^{-\beta\hbar\omega_0})^2} \delta(\Omega-\omega) \tag{6.152}$$

whence we can get either the band of absorption or the envelope.

It is worth noting that the weak field E_0 does not appear explicitly in the above formulae; its role is that of setting the z-axis, to highlight the directional effect of the interaction field E through the angle α, and to reduce the conservation of the angular momentum $\mathbf{L}$ to the conservation of only one component L_z. For comparison, we give here the result for free rotations, with the hamiltonian $H = L^2/2I$, energy levels $E_l = \hbar^2 l(l+1)/2I$, $l = 0, 1, 2, ...$, and eigenfunctions Y_{lm} (spherical harmonics). The interaction hamiltonian

$$H_{int} = -dE(\sin\alpha \sin\theta \cos\varphi + \cos\alpha \cos\theta) \cos\omega t \tag{6.153}$$

generates transitions according to the matrix elements of $\sin\theta\cos\varphi$ and $\cos\theta$. Since the rotations are free, we may take E directed along the z-axis, *i.e.* we may put $\alpha = 0$. The matrix elements of $\cos\theta$ are given by

$$(\cos\theta)_{l+1,m;l,m} = C_{lm} = -i\sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}} \ . \tag{6.154}$$

We get the absorbed power

$$P_q = \tfrac{\pi}{2\hbar} d^2E^2 \sum\nolimits_{m=-l}^{l} |C_{lm}|^2 \omega_l \delta(\omega_l - \omega) = \\ = \tfrac{\pi d^2E^2}{6\hbar} \omega_l (l+1) \delta(\omega_l - \omega) = \tfrac{\pi d^2E^2}{6I} (l+1)^2 \delta(\omega_l - \omega) \ , \tag{6.155}$$

where $\omega_l = \hbar(l+1)/I$, $l = 0, 1, 2, ...$ At finite temperatures

$$P_{q,th} = \tfrac{\pi d^2E^2}{2\hbar} \sum\nolimits_{m=-l}^{l} |C_{lm}|^2 [e^{-\beta\hbar^2 l(l+1)/2I} - \\ -e^{-\beta\hbar^2 (l+1)(l+2)/2I}] \omega_l \delta(\omega_l - \omega)/Z \ , \tag{6.156}$$

where

$$Z=\sum_{l=0}(2l+1)e^{-\beta\hbar^2 l(l+1)/2I}=\frac{2I}{\beta\hbar^2}\ ; \tag{6.157}$$

we get

$$\begin{aligned} P_{q,th}=&\tfrac{\pi d^2E^2}{12I}(l+1)^3\left(\tfrac{\beta\hbar^2}{I}\right)^2e^{-\beta\hbar^2 l(l+1)/2I}\delta(\omega_l-\omega)=\\ &=\tfrac{1}{2}P_q(l+1)\left(\tfrac{\beta\hbar^2}{I}\right)^2e^{-\beta\hbar^2 l(l+1)/2I}\ . \end{aligned} \tag{6.158}$$

A quasi-classical approximation can also be used for the dynamical variable $z=l\cos\theta$ (where l is the length of the dipole). We can see that the absorbed power for free rotations occurs for the same frequencies $\omega_l=\hbar(l+1)/I$, $l=0,1,2...$ as the frequencies $\omega_0=\hbar m/I$, $m=0,1,2...$ corresponding to the presence of a weak static field E_0, although the intensities of the spectral lines are different (compare equation (6.147) with equation (6.155), for instance, where an additional degeneracy is absent in the presence of the field, as expected); in addition, the parametric resonance is a new feature in the presence of the static electric field. It is also worth noting that the expansion of the effective potential function U_{eff} in powers of $\widetilde{\theta}$ is an approximation to free rotations with $L_z=const$, instead of $\mathbf{L}=const$.

It is also worth noting that a weak static field has an influence on the statistical behaviour. Indeed, the hamiltonian of rotations

$$H=\frac{1}{2}I(\dot{\theta}^2+\dot{\varphi}^2\sin^2\theta) \tag{6.159}$$

can also be written as

$$H=\frac{1}{2I}P_\theta^2+\frac{1}{2I\sin^2\theta}P_\varphi^2 \tag{6.160}$$

with the momenta (angular momenta) $P_\theta=I\dot{\theta}$ and $P_\varphi=I\dot{\varphi}\sin^2\theta$. The classical statistical distribution is

$$const\cdot dP_\theta dP_\varphi d\theta e^{-\beta P_\theta^2/2I}e^{-\beta P_\varphi^2/2I\sin^2\theta}\ , \tag{6.161}$$

or, integrating over momenta, $\frac{1}{2}\sin\theta d\theta$. In the presence of the field we have the distribution $\simeq \frac{1}{2}\sin\theta d\theta \cdot e^{\beta \mathbf{dE}_0}$ (since $\beta dE_0 \ll 1$), which leads, for example, to $\overline{\cos\theta} = \beta dE_0/3$ (the well-known Curie-Langevin-Debye law[15]). Similarly, in the quantum-mechanical regime, for $dE_0 \ll \hbar^2/I$, the interaction $-dE_0\cos\theta$ brings a second-order contribution to the energy levels $E_l = \hbar^2 l(l+1)/2I$, there appear diagonal matrix elements of $(\widetilde{\cos\theta})_{lm,lm}$ in the first-order of the perturbation theory, and the mean value is given by $\overline{\cos\theta} = \sum(\widetilde{\cos\theta})_{lm,lm}\Delta(\beta E_l)e^{-\beta E_l}/$ $/\sum e^{-\beta E_l} = \beta dE_0/3$.

6.8.3 Mathieu's equation

Mathieu's equation given by equation (6.141) is solved by means of the perturbation theory for $h \ll 1$.[16] Besides periodic solutions, it has also aperiodic solutions, which may increase exponentially in time. For the unperturbed solution $\cos\omega_0 t$, $\sin\omega_0 t$ the h-term in equation (6.141) gives rise to terms of the form $\cos(\omega_0 \pm \omega)t$, $\sin(\omega_0 \pm \omega)t$; and so on, in higher orders of the perturbation theory. It follows that a resonance may occur for $\omega = 2\omega_0 + \varepsilon$, $\varepsilon \ll \omega_0$; the solution is

$$\delta\theta \simeq a\cos(\omega_0 + \frac{\varepsilon}{2})t + b\sin(\omega_0 + \frac{\varepsilon}{2})t \ , \tag{6.162}$$

where a and b are slowly-varying functions of time. We get

$$2\dot{a} + (\varepsilon + h\omega_0/2)b = 0 \ , \ 2\dot{b} - (\varepsilon - h\omega_0/2)a = 0 \ , \tag{6.163}$$

with a, $b \sim e^{st}$, where $s^2 = \frac{1}{4}(h^2\omega_0^2/4 - \varepsilon^2)$, for $-h\omega_0/2 < \varepsilon < h\omega_0/2$. If the damping is included, the coefficients a and b go like $e^{(s-\gamma)t}$ and the resonance occurs for $-\sqrt{(h\omega_0)^2/4 - 4\gamma^2} < \varepsilon < \sqrt{(h\omega_0)^2/4 - 4\gamma^2}$; a threshold occurs now for the perturbation amplitude h.

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[15] P. Curie, "Lois experimentales du magnetisme. Proprietes magnetiques des corps a diverses temperatures", Ann. Chim. Phys. **5** 289 (1895); P. Langevin, "Sur la theorie du magnetisme", J. Physique **4** 678 (1905); P. Langevin, "Magnetism et theorie des electrons", Ann. Chim. Phys. **5** 70 (1905); P. Debye, "Einige Resultate einer kinetischen Theorie der Isolatoren", Phys. Z. **13** 97 (1912).

[16] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 1, *Mechanics*, Elsevier (1976).

For the sake of definiteness we may set $\varepsilon = 0$; the initial conditions for $\delta\theta$ and $\delta\dot{\theta}$ are provided by fluctuations; we can see that their mean values are vanishing. For illustrative purposes we may limit ourselves to a and write approximately

$$\delta\theta \simeq \pi e^{st} \cos\omega_0 t \ , \ s = \frac{1}{4} h\omega_0 \ , \tag{6.164}$$

or, for its Fourier transform,

$$\delta\theta(\omega) \simeq -\frac{\pi(s+i\omega)}{(\omega_0^2-\omega^2)+2is\omega} \ , \tag{6.165}$$

and

$$\delta\theta(\omega) \simeq -\frac{\pi}{2}\delta(\omega-\omega_0) \tag{6.166}$$

for ω close to ω_0. We can also write

$$\delta\theta(\omega) \simeq -\pi\delta(2\omega_0-\omega) = -\pi^2 \frac{\gamma/2}{(2\omega_0-\omega)^2+\gamma^2/4} \tag{6.167}$$

similar with the resonance electric field $E\cos 2\omega_0 t$. The energy absorbed per unit time is obtained from equation (6.127) as

$$P = -hI\omega_0^2 \overline{\delta\theta\delta\dot{\theta}\cos 2\omega_0 t} \ , \tag{6.168}$$

where s is set equal to zero and the damping parameter γ is included; we get $P = \frac{1}{4}a^2 hI\omega_0^2\gamma$.

Parametric resonance occurs also for $\omega = 2\omega_0/n$, $n = (1), 2, 3, ...$, within a more narrow ε-range.

The quasi-classical approximation can be applied for the problem described above with the interaction hamiltonian H_{1int}; it is a quasi-classical approximation for harmonic oscillators. For the Mathieu's equation, which implies transitions with frequency $2\omega_0$, corresponding to the matrix elements of $\delta\theta^2$ or $\widetilde{\theta}^2$ between harmonic-oscillator states n and $n+2$, we introduce the variable $\theta_2 = \delta\theta^2$, or $\theta_2 = \widetilde{\theta}^2$ and write the quasi-classical equation of motion

$$\ddot{\theta}_2 + 4\omega_0^2\theta_2 = -\frac{1}{2}h\omega_0^2\cos\omega t \tag{6.169}$$

for H_{2int} given by equation (6.140); similarly, we can use H_{2int} given by equation (6.146). Introducing the damping parameter γ we get the solution

$$\theta_2 = a\cos\omega t + b\sin\omega t \ , \tag{6.170}$$

where

$$\begin{aligned} a &= \tfrac{1}{8}h\omega_0 \tfrac{\omega-2\omega_0}{(\omega-2\omega_0)^2+\gamma^2/4} \ , \\ b &= -\tfrac{1}{8}h\omega_0 \tfrac{\gamma/2}{(\omega-2\omega_0)^2+\gamma^2/4} \ . \end{aligned} \tag{6.171}$$

Unfortunately, $\theta_2 = \delta\theta^2$ does not offer the possibility to compute the absorbed power; this would only be possible for $\delta\theta \simeq \delta\theta^2$, which would imply $\delta\theta \simeq 1$ or $\hbar/2I\omega_0 \simeq 1$ for small harmonic-oscillator quantum numbers; under such circumstances the absorbed power is $P = -hI\omega_0^2\omega b/4$, which is comparable with P_q given by equation (6.143) for $n = 0$ and $\hbar/2 \simeq I\omega_0$; the quasi-classical approximation has a limited applicability in these conditions.

It is also worth noting the difference between the quasi-classical variable $\theta_2 = \delta\theta^2$ and the classical variable $\delta\theta^2$: the amplitude of the classical variables $\delta\theta$ and $\delta\theta^2$ is determined from initial conditions, while it is determined by the interaction (driving force) for the quasi-classical variable θ_2. In this respect, the quasi-classical approximation resembles more the quantum-mechanical approach than the classical one.

7 Parametric Resonance in Rotation Molecular Spectra

7.1 Summary and introduction

The rotation molecular spectra, generated by the coupling of an external time-dependent electric field with the molecular electric dipole moment, are discussed in a few particular conditions which may be of some experimental interest. First, the classical dynamics of the molecule viewed as a spherical pendulum is presented, and the quantum-mechanical rotation spectrum is derived (transitions between rotation levels) at finite temperatures. Second, the same problem is analyzed in the presence of a static external electric field, in two particular cases, namely, strong and weak field. For a strong static electric field the dipoles are quenched in equilibrium positions, giving rise to a macroscopic electric polarization; they may execute small rotations and vibrations around these positions, which may exhibit a parametric resonance. This situation may be relevant for polar matter (like pyroelectrics, ferroelectrics), or for heavy impurities embedded in a polar solid, which may provide strong local static electric fields. A similar situation may also appear for a weak static electric field. Next, the dipolar interaction is analyzed in polar condensed matter, where it is shown that new polarization modes may appear for a spontaneous macroscopic value of the electric polarization (these modes are tentatively called "dipolons"); one of the polarization modes is also related to a parametric resonance. The extension of these considerations to magnetic dipoles is also briefly discussed.

Many molecules have a permanent electric dipole moment in their ground state, which may couple to an external electric field; such a coupling may give rise to changes (transitions) in the molecular rotation. An external time-dependent electric field may also cause vibrations of the induced dipole moment. Typically, the molecular vibration-rotation spectra have frequencies in the range $\nu = 10^{13} - 10^{11}$(angular frequency $\omega = 10^{14} - 10^{12}$, infrared region).[1] We introduce here a new feature in the rotation molecular spectra, which is a parametric resonance caused by the presence of an external static electric field. We present also a dipolar interaction model in polar matter, which generates new polarization modes (tentatively called "dipolons"), including parametric resonances. The discussion is briefly extended to similar features exhibited by magnetic moments.[2]

7.2 Free rotations

In many cases the free molecular rotations are described satisfactorily by using a spherical-pendulum model (spatial, rigid rotator, spherical top) for the molecule. A spherical pendulum consists of a point of mass M which rotates freely in space at the end of a radius $\mathbf{r} = r(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, as described by the hamiltonian

$$H = \frac{1}{2}M\dot{\mathbf{l}}^2 = \frac{1}{2}Ml^2(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) \ ; \tag{7.1}$$

if the point has a charge q, it is a dipole $\mathbf{d} = q\mathbf{r}$ which can couple to an external electric field $\mathbf{E}\cos\omega t$, with an interaction hamiltonian $H_{int}(t) = -dE\cos\theta\cos\omega t$. We take the electric field directed along the z-axis.

As it is well known, the angular momentum $\mathbf{L} = M\mathbf{r}\times\dot{\mathbf{r}}$ has the components $L_x = Mr^2(-\dot{\theta}\sin\varphi - \dot{\varphi}\sin\theta\cos\theta\cos\varphi)$, $L_y = Mr^2(\dot{\theta}\cos\varphi - \dot{\varphi}\sin\theta\cos\theta\sin\varphi)$, $L_z = Mr^2\dot{\varphi}\sin^2\theta$, so that the rotation hamiltonian can be written as

$$H = \frac{1}{2I}L^2 \ , \tag{7.2}$$

where $I = Mr^2$ is the moment of inertia. The quantum-mechanical

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[1] G. Herzberg, *Molecular Spectra and Molecular Structure*, vol.1, Van Nostrand, Princeton (1950).

[2] M. Apostol and L. C. Cune, "Molecular dynamics in high electric fields", Chem. Phys. **472** 262 (2016).

expression for L^2 is

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] \ , \tag{7.3}$$

with the eigenfunctions Y_{lm} (spherical harmonics) and the eigenvalues $\hbar^2 l(l+1)$, $l = 0, 1, ...$ The z-component of the angular momentum is $L_z = -i\hbar\frac{\partial}{\partial\varphi}$, with the same eigenfunctions Y_{lm}, $L_z Y_{lm} = \hbar m Y_{lm}$, $m = -l, -l+1, ...l$. Therefore, the energy levels of the spherical pendulum are $E_l = \frac{\hbar^2}{2I} l(l+1)$; they are degenerate with respect to the quantum number m which takes $2l+1$ values.

The classical dynamics of the free motion is governed by the equations

$$\ddot{\theta} = \dot{\varphi}^2 \sin\theta\cos\theta \ , \ I\frac{d}{dt}(\dot{\varphi}\sin^2\theta) = 0 \ ; \tag{7.4}$$

from the second equation (7.4) we get $\dot{\varphi} = L_z/I\sin^2\theta$, which indicates the conservation of the component L_z of the angular momentum. Moreover, making use of the equations of motion (7.4), we check easily the conservation of the other two components L_x and L_y of the angular momentum given above; indeed, the angular momentum $\mathbf{L}$ is conserved in the free motion of the spherical pendulum. The hamiltonian given by equation (7.1) can be written as

$$H = \frac{1}{2} I\dot{\theta}^2 + \frac{L_z^2}{2I\sin^2\theta} \ ; \tag{7.5}$$

the effective potential function $U_{eff} = L_z^2/2I\sin^2\theta$ has a minimum for $\theta = \pi/2$; the motion may be limited to small oscillations about the equatorial plane $\theta = \pi/2$. Indeed, introducing $\delta\vartheta = \theta - \pi/2$ we get

$$\frac{L_z^2}{2I\sin^2\theta} = \frac{L_z^2}{2I} + \frac{L_z^2}{2I}\delta\theta^2 + ... \tag{7.6}$$

and

$$H \simeq \frac{1}{2} I\delta\dot{\theta}^2 + \frac{L_z^2}{2I}\delta\theta^2 + \frac{L_z^2}{2I} \ , \tag{7.7}$$

$$\begin{gathered} L_x = I(-\delta\dot{\theta}\sin\varphi + \dot{\varphi}\delta\theta\cos\varphi) \ , \\ L_y = I(\delta\dot{\theta}\cos\varphi + \dot{\varphi}\delta\theta\sin\varphi) \ , \ \dot{\varphi} = L_z/I = \omega_0 \ , \end{gathered} \tag{7.8}$$

where we have introduced the frequency $\omega_0 = L_z/I$. We can see that there is a precession $\varphi = \omega_0 t$ about the z-axis and an oscillation $\delta\theta = A\cos(\omega_0 t + \delta)$, where A is an undetermined amplitude and δ is an undetermined phase, according to the small oscillations governed by the hamiltonian given by equation (7.7). We can check easily that the angular momentum given by equations (7.8) is conserved ($\dot{\mathbf{L}} = 0$); the components of the angular momentum are $L_x = IA\omega_0 \cos\delta$ and $L_y = IA\omega_0 \sin\delta$, and $L_z = I\omega_0$. We can rotate the equatorial plane $\theta = \pi/2$ by an angle given by $\sin\alpha = IA\omega_0/\sqrt{I^2\Omega^2 + I^2A^2\Omega^2} \simeq A$, such that the motion will be an in-plane motion.[3]

In the presence of the interaction the classical equations of motion are

$$\begin{gathered} \ddot{\theta} = \dot{\varphi}^2 \sin\theta\cos\theta - \tfrac{dE}{I}\sin\theta\cos\omega t \ , \\ I\tfrac{d}{dt}(\dot{\varphi}\sin^2\theta) = 0 \ ; \end{gathered} \tag{7.9}$$

we can see that the component $L_z = I\dot{\varphi}\sin^2\theta$ of the angular momentum is conserved, which leads again to the effective potential function $U_{eff} = \frac{L_z^2}{2I\sin^2\theta}$ in the hamiltonian given by equation (7.1); it follows that for low energies the angle θ oscillates around the minimum point $\theta = \pi/2$ of this potential function, and only for high energy values it may execute complete rotations. At usual temperatures and for usual electric fields the energies are low and l may acquire large values. In the classical limit, the spherical pendulum rotates as a quasi-planar rotator, with small oscillations around the equilibrium value $\theta = \pi/2$.[4] We limit ourselves to such small oscillations $\delta\theta$ around $\theta = \pi/2$, whose dynamics is governed by the harmonic-oscillator equation

$$\delta\ddot{\theta} + \omega_0^2\delta\theta = -\frac{dE}{I}\cos\omega t \ , \tag{7.10}$$

where $\omega_0 = L_z/I = \hbar m/I$; we include a damping term $2\gamma\delta\dot{\theta}$ and get the solution

$$\delta\theta = a\cos\omega t + b\sin\omega t \ , \tag{7.11}$$

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[3] For the classical dynamics of the spherical pendulum see A. Sommerfeld, *Vorlesungen uber Theoretische Physik*, Bd.1, *Mechanik*, Akad. Verlagsgeselschaft, Lepzig (1968); L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol.1, *Mechanics*, Elsevier, Oxford (1976).

[4] For low values of the electric field we may leave aside the coupling between vibrations and rotations.

where

$$a = \frac{dE}{2I\omega_0}\frac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2} \ , \ b = -\frac{dE}{2I\omega_0}\frac{\gamma}{(\omega-\omega_0)^2+\gamma^2} \tag{7.12}$$

for ω near ω_0; we can see that the classical dynamics yields a resonance for $\omega = \omega_0 = L_z/I$; the azimuthal angle $\varphi = \omega_0 t$ rotates freely. This approximation corresponds to $L_z \simeq L$ ($m \simeq l$, $L_x^2 + L_y^2 \ll L_z^2 \simeq L^2$). The mean absorbed power is

$$P = -dE\overline{\delta\dot{\theta}\cos\omega t} = -\frac{1}{2}dEb\omega_0 = \frac{d^2E^2}{4I}\frac{\gamma}{(\omega-\omega_0)^2+\gamma^2} \ , \tag{7.13}$$

which is a typical resonance function of ω.

For the interaction hamiltonian $H_{int}(t) = -dE\cos\theta\cos\omega t$ the transition rate of quantum jumps for $\omega_0 = (E_{l+1} - E_l)/\hbar = (\hbar/I)(l+1)$ is

$$\frac{\partial\left|c_{lm}\right|^2}{\partial t} = \frac{\pi d^2E^2}{2\hbar^2}\left|(\cos\theta)_{lm}\right|^2\delta(\omega_0-\omega) \ , \tag{7.14}$$

where

$$(\cos\theta)_{lm} = (\cos\theta)_{l+1,m;l,m} = -i\sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}} \tag{7.15}$$

(c_{lm} are the coefficients of the superpositions of the wavefunctions); the absorbed power is

$$\begin{gathered} P_q = \hbar\omega_0\sum\nolimits_{m=-l}^{l}\frac{\partial|c_{lm}|^2}{\partial t} = \\ = \frac{\pi d^2E^2}{2\hbar}\omega_0\sum\nolimits_{m=-l}^{l}\left|(\cos\theta)_{lm}\right|^2\delta(\omega_0-\omega) = \\ = \frac{d^2E^2}{6\hbar}\omega_0(l+1)\frac{\gamma}{(\omega-\omega_0)^2+\gamma^2} = \\ = \frac{d^2E^2}{6I}(l+1)^2\frac{\gamma}{(\omega-\omega_0)^2+\gamma^2} \end{gathered} \tag{7.16}$$

(for $\gamma \to 0^+$) and the net absorbed power at finite temperatures is given by

$$\begin{gathered} P_{q,th} = \frac{\pi d^2E^2}{2\hbar}\omega_0\times \\ \times\sum\nolimits_{m=-l}^{l}\left|(\cos\theta)_{lm}\right|^2\{e^{-\beta\hbar^2l(l+1)/2I}- \\ -e^{-\beta\hbar^2(l+1)(l+2)/2I}\}\delta(\omega_0-\omega)/Z \ , \end{gathered} \tag{7.17}$$

where

$$Z = \sum_{l=0}(2l+1)e^{-\beta\hbar^2 l(l+1)/2I} = \frac{2I}{\beta\hbar^2} \tag{7.18}$$

is the partition function ($\beta = 1/T$ is the reciprocal of the temperature T); we get

$$\begin{aligned} P_{q,th} = {} & \tfrac{\pi d^2 E^2}{12I}(l+1)^3\left(\tfrac{\beta\hbar^2}{I}\right)^2 e^{-\beta\hbar^2 l(l+1)/2I}\delta(\omega_0-\omega) = \\ & = \tfrac{1}{2}P_q(l+1)\left(\tfrac{\beta\hbar^2}{I}\right)^2 e^{-\beta\hbar^2 l(l+1)/2I} \end{aligned} \tag{7.19}$$

(the suffix q stands for "quantum-mechanical").

We use $I = 10^{-38} g \cdot cm^2$, which is a typical numerical value for the molecular moment of inertia (molecular mass $M = 10^5$, electronic mass $m = 10^{-27} g$, the dipole length $r = 10^{-8} cm$ (1Å)), and get $\hbar/I = 10^{11} s^{-1} \simeq 1K$ ($\omega_0 = \hbar m/I$, or $\omega_0 = \hbar(l+1)/I$); at room temperature there are many levels occupied, and we may use $\beta\hbar^2(l+1)/I \ll 1$). It is worth noting that $\delta P_q = (\partial P_q/\partial l)\ (\delta l = 1)$, as given by equation (7.16) resembles very much the power absorbed in the classical motion (after multiplying with the degeneracy factor $2l+1$), given by equation (7.13) (up to an irrelevant numerical factor); this is the expression of the quasi-classical approximation. Indeed, the quantum-mechanical transitions for the harmonic-oscillator given by equation (7.7) give an absorbed power $P = (\pi d^2 E^2/4I)(n+1)\delta(\omega_0-\omega)$ (where we have used the matrix elements $(\delta\theta)_{n+1,n} = \sqrt{\hbar(n+1)/2I\omega_0}$), which is very close to $\delta P_q = (\pi d^2 E^2/3I)(l+1)\delta(\omega_0-\omega)$ given by equation (7.16), providing $n \simeq l \simeq m$; the additional factor $l+1$ in equation (7.16) originates in the removal of the rotational degeneracy of the spherical pendulum in the harmonic-oscillator approximation. As a matter of fact, the harmonic-oscillator approximation used here is valid for $(\delta\theta)_{n+1,n} \ll 1$, which, using $\omega_0 = L_z/I = m\hbar/I$, yields $n+1 \ll 2m$; summing up the absorbed power $P = (\pi d^2 E^2/4I)(n+1)\delta(\omega_0-\omega)$ with respect to n, we get a total power very similar with the exact result given by equation (7.16). We conclude that the separation of the azimuthal and zenithal motions for heavy molecules is a satisfactory approximation for the molecular rotations.

7.3 Strong static field

Consider a constant, uniform electric field $\mathbf{E}_0 = E_0(0,0,1)$ oriented along the z-axis; the potential energy of an electric dipole $\mathbf{d} = d(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ of arbitrary orientation θ, φ is $U = -dE_0\cos\theta$. The hamiltonian of rotation in this field is given by

$$H = \frac{1}{2}I(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) - dE_0\cos\theta \ , \tag{7.20}$$

where I is the moment of inertia of the dipole, considered as a sherical pendulum (spherical top). The equation of motion

$$I\frac{d}{dt}(\dot{\varphi}\sin^2\theta) = 0 \tag{7.21}$$

indicates that the component L_z of the angular momentum is conserved, $\dot{\varphi}\sin^2\theta = L_z/I$; consequently, an effective potential function

$$U_{eff} = \frac{L_z^2}{2I\sin^2\theta} - dE_0\cos\theta \tag{7.22}$$

occurs in the hamiltonian. We assume that the dipole energy dE_0 is much greater than the rotation energy L_z^2/I, which is of the order of the temperature T. For typical value $d = 10^{-18}esu$ and temperature $T = 300K \simeq 4\times10^{-14}erg$ this condition requires an electric field $E_0 \gg T/d = 4\times10^4 statvolt/cm \simeq 1.2\times10^9 V/m$. This is a strong electric field; for comparison, the electric field created by an electron charge at distance $1\mathring{A} = 10^{-8}cm$ is $4.8\times10^{-10}/10^{-16} = 4.8\times10^6 stavolt/cm$ (atomic fields). A strong static electric field may appear as an internal field in polar condensed matter (*e.g.*, pyroelectrics, ferroelectrics). At low temperatures the free molecular rotations may be hindered, and the dipoles get quenched in parallel, equilibrium positions; they may only execute small rotations and vibrations around these equilibrium positions. The transitions from free rotations to small vibrations around quenched positions in polar matter is seen in the curve of the heat capacity *vs* temperature.[5] The

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[5] L. Pauling, "The rotational motion of molecules in crystals", Phys. Rev. **36** 430 (1930); T. E. Stern, "The symmetrical spherical oscillator, and the rotational motion of homopolar molecules in crystals", Proc. Roy. Soc. **A130** 551 (1931).

electric field produced by the nearest neighbours, averaged over their small vibrations and rotations, give rise to a local, static (mean) electric field, which can be as high as the atomic fields. The condition $E_0 \gg T/d$ shows that at lower temperatures (and high values of the electric dipoles) the field E_0 may be weaker. Similarly, strong static electric fields may appear locally near polar impurities with large moments of inertia, embedded in polar matter. Under such conditions the effective potential given by equation (7.22) has a minimum value for $\theta_0 \simeq (L_z^2/IdE_0)^{1/4} \simeq (T/dE_0)^{1/4} \ll 1$; it can be expanded in powers of $\delta\theta = \theta - \theta_0$ around this minimum value as

$$U_{eff} \simeq -dE_0 + 2dE_0\delta\theta^2 \ ; \tag{7.23}$$

the hamiltonian given by equation (7.20) becomes

$$H \simeq \frac{1}{2}I\delta\dot{\theta}^2 + \frac{1}{2}I\omega_0^2\delta\theta^2 - dE_0 \ , \tag{7.24}$$

where $\omega_0 = 2\sqrt{dE_0/I}$ is sometimes known as Rabi's frequency;[6] according to our condition of strong field, we have $\omega_0 \gg 10^{12}s^{-1}$. Therefore, the dipoles are quenched in the static electric field E_0, where they execute small oscillations and rotations. The angle φ rotates freely with the frequency $\dot{\varphi} \simeq L_z/I\sin^2\theta_0 = \frac{1}{2}\omega_0$ ($\varphi = \frac{1}{2}\omega_0 t$). It is worth noting that the frequency ω_0 is given by the static field E_0.

Consider an external time-dependent field $\mathbf{E}(t) = E(t)(\sin\alpha, 0, \cos\alpha)$, $E(t) = E\cos\omega t$, which makes an angle α with the z-axis; its interaction with the dipole is

$$H_{int} = -dE(t)(\sin\alpha\sin\theta\cos\varphi + \cos\alpha\cos\theta) \ , \tag{7.25}$$

which provides two relevant interaction hamiltonians:

$$\begin{gathered} H_{1int} = -\tfrac{1}{2}dE\sin\alpha\left[\cos(\omega + \tfrac{1}{2}\omega_0)t + \cos(\omega - \tfrac{1}{2}\omega_0)t\right]\delta\theta \ , \\ H_{2int} = \tfrac{1}{2}dE\cos\alpha\cos\omega t \cdot \delta\theta^2 \ . \end{gathered} \tag{7.26}$$

The interaction hamiltonian H_{1int} produces transitions between the harmonic-oscillator states n and $n+1$ with the resonance frequency

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[6] I. I. Rabi, "On the process of space quantization", Phys. Rev. **49** 324 (1936); I. I. Rabi, "Space quantization in a gyrating magnetic field", Phys. Rev. **51** 652 (1937).

$\Omega = \frac{1}{2}\omega_0$, $\frac{3}{2}\omega_0$. In general, for an interaction $H_{int} = h\cos\omega t$, the rate of transition between two states n and $n+s$, with energies E_n, E_{n+s} is

$$\frac{\partial\left|c_{n+s,n}\right|^2}{\partial t} = \frac{\pi}{2\hbar^2}\left|h_{n+s,n}\right|^2\delta(\omega_{n;s}-\omega) \tag{7.27}$$

in the first order of the perturbation theory, where $\omega_{n;s} = (E_{n+s} - E_n)/\hbar$ and $c_{n+s,n}$ are the coefficients of the superposition of the wavefunctions. For H_{1int} we get

$$\frac{\partial\left|c_{n+1,n}\right|^2}{\partial t} = \frac{\pi}{16\hbar I\omega_0}d^2E^2(n+1)\sin^2\alpha\delta(\omega-\Omega) \tag{7.28}$$

and the absorbed power

$$\begin{aligned} P_q = \hbar\Omega\tfrac{\partial|c_{n+1,n}|^2}{\partial t} = \tfrac{\pi}{16I\omega_0}d^2E^2\Omega(n+1)\sin^2\alpha\delta(\omega-\Omega) = \\ = \tfrac{1}{16I\omega_0}d^2E^2\Omega(n+1)\sin^2\alpha\tfrac{\gamma}{(\omega-\Omega)^2+\gamma^2}\ ,\ \gamma\rightarrow 0^+\ , \end{aligned} \tag{7.29}$$

which is a typical resonance curve. In order to compute the mean power the thermal weigths $e^{-\beta\hbar\omega_0 n}/\sum e^{-\beta\hbar\omega_0 n}$ should be inserted, where $\beta = 1/T$ is the inverse of the temperature T; in addition, the reverse transitions must be taken into account. Since $\beta\hbar\omega_0 \gg 1$, only the lowest states n are excited by interaction. The temperature dependence is given by

$$\begin{aligned} P_{q,th} = \tfrac{\pi}{16I\omega_0}d^2E^2\Omega\textstyle\sum_{n=0}(n+1)\cdot \\ \cdot\left[e^{-\beta\hbar\omega_0 n} - e^{-\beta\hbar\omega_0(n+1)}\right]\times \\ \times\sin^2\alpha\delta(\omega-\Omega)/\textstyle\sum_{n=0}e^{-\beta\hbar\omega_0 n}\ , \end{aligned} \tag{7.30}$$

where the summation over n is, in principle, limited.

We should limit ourselevs to the lowest states of the harmonic oscillator, since the oscillation amplitude $\delta\theta$ must be much smaller than the angle θ_0. The matrix element $(\delta\theta)_{n+1,n} = \sqrt{\hbar/2I\omega_0}\sqrt{n+1}$ for the harmonic oscillator should be much smaller than $\theta_0 \simeq (L_z^2/IdE_0)^{1/4}$, which implies $\hbar(n+1) \ll 4L_z \simeq 4\sqrt{IT}$; for typical values $I = 10^{-38}g\cdot cm^2$ (10^5 electronic mass for the molecular mass, $10^{-8}cm$

for the dipole length) we get $n \ll 80$ for $T = 300K$ (and $n \ll 8$ for $T = 3K$). Consequently, for $\beta\hbar\omega_0 \gg 1$ we may extend the summation in equation (7.30) to $n = \infty$; we get $P_{q,th}$ independent of temperature. Making use of the expressions $L_x = I(-\dot{\theta}\sin\varphi - \dot{\varphi}\sin\theta\cos\theta\cos\varphi)$, $L_y = I(\dot{\theta}\cos\varphi - \dot{\varphi}\sin\theta\cos\theta\sin\varphi)$, we get $L_x \simeq -(1/2)I\omega_0\theta_0\cos\omega_o t/2$ and $L_y \simeq -(1/2)I\omega_0\theta_0\sin\omega_o t/2$ for the transverse components of the angular momentum, which show that the high-field approximation corresponds to $L_x^2 + L_y^2 \simeq L^2 \gg L_z^2$.

Under the same conditions, the harmonic-oscillator hamiltonian given by equation (7.24) and the interaction hamiltonian H_{2int} given by equation (7.26),

$$H^{'} = H + H_{2int} = \frac{1}{2}I\delta\dot{\theta}^2 + \frac{1}{2}I\omega_0^2(1 + h\cos\omega t)\delta\theta^2 \ , \tag{7.31}$$

where $h = \frac{E}{2E_0}\cos\alpha$, lead to the classical equation of motion

$$\delta\ddot{\theta} + \omega_0^2(1 + h\cos\omega t)\delta\theta = 0 \ , \tag{7.32}$$

which is the well-known equation of parametric resonance (Mathieu's equation).[7] As it is well known, besides periodic solutions, the classical equation (7.32) has also aperiodic solutions, which may grow indefinitely with increasing time; these are (parametrically) resonant solutions, which occur for ω in the neighbourhood of $2\omega_0/n$, $n = 1, 2, 3...$. As we can see immediately, the solutions of equation (7.32) are determined by the initial conditions $\delta\theta(t = 0)$ and $\delta\dot{\theta}(t = 0)$ (as for any homogeneous equation). The initial conditions are vanishing due to thermal fluctuations, so the classical solutions of equation (7.32) are ineffective.

The quantum-mechanical dynamics is different. The interaction hamiltonian H_{2int} produces transitions between the harmonic-oscillator states n and $n + 2$ (due to the matrix elements of $\delta\theta^2$; this is an example of a double-quanta process[8]). These transitions have frequency $2\omega_0$, in accordance with the classical dynamics. The transition rate is

$$\frac{\partial\left|c_{n+2,n}\right|^2}{\partial t} = \frac{\pi h^2}{128}\omega_0^2(n + 1)(n + 2)\delta(2\omega_0 - \omega) \tag{7.33}$$

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[7] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, Cambridge (1996).

[8] M. Goppert-Mayer, "Uber Elementarakte mit zwei Quantensprungen", Ann. Physik **401** 273 (1931).

and the absorbed power

$$\begin{aligned} P_q = 2\hbar\omega_0 \tfrac{\partial |c_{n+2,n}|^2}{\partial t} = \tfrac{\pi h^2}{64}\hbar\omega_0^3 (n+1)(n+2)\delta(2\omega_0-\omega) = \\ = \tfrac{h^2}{64}\hbar\omega_0^3 (n+1)(n+2)\tfrac{\gamma}{(2\omega_0-\omega)^2+\gamma^2} \ , \ \gamma \to 0^+ \ , \end{aligned} \tag{7.34}$$

where we may restrict, in principle, to the lowest states. The intensity given by equation (7.34) is small, because, especially, of the factor $(E/E_0)^2$. The temperature dependence is given by

$$\begin{aligned} P_{q,th} = \tfrac{\pi h^2}{64}\hbar\omega_0^3 \textstyle\sum_{n=0}(n+1)(n+2)\times \\ \times \left[e^{-\beta\hbar\omega_0(2n+1)} - e^{-\beta\hbar\omega_0(2n+3)}\right]\cdot \\ \cdot\delta(2\omega_0-\omega)/\left[\textstyle\sum_{n=0} e^{-\beta\hbar\omega_0 n}\right]^2 \ , \end{aligned} \tag{7.35}$$

in accordance with the direct transitions $n \to n+1 \to n+2$ and the corresponding reverse transitions; $P_{q,th}$ is also diminished by the thermal factor $e^{-\beta\hbar\omega_0}$ for $\beta\hbar\omega_0 \gg 1$.

The parametric resonance disappears for $\alpha = \frac{\pi}{2}$, *i.e.* for the applied field $\mathbf{E}$ at right angle with the quenching field $\mathbf{E}_0$. The effect of the parametric resonance depends on the orientation of the crystal; in amorphous samples the average over angles α should be taken $(\overline{\cos^2\alpha} = \frac{1}{3})$. The parameter γ in equation (7.34), which gives the width of the absorption line, is a damping parameter; in solids it originates, very likely, in the dipolar interaction. Since the dipolar interaction is taken mainly in the quenching effect, we may expect a small damping, and, consequently, rather sharp resonance lines. In liquids, besides the random distribution of the dipoles (and the average over angle α), we may expect the usual motional narrowing of the line. In gases the quenching field is weak, and the parametric resonance is not likely to occur.

7.4 Weak static field

Consider now the opposite case, when the field E_0 is weak, such that $dE_0 \ll L_z^2/I$. The effective potential U_{eff} given by equation (7.22) has a minimum value for $\theta \simeq \frac{\pi}{2}$ and the hamiltonian given by equation (7.20) reduces to

$$H \simeq \frac{1}{2} I \dot{\widetilde{\theta}}^2 + \frac{1}{2} I \omega_0^2 \dot{\widetilde{\theta}}^2 \quad , \tag{7.36}$$

where $\widetilde{\theta} = \theta - \frac{\pi}{2}$ and $\omega_0 = L_z / I$; the field E_0 brings only a small correction to the $\pi/2$-shift in θ, while its contribution to the hamiltonian is a second-order effect. The angle φ moves freely with angular velocity $\dot{\varphi} = \omega_0$. In contrast with the strong-field case, where the frequency $\dot{\varphi}$ is fixed by the static field E_0, in the weak-field case we may quantize the φ-motion, according to $L_z = \hbar m$, m integer, such that $\omega_0 = \frac{\hbar}{I} m$; the lowest value of this frequency is $\hbar / I \simeq 10^{11} s^{-1}$ for typical values $I = 10^{-38} g \cdot cm^2$ (10^5 electronic mass for the molecular mass, $10^{-8} cm$ for the dipole length). We can see that the molecular rotations are described by a set of harmonic oscillators with frequencies $\omega_0 = \frac{\hbar}{I} m$, besides the φ-precession (which has the same frequencies ω_0). The energy quanta are $\hbar \omega_0 = \frac{\hbar^2}{I} m$, with the lowest value $\frac{\hbar^2}{I} = 1K$ (for our numerical values). The approximation described above is valid for $\widetilde{\theta}_{n+1,n} = \sqrt{\hbar (n+1) / 2 I \omega_0} \ll 1$, which leads to $\hbar (n+1) \ll 2 L_z$, or $n \ll m$. Similarly, the transverse components of the angular momentum are very small, $L_x^2 + L_y^2 \ll L^2 \simeq L_z^2$ ($m \simeq l$); at room temperature m may acquire as high values as $m = 300$.

The interaction hamiltonian given by equation (7.25) leads to two relevant interactions

$$\begin{gathered} H_{1int} = dE \cos\alpha \cos\omega t \cdot \widetilde{\theta} \ , \\ H_{2int} = \tfrac{1}{4} dE \sin\alpha \left[\cos(\omega + \omega_0) t + \cos(\omega - \omega_0) t \right] \cdot \widetilde{\theta}^2 \ . \end{gathered} \tag{7.37}$$

The interaction H_{1int} produces transitions between the harmonic-oscillator states n and $n+1$, with an absorbed power

$$P_q = \frac{\pi}{4I} d^2 E^2 (n+1) \cos^2 \alpha \delta(\omega_0 - \omega) \ . \tag{7.38}$$

For n, m ($n \ll m$) we restrict ourselves to small values of n in equation (7.38) and sum over a few values of m in $\delta(\omega_0 - \omega) = \delta(\hbar m / I - \omega)$ with the statistical weight $e^{-\beta \hbar^2 m^2 / 2I}$. As long as $\hbar / I \gg \gamma$, where γ is the resonance width, the spectrum exhibits a few, distinct absorption lines at frequencies $\omega_0 = \hbar m/I$ (a band of absorption). In general, the temperature dependence is given by

$$\begin{gathered} P_{q,th} = \tfrac{\pi}{4I} d^2 E^2 \cos^2\alpha \cdot C \textstyle\sum_{m>0} e^{-\beta\hbar^2 m^2/2I} \times \\ \times \{ \textstyle\sum_{n=0} (n+1) \left[e^{-\beta\hbar\omega_0 n} - e^{-\beta\hbar\omega_0 (n+1)} \right] / \\ / \textstyle\sum_{n=0} e^{-\beta\hbar\omega_0 n} \} \delta(\omega_0 - \omega) \ , \end{gathered} \tag{7.39}$$

where $\omega_0 = \hbar m/I$ and $C \sum_{m>0} e^{-\beta\hbar^2 m^2/2I} = 1$. At room temperature we may extend the summation over n, m and get the envelope of this function

$$P_{q,th} = \frac{\pi}{4} d^2 E^2 \cos^2\alpha \sqrt{\frac{2\pi\beta}{I}} e^{-\beta I \omega^2/2} \ . \tag{7.40}$$

The interaction hamiltonian H_{2int} given by equation (7.37) produces transitions between states n and $n+2$ (separated by frequency $2\omega_0$) for external frequencies $\Omega = \omega_0$, $3\omega_0$. The absorbed power is

$$P_q = \frac{\pi\hbar\Omega}{128 I^2 \omega_0^2} d^2 E^2 (n+1)(n+2) \sin^2\alpha \delta(\Omega - \omega) \ . \tag{7.41}$$

These parametric resonances occurring at frequencies $\Omega = \omega_0$, $3\omega_0$ are superposed over the transitions produced by H_{1int}. The temperature dependence is given by

$$\begin{gathered} P_{q,th} = \tfrac{\pi\hbar}{128 I^2} d^2 E^2 \sin^2\alpha \cdot C \textstyle\sum_{m>0} \tfrac{\Omega}{\omega_0^2} e^{-\beta\hbar^2 m^2/2I} \times \\ \times \{ \textstyle\sum_{n=0} (n+1)(n+2) \left[e^{-\beta\hbar\omega_0 (2n+1)} - e^{-\beta\hbar\omega_0 (2n+3)} \right] / \\ / \left[\textstyle\sum_{n=0} e^{-\beta\hbar\omega_0 n} \right]^2 \} \delta(\Omega - \omega) \ ; \end{gathered} \tag{7.42}$$

summation over n gives

$$\begin{gathered} P_{q,th} = \tfrac{\pi\hbar}{64 I^2} d^2 E^2 \sin^2\alpha \cdot C \textstyle\sum_{m>0} \tfrac{\Omega}{\omega_0^2} e^{-\beta\hbar^2 m^2/2I} \cdot \\ \cdot \tfrac{e^{-\beta\hbar\omega_0}}{(1+e^{-\beta\hbar\omega_0})^2} \delta(\Omega - \omega) \end{gathered} \tag{7.43}$$

whence we can get either the band of absorption or the envelope.

It is worth noting that the low field E_0 does not appear explicitly in the above formulae; its role is that of setting the z-axis, to highlight the directional effect of the interaction field E through the angle α, and to reduce the conservation of the angular momentum $\mathbf{L}$ to the conservation of only one component L_z. In addition, the parametric resonances are a new feature in the presence of the electric field. It is also worth noting that the expansion of the effective potential function U_{eff} in powers of $\widetilde{\theta}$ is an approximation to free rotations with $L_z = const$, instead of $\mathbf{L} = const$.

It is also worth noting that a weak static electric field has an influence on the statistical behaviour, as it is well known. Indeed, the hamiltonian of rotations

$$H = \frac{1}{2} I(\dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta) \tag{7.44}$$

can also be written as

$$H = \frac{1}{2I} P_\theta^2 + \frac{1}{2I \sin^2 \theta} P_\varphi^2 \tag{7.45}$$

with the momenta (angular momenta) $P_\theta = I\dot{\theta}$ and $P_\varphi = I\dot{\varphi}\sin^2\theta$. The classical statistical distribution is

$$const \cdot dP_\theta dP_\varphi d\theta e^{-\beta P_\theta^2/2I} e^{-\beta P_\varphi^2/2I\sin^2\theta} \quad , \tag{7.46}$$

or, integrating over momenta, $\frac{1}{2}\sin\theta d\theta$. In the presence of the field we have the distribution $\simeq \frac{1}{2}\sin\theta d\theta \cdot e^{\beta \mathbf{dE}_0}$ (since $\beta dE_0 \ll 1$), which leads, for example, to $\overline{\cos\theta} = \beta dE_0/3$. This is the well-known Curie-Langevin-Debye law.[9] In the quantum-mechanical regime, for $dE_0 \ll \hbar^2/I$, the interaction $-dE_0\cos\theta$ brings a second-order contribution to the energy levels $E_l = \hbar^2 l(l+1)/2I$, there appear diagonal matrix elements of $\widetilde{(\cos\theta)}_{lm,lm}$ in the first-order of the perturbation theory, and the mean value is given by $\overline{\cos\theta} = \sum \widetilde{(\cos\theta)}_{lm,lm}\Delta(\beta E_l)e^{-\beta E_l}/$ $/\sum e^{-\beta E_l} = \beta dE_0/3$.

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[9] P. Curie, "Lois experimentales du magnetisme. Proprietes magnetiques des corps a diverses temperatures", Ann. Chim. Phys. **5** 289 (1895); P. Langevin, "Sur la theorie du magnetisme", J. Physique **4** 678 (1905); P. Langevin, "Magnetism et theorie des electrons", Ann. Chim. Phys. **5** 70 (1905); P. Debye, "Einige Resultate einer kinetischen Theorie der Isolatoren", Phys. Z. **13** 97 (1912).

7.5 Dipolar interaction

Although many molecules possess an electric dipole moment d, even in their ground state, usually the dipole-dipole interaction is neglected in rarefied condensed matter, on the ground that the distance between the dipoles is large. In these conditions, at finite temperatures, the electric dipoles are randomly distributed; they get slightly aligned in the presence of a static external electric field $\mathbf{E}_0$, which provides a small interaction energy, leading to an induced orientational polarization $\overline{d} = \beta d^2 E_0/3$, known as the Curie-Langevin-Debye law, as noted above ($\beta = 1/T$ is the inverse of the temperature T).

For typical values of the dipole moments $d = 10^{-18} esu$ separated by distance $a = 10^{-8} cm$ (1Å) the interaction energy is $\simeq d^2/a^3 = 10^{-12} erg \simeq 10^3 K$ ($1eV = 1.6 \times 10^{-12} erg$, $1K = 1.38 \times 10^{-16} erg$, $1eV = 1.1 \times 10^4 K$). This is not a small energy, and, apart from special circumstances, the electric dipole-dipole interaction cannot be neglected in condensed matter. The corresponding dipolar field is of the order $d/a^3 = 10^6 statvolt/cm$ (*i.e.*, of the order of the atomic fields).

The interaction energy of two dipoles $\mathbf{d}_1$ and $\mathbf{d}_2$ separated by distance $\mathbf{a}$ (much longer than the dimension of the dipoles) is given by

$$U = -\frac{3(\mathbf{d}_1\mathbf{d}_2)a^2 - (\mathbf{d}_1\mathbf{a})(\mathbf{d}_2\mathbf{a})}{a^5} \ . \tag{7.47}$$

We introduce the angles (θ_1, φ_1) and (θ_2, φ_2) for the directions of the two dipoles with respect to the axis $\mathbf{a}$ and the interaction energy becomes

$$U = -\frac{d_1 d_2}{a^3}[2\cos\theta_1\cos\theta_2 + 3\sin\theta_1\sin\theta_2\cos(\varphi_1 - \varphi_2)] \ ; \tag{7.48}$$

this energy has four extrema for $\theta_1 = \theta_2 = 0$, $\pi/2$ and $\varphi_1 - \varphi_2 = 0$, π; only for $\theta_1 = \theta_2 = \pi/2$, $\varphi_1 - \varphi_2 = 0$ the interaction energy has a local minimum; in the neighbourhood of this minimum value the interaction energy behaves like

$$\begin{gathered}U=\tfrac{d_1d_2}{a^3}[-3+\tfrac{3}{2}(\delta\theta_1^2+\delta\theta_2^2)-\\-2\delta\theta_1\delta\theta_2+\tfrac{3}{2}(\delta\varphi_1-\delta\varphi_2)^2]=\\=\tfrac{d_1d_2}{a^3}[-3+\tfrac{1}{4}(\delta\theta_1+\delta\theta_2)^2+\\+\tfrac{5}{4}(\delta\theta_1-\delta\theta_2)^2+\tfrac{3}{2}(\delta\varphi_1-\delta\varphi_2)^2]\ ,\end{gathered}\tag{7.49}$$

where $\delta\theta_{1,2}=\theta_{1,2}-\pi/2$ are small deviations of the angles $\theta_{1,2}$ from the polarization axis $\pi/2$; similarly, $.\delta\varphi_{1,2}$ are small deviations of the angles $\varphi_{1,2}$ from their equilibrium values $\varphi_{1,2}$, subject to the condition $\varphi_1-\varphi_2=0$. It follows that the electric dipoles are quenched in the equilibrium positions $\theta_1=\theta_2=\pi/2$, $\varphi_1-\varphi_2=0$, such that they are parallel to each other and perpendicular to the distance between them; they may execute small rotations and vibrations around these equilibrium positions. For the other three extrema the interaction energy has either a saddle point ($\theta_1=\theta_2=0$, $\varphi_1-\varphi_2=0,\pi$) or a maximum ($\theta_1=\theta_2=\pi/2$, $\varphi_1-\varphi_2=\pi$). It is very likely that the structural environment is distorted such as the dipoles take advantage of the energy minimum. For instance, a structural elongation along the direction $\theta_1=\theta_2=0$ decreases appreciably the dipolar interaction along this direction (which goes like $1/a^3$!), such that the corresponding contribution to the energy may be neglected. Under such circumstances, we may expect the dipoles to be (spontaneously) aligned along an arbitrary axis, giving rise to an electric (macroscopic) polarization along such an axis. The neglect of the interaction along the direction $\theta_1=\theta_2=0$ makes this model highly anisotropic, with a layered structure of the aligned dipoles.

As it is well known, substances that have a permanent electric polarization are called pyroelectrics (or electrets);[10] if the polarization is singular just below a critical temperature and vanishes above, those substances are called ferroelectrics (in the state above the critical temperature they are also called paraelectrics); they exhibit a second-order phase transition; it seems that all these substances aret piezo-

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[10] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol.8, *Electrodynamics of Continuous Media*, Elsevier, Oxford (1993).

electric. There are also structural modifications associated with finite discontinuities in polarization (first-order phase transitions), a typical example being barium titanate ($BaTiO_3$); the dimension of the elementary cell in the crystal of $BaTiO_3$ is $a \simeq 4 \times 10^{-8} cm$ (4Å); the dipole of a cell is $d \simeq 5 \times 10^{-18} esu$ (the saturation polarization - the dipole moment per unit volume - at room temperature is $8 \times 10^4 esu$); if Ba^{2+} and Ti^{4+} are displaced by δ with respect to O^{2-}, then the dipole moment d is achieved for a slight displacement $\delta = 0.1$Å; we can see that the distance a between the dipoles is much longer than the dimension δ of the dipoles. In addition, $BaTiO_3$ exhibits several structural modifications (from cubic to tetragonal to monoclinic to rhombohedral with decreasing temperature), in all polarized phases the structure being elongated along the direction of the polarization.[11]

In a continuum model of polarized substance the dipolar interaction given by equation (7.49) (with identical dipoles d) gives the interaction hamiltonian

$$H_{int} = \frac{1}{a^3} \int d\mathbf{r} \left[\frac{d^2}{a^3} \delta\theta^2 + \frac{5d^2}{4a} (grad\delta\theta)^2 + \frac{3d^2}{2a} (grad\delta\varphi)^2 \right] \ , \quad (7.50)$$

which, together with the kinetic part, leads to the full hamiltonian

$$\begin{gathered} H = \tfrac{1}{a^3} \int d\mathbf{r} [\tfrac{1}{2} I \dot{\delta\theta}^2 + \tfrac{1}{2} I \dot{\delta\varphi}^2 + \tfrac{1}{2} I \omega_0^2 \delta\theta^2 + \\ + \tfrac{1}{2} I v_\theta^2 (grad\delta\theta)^2 + \tfrac{1}{2} I v_\varphi^2 (grad\delta\varphi)^2 \ , \end{gathered} \quad (7.51)$$

where I is the moment of inertia of the dipoles and $\omega_0^2 = 2d^2/Ia^3$, $v_\theta^2 = 5d^2/2Ia = 5\omega_0^2 a^2/4$, $v_\varphi^2 = 3d^2/Ia = 3\omega_0^2 a^2/2$. The dipole density $1/a^3$ should include the number of nearest neighbours; if we restrict ourselevs to the highly anisotropic (layered) model, then the hamiltonian density in equation (7.51) is two-dimensional. We can see that the dipolar interaction may generate dipolar waves (waves of orientational polarizability), governed by the wave equations

$$\ddot{\delta\theta} + \omega_0^2 \delta\theta - v_\theta^2 \Delta\delta\theta = 0 \ , \ \ddot{\delta\varphi} - v_\varphi^2 \Delta\delta\varphi = 0 \ ; \quad (7.52)$$

the spectrum of these dipolar waves is given by $\omega_\theta^2 = \omega_0^2 + v_\theta^2 k^2$ and $\omega_\varphi^2 = v_\varphi^2 k^2$ (in the layered model the wavevector $\mathbf{k}$ is two-dimensional);

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[11] Ch. Kittel, *Introduction to Solid State Physics*, Wiley, NJ (2005).

for typical values $d = 10^{-18} esu$, $a = 10^{-8} cm$ and $I = 10^{-38} g \cdot cm^2$ (10^5 electronic mass for the molecular mass, $10^{-8} cm$ for the dipole length) we get the frequency $\omega_0 \simeq 10^{13} s^{-1}$ (infrared region) and the wave velocities $v_{\theta,\varphi} \simeq 10^5 cm/s$ (the wavelengths are $\lambda_{\theta,\varphi} \simeq \pi\sqrt{5}a$, $\pi\sqrt{6}a$). It is worth noting that the coordinates $\delta\theta$, $\delta\varphi$ are the tilting angles of the polarization with respect to its equilibrium direction. Tentatively, we may call these polar-matter modes "dipolons". They contribute to the anomalous heat-capacity curve *vs* temperature.

The dipolar waves can couple to an external time-dependent electric field. Let $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}\cos(\omega t - \mathbf{kr})$ be a radiation electric field (plane wave) which makes an angle α with the polarization direction; the interaction hamiltonian is

$$H^{'} = -\frac{1}{a^3}\int d\mathbf{r}\mathbf{d}\mathbf{E}\cos(\omega t - \mathbf{kr}) \ , \tag{7.53}$$

where $\mathbf{E} = E(\sin\alpha\cos\varphi^{'}, \sin\alpha\sin\varphi^{'}, \cos\alpha)$ and $\mathbf{d} = d(\sin\delta\theta\cos\varphi, \sin\delta\theta\sin\varphi, \cos\delta\theta)$; we may limit ourselves to $\varphi = \varphi^{'}$, and get

$$H^{'} = -\frac{1}{a^3}\int d\mathbf{r} dE(\delta\theta\sin\alpha - \frac{1}{2}\delta\theta^2\cos\alpha)\cos(\omega t - \mathbf{kr}) \tag{7.54}$$

(up to irrelevant terms); we can see that the φ-waves do not couple to the external electric field (within the present approximation). Moreover, since the wavelength of the radiation field is much longer than the wavelength of the dipolar interaction ($v_{\theta,\varphi} \ll c$, where c is the speed of light), we may drop out the spatial dependence (spatial dispersion) both in equation (7.52) and in the interaction hamiltonian $H^{'}$; we are left with the equation of motion of a harmonic oscillator under the action of an external force,

$$\ddot{\delta\theta} + \omega_0^2\delta\theta = \frac{dE}{I}\sin\alpha\cos\omega t - \frac{dE}{I}\delta\theta\cos\alpha\cos\omega t \ . \tag{7.55}$$

The first interaction term gives

$$\ddot{\delta\theta}_1 + \omega_0^2\delta\theta_1 + 2\gamma\dot{\delta\theta}_1 = \frac{dE}{I}\sin\alpha\cos\omega t \ \ , \tag{7.56}$$

where a damping term has been introduced; this is the equation of motion of a harmonic oscillator under the action of a harmonic force;

the (particular) solution is

$$\delta\theta_1 = a\cos\omega t + b\sin\omega t \ , \tag{7.57}$$

where

$$\begin{aligned} a &= -\tfrac{dE}{2I\omega_0}\sin\alpha\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2} \ , \\ b &= \tfrac{dE}{2I\omega_0}\sin\alpha\tfrac{\gamma}{(\omega-\omega_0)^2+\gamma^2} \end{aligned} \tag{7.58}$$

for ω near ω_0; we get a resonance for $\omega = \omega_0$; the absorbed mean power is

$$\begin{aligned} P &= dE\sin\alpha\overline{\cos\omega t\dot{\delta\theta_1}} = \tfrac{1}{2}dE\sin\alpha\cdot b\omega_0 = \\ &= \tfrac{\pi}{4I}d^2E^2\sin^2\alpha\delta(\omega_0-\omega) \ . \end{aligned} \tag{7.59}$$

The second interaction term in equation (7.55) gives the Mathieu's equation

$$\ddot{\delta\theta_2} + \omega_0^2(1 + h\cos\omega t)\delta\theta_2 = 0 \ , \tag{7.60}$$

where $h = (dE/I\omega_0^2)\cos\alpha$ (a damping term can be included). As it is well known, the Mathieu's equation has both periodic and aperiodic solutions; the latter, which may increase indefinitely, give the parametric resonances occurring at $\omega = 2\omega_0/n$, $n = 1, 2, 3, ...$. The parameter h acquires, usually, very small values (it dictates the rate of the increase in time of the resonant solutions). The thermal fluctuations wipe out these parametric resonances, as discussed before. All the above considerations are valid for a classical dynamics. The quantization of the hamiltonians H and $H^{'}$ given by equations (7.51) and (7.54) (which is performed according to the well-known standard rules), leads to standard absorption and emission processes, and to quantum transitions (jumps) similar with equations (7.33)-(7.35). It is worth noting that the static electric field E_0 in equations (7.33)-(7.35) is replaced here by $E_0 = d/2a^3$ (by comparing the frequencies ω_0 given in equations (7.24) and (7.51)), as expected for a (high) electric field generated by a dipolar interaction.

The spontaneous polarization caused by the dipolar interaction as described above may appear in polarization domains, randomly distributed in polar matter (pyroelectrics, ferroelectrics), or in granular matter, where charges may accumulate at the interfaces.[12] This is known as the Maxwell-Wagner-Sillars effect (an average over the angle α should then be taken in the absorbed power). In the latter case the distance between the dipoles is much larger than the atomic distances and, consequently, the characteristic frequency ω_0 is much lower; for instance, for a distance $a = 1\mu m$ (10^4Å) we get a frequency $\omega_0 \simeq 10MHz$.

7.6 Discussion and conclusions

We have shown here that the rotations of a molecule viewed as a spherical pendulum can be approximated by azimuthal rotations and zenithal oscillations. In the presence of a time-dependent external electric field the molecular electric dipole moment couples to the electric field giving rise to molecular rotation (and vibration) spectra. Arguments have been given that in polar matter there could appear local strong static electric fields, which may lead to quenched dipoles and a macroscopic electric polarization. The small rotations and oscillations which these dipoles may execute about their equilibrium positions give rise to special features in the spectrum, in particular to parametric resonances. A similar situation may also appear in the presence of weak static electric fields. The dipole-dipole interaction has also been examined and it was found that indeed it may lead to an equilibrium state of quenched dipoles; this state possesses a macroscopic polarization, whose motion proceeds by particular modes which have been tentatively called "dipolons". The excitation of these modes may also lead to parametric resonances.

All the discussion made in this paper for electric dipole moments can also be applied, in principle, to magnetic moments, magnetic fields,

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[12] J. C. Maxwell, *Lehrbuch der Elektrizitat und der Magnetismus*, vol. 1, Art. 328, Berlin (1983); K. W. Wagner, "Erklarung der dielektrischen Nachwirkungsvorgange auf Grund Maxwellscher Vorstellungen", Electr. Eng. (Archiv fur Elektrotechnik) **2** 371 (1914); K. W. Wagner, *Die Isolierstoffe der Elektrotechnik*, H. Schering ed., Springer, Berlin (1924); R. W. Sillars, "The properties of a dielectric containing semiconducting particles of various shapes", J. Inst. Electr. Engrs. (London) **80** 378 (1937); A. von Hippel, *Dielectrics and Waves*, Wiley, NY (1954); D. E. Aspnes, "Local-field effects and effective-medium theory: a microscopic perspective", Am. J. Phys. **50** 704 (1982).

magnetization and magnetic matter (*e.g.*, ferromagnets). The main difference is the magnitude; the nuclear magnetic moments are five orders of magnitude smaller than the electric dipole moments ($\mu \simeq 10^{-23} erg/Gs$); if the magnetic moments are in thermal equilibrium their interaction energy $\mu^2/a^3 \simeq 10^{-6}K$ is effective at much lower temperatures; the characteristic frequency of "electric dipolons" $\omega_0 = \sqrt{2d^2/Ia^3} \simeq 10^{13}s^{-1}$ becomes $\omega_0 = \sqrt{2\mu^2/Ia^3} \simeq 10^8 s^{-1}$ for "magnetic dipolons". For electronic magnetic moments $\mu \simeq 10^{-20} erg/Gs$ the interaction energy is $\simeq 1K$ and the characteristic frequency is $\omega_0 \simeq 10^{11}s^{-1}$. If the magnetic moment is higher by a factor of, say, 5 and the number of nearest neighbours is 4, then the effective magnetic dipolar energy increases to $\simeq 100K$, which is of the order of magnitude of usual ferromagnetic transitions temperatures; then, the "magnetic dipolons" become magnons (ferromagnetic resonances). The dipole interaction as source of ferromagnetism is different from the Weiss mean field approach (which requires a great exchange magnetic field since it employs the comparison with the very small magnetization at finite temperature); it seems to be closer to Bloch theory of magnons.[13]

7.7 Highly-oscillating electric fields

High-power lasers may provide strong electric fields which oscillate in time with a frequency ω_h much higher than the frequencies of molecular rotations or vibrations. Usually, the frequency ω_h is in the optical range, $\omega_h = 2\pi \times 10^{15}s^{-1}$, and the strength of the electric field may attain values of the order $E_0 = 10^9 statvolt/cm$ for laser intensities $10^{20} w/cm^2$. Under the action of such strong fields the molecules are usually ionized, but the molecular ions retain their electric dipoles which perform a non-relativistic motion. (Indeed, the non-relativistic approximation is ensured by the inequality $\eta = qA_0/2Mc^2 \ll 1$, where q is the charge of the particle with masss M and A_0 is the amplitude of the vector potential; for a proton in a potential $A_0 = 5 \times 10^3 statvolt$, corresponding to the field amplitude $E_0 = 10^9 statvolt/cm$, we get $\eta = 10^{-3} \ll 1$).

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[13] P. W. Anderson, "Two comments on the limits of validity of the P. R. Weiss theory of ferromagnetism", Phys. Rev. **80** 922 (1950).

Consider an electric field $E_0 \cos \omega_h t$ oriented along the z-axis. An electric dipole d acted by this field performs rapid oscillations of an angle α about, in general, a certain angle θ measured with respect to the z-axis, which may perform slow oscillations; we assume $\alpha \ll \theta$. The equation of motion can be written as

$$I\ddot{\alpha} = -dE_0 \sin(\theta + \alpha) \cos \omega_h t \simeq -dE_0 \sin \theta \cos \omega_h t \ ; \tag{7.61}$$

the corresponding kinetic energy is $E_{kin} = I\dot{\alpha}^2/2 = (d^2 E_0^2/2I\omega_h^2) \sin^2 \theta \sin^2 \omega_h t$; its time average

$$\overline{E}_{kin} = \frac{d^2 E_0^2}{4I\omega_h^2} \sin^2 \theta \tag{7.62}$$

replaces the interaction energy $-dE_0 \cos \theta$ of the static field in the effective potential energy U_{eff} given by equation (7.22); the effective potential becomes

$$U_{eff} = \frac{L_z^2}{2I \sin^2 \theta} + \frac{d^2 E_0^2}{4I\omega_h^2} \sin^2 \theta \ . \tag{7.63}$$

This function has a minimum value for $\widetilde{\theta}_0 = \arcsin \theta_0 / R^{1/4}$ and $\widetilde{\theta'}_0 = \pi - \widetilde{\theta}_0$, where $R = dE_0/2I\omega_h^2$ is a renormalization factor and $\theta_0 = (L_z^2/IdE_0)^{1/4} < R^{1/4}$, *i.e.* for strong fields; it is worth noting that there are two values of the equilibrium angle: $\widetilde{\theta}_0$ and $\pi - \widetilde{\theta}_0$. The dipole may perform small vibrations about these equilibrium angles with the frequency $\widetilde{\omega}_0 = \omega_0 \sqrt{3R/4}$, where $\omega_0 = 2\sqrt{dE_0/I}$ is the frequency for strong static fields given in equation (7.24) (for$\widetilde{\theta}_0 \ll 1$). We can see that for highly-oscillating electric fields we get the results for static fields renormalized according to $E_0 \rightarrow \widetilde{E}_0 = E_0 R$.

From $\theta_0/R^{1/4} < 1$ and $\alpha = (dE_0/I\omega_h^2)\widetilde{\theta}_0 \ll \widetilde{\theta}_0$ we get the inequalities

$$\frac{L_z^2}{IdE_0} < \frac{dE_0}{2I\omega_h^2} \ll 1 \tag{7.64}$$

(which are compatible because $L_z \ll I\omega_h$); these inequalities imply

$$\frac{\sqrt{2} L_z \omega_h}{d} < E_0 \ll \frac{2I\omega_h^2}{d} \ . \tag{7.65}$$

For $L_z^2/I = T$ and our numerical parameters $I = 10^{-38} g \cdot cm^2$, $T = 300K = 4\times10^{-14} erg$, $d = 10^{-18} statcoulomb{\cdot}cm$ and $\omega_h = 2\pi{\cdot}10^{15} s^{-1}$ we get approximately $10^8 statvolt/cm < E_0 \ll 10^{10} statvolt/cm$, which corresponds to a renormalization parameter $R = 10^{-10}E_0/8\pi^2 \ll 1$. We conclude that in strong, highly-oscillating electric fields, like those provided by high-power lasers, the molecular rotation spectra are affected in the same manner as in static electric field, providing the time-dependent field strength is renormalized by the factor $R \ll 1$ introduced here. It is worth noting that the interaction $-dE_0 \cos\theta \cos\omega_h t$ linear in the field is replaced by an effective interaction which is quadratic in the field, as shown in equation (7.63); while this effective interaction affects the slow rotation motion, it does not affect the (slow) translation motion.

7.8 Appendix

For convenience, we give here a few elements for the Mathieu's equation. Mathieu's equation (7.32) is solved by means of the perturbation theory for $h \ll 1$.[14] Besides periodic solutions, it has also aperiodic solutions, which may increase exponentially in time. For the unperturbed solutions $\cos\omega_0 t$, $\sin\omega_0 t$ the h-term in equation (7.32) gives rise to terms of the form $\cos(\omega_0 \pm \omega)t$, $\sin(\omega_0 \pm \omega)t$; and so on, in higher orders of the perturbation theory. It follows that a resonance may occur for $\omega = 2\omega_0 + \varepsilon$, $\varepsilon \ll \omega_0$; the solution is

$$\delta\theta \simeq a\cos(\omega_0 + \frac{\varepsilon}{2})t + b\sin(\omega_0 + \frac{\varepsilon}{2})t \ , \tag{7.66}$$

where a and b are slowly-varying functions of time. We get

$$2\dot{a} + (\varepsilon + h\omega_0/2)b = 0 \ , \ 2\dot{b} - (\varepsilon - h\omega_0/2)a = 0 \ , \tag{7.67}$$

with a, $b \sim e^{st}$, where $s^2 = \frac{1}{4}(h^2\omega_0^2/4 - \varepsilon^2)$, for $-h\omega_0/2 < \varepsilon < h\omega_0/2$. If the damping is included, the coefficients a and b go like $e^{(s-\gamma)t}$ and the resonance occurs for $-\sqrt{(h\omega_0)^2/4 - 4\gamma^2} < \varepsilon < \sqrt{(h\omega_0)^2/4 - 4\gamma^2}$; a threshold occurs now for the perturbation amplitude h.

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[14] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol.1, *Mechanics*, Elsevier, Oxford (1976).

For the sake of definiteness we may set $\varepsilon = 0$; the initial conditions for $\delta\theta$ and $\delta\dot{\theta}$ are provided by fluctuations; we can see that their mean values are vanishing. The amplitude a can be written approximately as

$$\delta\theta \simeq \pi e^{st} \cos \omega_0 t \ , \ s = \frac{1}{4} h\omega_0 \ ; \tag{7.68}$$

its Fourier transform is

$$\delta\theta(\omega) \simeq -\frac{\pi(s + i\omega)}{(\omega_0^2 - \omega^2) + 2is\omega} \ , \tag{7.69}$$

or

$$\delta\theta(\omega) \simeq -\frac{\pi}{2}\delta(\omega - \omega_0) \tag{7.70}$$

for ω close to ω_0; the energy absorbed per unit time is obtained from equation (7.32) as

$$P = -hI\omega_0^2 \overline{\delta\theta\delta\dot{\theta}\cos 2\omega_0 t} \ , \tag{7.71}$$

where s is set equal to zero and the damping parameter γ is included; we get $P = \frac{1}{4}a^2 hI\omega_0^2\gamma$.

Parametric resonance occurs also for $\omega = 2\omega_0/n$, $n = (1), 2, 3, ...$, within a more narrow ε-range.

8 Magnetic Resonance II

8.1 Classical magnetic moments

At the molecular level matter may exhibit electric currents known as "Ampere currents". Their density $\mathbf{j}_m$ occurs in the Maxwell-Ampere equation

$$curl\mathbf{B} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c}\mathbf{j}_0 + \frac{\boldsymbol{4\pi}}{\mathbf{c}}\mathbf{j}_m \tag{8.1}$$

and generates magnetic induction; in equation (8.1) $\mathbf{B}$ is the magnetic induction, $\mathbf{D}$ is the electric displacement and $\mathbf{j}_0$ is the density of external currents. It is customary to introduce the magnetization $\mathbf{M}$ through

$$\mathbf{j}_m = c \cdot curl\mathbf{M} \tag{8.2}$$

and write the above equation as

$$curl\mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c}\mathbf{j}_0 \ \ , \tag{8.3}$$

where $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$ is the magnetic field. We can see that $\mathbf{B}$, $\mathbf{M}$ and $\mathbf{H}$ have the same nature, that of a magnetic field. It is also worth noting that $div\mathbf{j}_m = 0$, *i.e.* there is no time variation of the charge, $\partial\rho_m/\partial t = 0$, where ρ_m is the charge density; since the magnetic field is not related to a magnetic charge, we set, in fact, $\rho_m = 0$. The solution of equation (8.2) is

$$\mathbf{M} = \frac{1}{2c}\mathbf{j}_m \times \mathbf{R} \ \ , \tag{8.4}$$

where $\mathbf{R}$ is the position vector from the location of $\mathbf{j}_m$; indeed, we have

$$\begin{aligned} (curl\mathbf{M})_i &= \tfrac{1}{2c}\varepsilon_{ijk}\partial_j\varepsilon_{klr}j_{ml}X_r = \\ &= \tfrac{1}{2c}(\delta_{il}\delta_{jr} - \delta_{ir}\delta_{jl})\delta_{jr}j_{ml} = \tfrac{1}{c}j_{mi} \ \ , \end{aligned} \tag{8.5}$$

where ε_{ijk} is the totally antisymmetric symbol of rank three and δ_{ij} is the Kronecker symbol. It is convenient to introduce the position vector $\mathbf{r}_m = -\mathbf{R}$ of the current $\mathbf{j}_m$ and the current $\mathbf{J}_m = V\mathbf{j}_m = q_m\mathbf{v}_m$, where V is the volume wherein the (point) charge q_m moves with velocity $\mathbf{v}_m$;

$$\overrightarrow{\mu} = V\mathbf{M} = \frac{q_m}{2c}\mathbf{r}_m \times \mathbf{v}_m \tag{8.6}$$

is called magnetic moment, located at $\mathbf{r}_m$ and generated by a moving charge, *i.e.* by a current. For convenience we may give up the suffix m and write $\overrightarrow{\mu} = (q/2c)\mathbf{r}\times\mathbf{v}$. Usually, an average is taken upon the finite motion of the charge at the molecular level; in this case, the magnetic moments are constant, they do not depend on the rapid movements of the charges at the molecular level; their only dependence on the time is caused by external magnetic fields. For a finite motion which covers an area $\mathbf{S}$ we have $(1/2)\mathbf{r} \times \mathbf{v} = d\mathbf{S}/dt$; with $qd\mathbf{S} = \mathbf{S}dq$ and the current intensity $dq/dt = I$, we get $\overrightarrow{\mu} = I\mathbf{S}/c$. Magnetization is the magnetic moment of the unit volume. From definition 8.6 the magnetic moment is proportional to the angular momentum $\mathbf{l}$,

$$\overrightarrow{\mu} = \frac{q}{2mc}\mathbf{r} \times m\mathbf{v} = \frac{q}{2mc}\mathbf{l} \ , \tag{8.7}$$

where m is the charge mass (and $m\mathbf{v}$ is the momentum in the non-relativistic limit)); for an assembly of charges

$$\overrightarrow{\mu} = \sum_a \frac{q_a}{2m_a c}\mathbf{l}_a \ ; \tag{8.8}$$

if the charge-to-mass ratios are the same,

$$\overrightarrow{\mu} = \frac{q}{2mc}\mathbf{L} \ , \tag{8.9}$$

where $\mathbf{L} = \sum_a \mathbf{l}_a$ is the total angular momentum; $\gamma = q/2mc$ is called gyromagnetic factor.

The Lorentz force acting upon an assembly of charges in a constant magnetic field $\mathbf{H}$,

$$\mathbf{F} = \sum_a \frac{q_a}{c}\mathbf{v}_a \times \mathbf{H} = \sum_a \frac{q_a}{c}\frac{d}{dt}(\mathbf{r}_a \times \mathbf{H}) \ , \tag{8.10}$$

is vanishing as an average over finite motion. The average of its torque is

$$\begin{gathered}\mathbf{K}=\sum_a\tfrac{q_a}{c}\mathbf{r}_a\times(\mathbf{v}_a\times\mathbf{H})=\\=\sum_a\tfrac{q_a}{c}[\mathbf{v}_a(\mathbf{r}_a\mathbf{H})-\mathbf{H}(\mathbf{v}_a\mathbf{r}_a)]=\\=\sum_a\tfrac{q_a}{c}[\mathbf{v}_a(\mathbf{r}_a\mathbf{H})-\tfrac{1}{2}\tfrac{d}{dt}(\mathbf{H}r_a^2)]=\\=\sum_a\tfrac{q_a}{c}\mathbf{v}_a(\mathbf{r}_a\mathbf{H})=\\=\sum_a\tfrac{q_a}{2c}\left\{\mathbf{v}_a(\mathbf{r}_a\mathbf{H})-\mathbf{r}_a(\mathbf{v}_a\mathbf{H})+\tfrac{d}{dt}[\mathbf{r}_a(\mathbf{r}_a\mathbf{H})]\right\}=\\=\sum_a\tfrac{q_a}{2c}[\mathbf{v}_a(\mathbf{r}_a\mathbf{H})-\mathbf{r}_a(\mathbf{v}_a\mathbf{H})]\ ,\end{gathered}\tag{8.11}$$

or

$$\mathbf{K}=\sum_a\frac{q_a}{2c}(\mathbf{r}_a\times\mathbf{v}_a)\times\mathbf{H}=\overrightarrow{\mu}\times\mathbf{H}\ .\tag{8.12}$$

It is worh noting that here the magnetic moments are averaged over the molecular motion.

The equation of motion of the angular momentum,

$$\frac{d\mathbf{L}}{dt}=\mathbf{K}=\overrightarrow{\mu}\times\mathbf{H}\tag{8.13}$$

leads to the equation of motion of the (averaged) magnetic moment (in a constant magnetic field)

$$\frac{d\overrightarrow{\mu}}{dt}=\gamma\overrightarrow{\mu}\times\mathbf{H}\ ,\ \gamma=q/2mc\ ,\tag{8.14}$$

or

$$\frac{d\overrightarrow{\mu}}{dt}=-\overrightarrow{\Omega}\times\overrightarrow{\mu}\ ,\ \frac{d\mathbf{L}}{dt}=-\overrightarrow{\Omega}\times\mathbf{L}\ ,\ \overrightarrow{\Omega}=\gamma\mathbf{H}\ ;\tag{8.15}$$

this is called the Larmor equation, and $\overrightarrow{\Omega}=qH/2mc$ is called the Larmor frequency; equation (8.15) describes the rotation of the reference frame with frequency $\overrightarrow{\Omega}$. The same equation governs the motion of the magnetization **M**. For **H** oriented along the z-axis we get $\dot{\mu}_x=\gamma H\mu_y$, $\dot{\mu}_y=-\gamma H\mu_x$, and the magnetic moment oscillates (precesses, rotates about **H**) with the Larmor frequency $\Omega=\gamma H=qH/2mc$. In the same situation, the motion of a charge q, mass m, under the action of the Lorentz force is governed by the equations $m\dot{v}_x = (q/c)Hv_y$, $m\dot{v}_y = -(q/c)Hv_x$, and the velocities oscillate (rotate) with the frequency $\omega_c = |q|\,H/mc = \Omega/2$, which is half the Larmor frequency; the frequency $\omega_c = |q|\,H/mc$ is called cyclotron frequency. The connection of the magnetic moment with the angular moment gives rise to the "rotation by magnetization" (Einstein-de Haas effect) and "magnetization by rotation" (Barnett effect).

A (uniform) magnetic field $\mathbf{H}$ is produced by a vector potential $\mathbf{A} = (1/2)\mathbf{H}\times\mathbf{r}$; the interaction lagrangian is

$$L_{int} = \frac{1}{c}q\mathbf{v}\mathbf{A} = \frac{q}{2c}\mathbf{v}(\mathbf{H}\times\mathbf{r}) = \frac{q}{2c}(\mathbf{r}\times\mathbf{v})\mathbf{H} = \overrightarrow{\mu}\mathbf{H} \tag{8.16}$$

and the interaction energy is

$$H_{int} = -L_{int} = -\overrightarrow{\mu}\mathbf{H} \ , \tag{8.17}$$

where the average is taken over molecular motion. A force may act upon the magnetic moment (or magnetization) in this case, given by $\mathbf{F} = grad(\overrightarrow{\mu}\mathbf{H})$. (The equation of motion of the charge q, either with the Lagrange-Euler or Hamilton equations, leads to the Lorentz force, whose (averaged) torque governs the motion of the magnetic moment).

The molecular currents produce a potential vector

$$\begin{aligned}\mathbf{A}(\mathbf{r},t) &= \tfrac{1}{c}\int d\mathbf{r}'\,\frac{\mathbf{j}_m(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|} = \\ &= \int d\mathbf{r}'\,\frac{curl'\,\mathbf{M}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|} \ ,\end{aligned} \tag{8.18}$$

or, integrating by parts,

$$\mathbf{A}(\mathbf{r},t) = \int d\mathbf{r}'\,\frac{\mathbf{M}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)\times(\mathbf{r}-\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|^3} \ ; \tag{8.19}$$

for an infinitesimal volume $d\mathbf{r}'$ placed at the origin we get

$$\mathbf{A}(\mathbf{r},t) = -\overrightarrow{\mu}\times grad\frac{1}{r} = \frac{\overrightarrow{\mu}\times\mathbf{r}}{r^3} \tag{8.20}$$

(and the magnetic field $\mathbf{H} = curl\mathbf{A}$). Here, the magnetic moment is taken at the retarded time $t-r/c$; for distances much smaller than the wavelength (the quasi-stationary regime) we get the magnetic field

$$\mathbf{H} = curl\mathbf{A} = 4\pi\overrightarrow{\mu}\delta(\mathbf{r}) + \frac{3\mathbf{r}(\overrightarrow{\mu}\mathbf{r}) - \overrightarrow{\mu}r^2}{r^5} \ ; \tag{8.21}$$

indeed,

$$\begin{gathered} H_i = (curl\mathbf{A})_i = -\varepsilon_{ijk}\partial_j\varepsilon_{klm}\mu_l\partial_m\tfrac{1}{r} = \\ = -(\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl})\mu_l\partial_j\partial_m\tfrac{1}{r} \ , \end{gathered} \tag{8.22}$$

whence equation (8.21) ($\Delta(1/r) = -4\pi\delta(r)$). A similar field is also produced by magnetization. Equation (8.21) may serve to compute the force acting between two magnetic moments.

In condensed matter the statistical averages are relevant. The classical statistical distribution (Maxwell distribution) is quadratic in velocities, while the classical magnetic moments are linear in velocities; consequently, the statistical averages of classical magnetic moments (as well as classical orbital currents) are vanishing (this is known as Bohr-van Leuween theorem): classically, there is no magnetic moment, and no magnetism.[1] The origin of the magnetic moments is quantum-mechanical and relativistic. (The quantum average of orbital currents (momenta) over bound states in centrally symmetric fields is also vanishing, due to the parity conservation).

8.2 Magnetic moments of the particles

All known elementary particles (quarks and leptons) have spin 1/2 (and all known fields have spin 1); all elementary particles, except neutrinos, have mass and electric charge and obey the Dirac equation; as a consequence, all of these particles possess a magnetic moment $\overrightarrow{\mu}$, which is proportional to their spin $\mathbf{s}$. In the first relativistic approximation, such a particle with mass m and charge q in an external electromagnetic field with potentials $\mathbf{A}$ and Φ has the hamiltonian

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[1] N. Bohr, Disertation, Copenhagen (1911); J. H. van Leeuwen, Disertation, Leiden (1919); J. H. van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford (1932).

$$\mathcal{H}=\frac{1}{2m}(\mathbf{p}-\frac{q}{c}\mathbf{A})^2-\overrightarrow{\mu}\mathbf{H}+q\Phi \ , \tag{8.23}$$

where $\mathbf{H}=curl\mathbf{A}$ is the magnetic field and $\mathbf{p}$ denotes the momentum; $i\hbar\partial\psi/\partial t=H\psi$ is Pauli's equation for the spinor ψ. It is worth noting the interaction energy

$$H_{int}=-\overrightarrow{\mu}\mathbf{H} \ , \tag{8.24}$$

known as the Zeeman energy. Within the same approximation, making use of the velocity $\mathbf{v}=\mathbf{p}/m-q\mathbf{A}/mc$ we can write the current density of the type $\mathbf{j}=nq\mathbf{v}$, where n is the density; in addition, the magnetization current must be added; we get the mean value of the current density

$$\begin{gathered}\mathbf{j}=-\tfrac{iq\hbar}{2m}[\psi^*(grad\psi)-(grad\psi^*)\psi]-\\ -\tfrac{q^2}{mc}\mathbf{A}\left|\psi\right|^2+c\cdot curl(\psi^*\overrightarrow{\mu}\psi) \ ;\end{gathered} \tag{8.25}$$

the matrix elements can be written similarly. We can check easily that the continuity equation $\partial\rho/\partial t+div\mathbf{j}=0$ is preserved, where the charge density is $\rho=q\left|\psi\right|^2$. Since the field potentials are defined up to a gauge transformation $\mathbf{A}\rightarrow\mathbf{A}+grad\chi$, $\Phi\rightarrow\Phi-(1/c)\partial\chi/\partial t$, where χ is an arbitrary function (for the Lorenz gauge $div\mathbf{A}+(1/c)\partial\Phi/\partial t=0$ it satisfies the wave equation $(1/c^2)\partial^2\Phi/\partial t^2-\Delta\Phi=0$), the wave function (spinor) must obey the gauge change $\psi\rightarrow\psi e^{\frac{i}{\hbar}(q\chi/c)}$; under these transformations the current density given by equation (8.25) remains unchanged.

The first term in equation (8.25) is the orbital current; it corresponds to a "classical" magnetic moment of the form $(1/2c)\mathbf{r}\times\mathbf{j}_{orb}$, where, noteworthy, in the orbital current $\mathbf{j}_{orb}=nq\mathbf{p}/m$ the momentum occurs instead of velocity. The second term in equation (8.25) corresponds to a diamagnetic, induced current $\mathbf{j}_d=-(nq^2/mc)\mathbf{A}$; indeed, for a uniform magnetic field $\mathbf{A}=(1/2)\mathbf{H}\times\mathbf{r}$ and the spatial average of the magnetic moment $\overrightarrow{\mu_d}=(1/2c)\mathbf{r}\times\mathbf{j}_d$ gives the well-known diamagnetic moment $\overline{\overrightarrow{\mu_d}}=-(nq^2\overline{r^2}/6mc^2)\mathbf{H}$. $\chi_d=-(nq^2\overline{r^2}/6mc^2)$ is the diamagnetic susceptibility and the corresponding interaction energy is $\Delta E_d=-(1/2)\chi_d H^2$ (since $\overline{\overrightarrow{\mu_d}}=-\partial\Delta E_d/\partial\mathbf{H}$) (Langevin's diamagnetism); we can see that the diamagnetism is a relativistic effect.

For the electron we have

$$\overrightarrow{\mu} = \frac{e\hbar}{mc}\mathbf{s} = \frac{e\hbar}{2mc}\overrightarrow{\sigma} \ , \tag{8.26}$$

where $\overrightarrow{\sigma}$ are Pauli's matrices;

$$\mu_B = \frac{|e|\,\hbar}{2mc} = 0.927 \times 10^{-20} erg/Gs \tag{8.27}$$

is called the Bohr's magneton ($1Gs = 10^{-4}Ts$); the spin $\mathbf{s}$ in equation (8.26) is taken without the Planck's constant $\hbar$ ($s = 1/2$). It is also customary to write $\overrightarrow{\mu} = g\mu_B\mathbf{s}$, where $g \simeq -2$ is called the Lande factor (electron mass $m = 10^{-27}g$, electron charge $e = -4.8 \times 10^{-10} statcoulomb\,(esu)$, Planck's constant $\hbar = 10^{-27}erg \cdot s$, the speed of light $c = 3 \times 10^{10}cm/s$). We see that the intrinsic magnetic momentum of the electron is opposed to the intrinsic angular momentum (the spin) and the proportionality coefficient (e/mc) is twice as large as the proportionality coefficient corresponding to the angular momentum (gyromagnetic factor, $e/2mc$, equation (8.7)). It is also convenient to write the magnetic moment of the electron as $\overrightarrow{\mu} = \gamma\hbar\mathbf{s}$, where $\gamma = e/mc = g\mu_B/\hbar = -1.8 \times 10^7 s^{-1}Gs^{-1}$ is also called gyromagnetic factor; from $H_{int} = -\overrightarrow{\mu}\mathbf{H} = -\gamma\hbar\mathbf{s}\mathbf{H}$, we can see that $-\gamma H$ is a frequency. In a mechanical model, the Bohr magneton corresponds to the quantization $\hbar/L = mv$ of the momentum mv for a particle with mass m and velocity v moving along the length L; indeed, the angular momentum $l = mvL$ is then $\hbar$ and we get a magnetic moment $\mu = (e/2mc)l = e\hbar/2mc$. Another mechanical model assumes that the electron moves along a circumference $2\pi\lambda$ (with the speed of light c!), where $\lambda = \hbar/mc = 3.8 \times 10^{-11}cm$ is the Compton wavelength, covering an area $S = \pi\lambda^2$; it produces a current intensity $I = ec/2\pi\lambda$ and has a magnetic moment $\mu = IS/c = e\lambda/2 = e\hbar/2mc$, *i.e.* the Bohr magneton.

The magnetic moment given by equation (8.26) is a quantum-mechanical operator (like the spin $\mathbf{s}$); the quantity $\mu_e = (e\hbar/2mc) = -\mu_B$ is also called the magnetic moment of the electron; we can see that it is the maximum eigenvalue of the operator μ_z. We can write $\mu_e = (e\hbar/mc)s = g\mu_B s = \gamma\hbar s$.

The nucleons also possess a magnetic moment: $\mu_p = 2.79\mu_0 = 1.4 \times 10^{-23}erg/Gs$ (parallel to the spin) for the proton and $\mu_n = -1.91\mu_0 =$

$-0.96 \times 10^{-23} erg/Gs$ for the neutron (antiparallel to the spin), where $\mu_0 = |e|\hbar/2M_pc = 5 \times 10^{-24} erg/Gs$ is the nuclear Bohr magneton ($M_p = 1.67 \times 10^{-24} g$ is the mass of the proton). These moments should come from the quarks, which are the constituents of the nucleons. It is also convenient to write $\overrightarrow{\mu} = g\mu_0\mathbf{I}$ for the quantum-mechanical operator of the magnetic moments of the nucleons, where g is a Lande factor and I $(= 1/2)$ is the nucleon spin (in units of $\hbar$); or, similarly, $\overrightarrow{\mu} = \gamma\hbar\mathbf{I}$, where γ is a gyromagnetic factor. For instance, for the proton $\gamma_p = 2.7 \times 10^4 s^{-1} Gs^{-1}$, while for the neutron $\gamma_n = -1.84 \times 10^4 s^{-1} Gs^{-1}$. If we compare the nuclear Bohr magneton $\mu_0 = |e|\hbar/2M_pc = 5 \times 10^{-24} erg/Gs$ with a mechanical model for a particle with charge $|e|$ moving with velocity v in a nucleus with radius R, $\mu = |e| Rv/2c \simeq 10^{-25}(v/c) erg/Gs$, we get $\mu_0 \gg \mu$, *i.e.* $\hbar/R \gg M_pv$, which indicates that the nucleon moves over much shorter distances. In fact, the magnetic moment includes the Compton wavelength $\hbar/M_pc$, which for proton is $\hbar/M_pc = 0.2 fm$ ($1 fm = 10^{-13} cm$), much smaller than the inter-nucleon separation in nucleus.

For composite particles, or assemblies of particles, the magnetic moment is given by the sum of angular momenta in the general formula $\overrightarrow{\mu} = \gamma\hbar\mathbf{J}$, with the corresponding gyromagnetic factors; its effect in an external magnetic field is computed by the perturbation theory, which implies the average over quantum states. For instance, the magnetization current $\mathbf{j}_m = c\gamma\hbar curl(\psi^*\mathbf{s}\psi)$ in equation (8.25) gives rise to a magnetization (density of magnetic moment) $\mathbf{M} = (1/2c)\mathbf{r} \times \mathbf{j}_m$ and a magnetic moment

$$\overrightarrow{\mu} = \int d\mathbf{r}\frac{1}{2}\gamma\hbar\mathbf{r} \times curl(\psi^*\mathbf{s}\psi) = \gamma\hbar\int d\mathbf{r}(\psi^*\mathbf{s}\psi) \ . \tag{8.28}$$

For a uniform magnetic field $\mathbf{A} = (1/2)\mathbf{H} \times \mathbf{r}$ and the hamiltonian given by equation (8.23) becomes

$$\mathcal{H} = \frac{1}{2m}p^2 - \frac{q}{2mc}(\mathbf{l} + 2\mathbf{s})\mathbf{H} + \frac{q^2}{8mc^2}(\mathbf{H} \times \mathbf{r})^2 \tag{8.29}$$

(here the product of $\mathbf{p}$ by $\mathbf{A}$ was symmetrized). The last term in equation (8.29) gives the diamagnetism. When applied to an atom the term including the orbital moment and the spin gives a magnetic moment $\overrightarrow{\mu_{at}} = -\mu_B(\mathbf{J}+\mathbf{S})$, where $\mathbf{J} = \mathbf{L}+\mathbf{S}$ is the total angular momentum and $\mathbf{S}$ is the total spin. The average over quantum states (all spin orientations) implies $\mathbf{S} = C\mathbf{J}$ and

$$\mathbf{SJ} = C\cdot J(J+1) = \frac{1}{2}[J(J+1) - L(L+1) + S(S+1)] \ , \quad (8.30)$$

where C is a constant determined by equation (8.30). Therefore, the energy in the first order of the perturbation theory is

$$\Delta E = g_{at}\mu_B M_J H \ , \quad (8.31)$$

where M_J is the quantum number of the projection of the total angular momentum $\mathbf{J}$ on the z-axis (the axis of the magnetic field $\mathbf{H}$) and

$$g_{at} = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (8.32)$$

is the atomic Lande factor; after this averaging, we can say that the atomic magnetic moment is $\overrightarrow{\mu_{at}} = g_{at}\mu_B\mathbf{J}$ (and $\mu_{at} = g_{at}\mu_B J$). The magnetic field splits the energy levels according to equation (8.31); this is the Zeeman splitting. If $S=0$, then $J=L$ and $g_{at}=1$; if $L=0$, then $J=S$ and $g_{at}=2$. For $\mathbf{J}=0$ (but $\mathbf{L}$, $\mathbf{S}\neq 0$) we should compute the second-order contribution of the interaction term $-\overrightarrow{\mu_{at}}\mathbf{H}$ (the result is known as van Vleck's paramagnetic moment). If the magnetic field is strong enough as the splitting produced by it exceeds the fine structure, then the effect is known as the Paschen-Back effect; it remains linear in the magnetic field, but it depends on $M_L + 2M_S$, where M_L and M_S are the quantum numbers of the z-components of the orbital moment and the spin (magnetic numbers), respectively, the magnetic field being oriented along the z-axis. Particles, or assemblies of particles with positive magnetic moments are called paramagnetic, in contrast with diamagnetic particles, whose magnetic moment is induced and opposed to the magnetic field (second-order magnetic moment in the perturbation theory is paramagnetic and induced). Ordered magnetic moments give ferromagnetism (with all its varieties).

The Zeeman splitting of energy $\mathcal{E} = -\overrightarrow{\mu}\mathbf{H}$ in a non-uniform magnetic field $\mathbf{H}$ (or a non-uniform distribution of magnetic moments) gives rise to a force $grad\mathcal{E}$, which was used to visualize the magnetic moment (the spin) by Stern and Gerlach, as well as to measure the magnetic moments in molecular beams experiments by Rabi.

In the non-relativistic approximation the atomic orbital momentum **L** is conserved (central field) and the total spin **S** is also conserved; the states are degenerate with respect to the spatial orientations of these vectors. The relativistic effects arise from the spin-orbit coupling and spin-spin interaction; both are small and can be treated as a perturbation which splits the degenerate energy levels; they give the fine structure of the atomic energy levels; the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is conserved. The electrons move in a mean field (self-consistent field, centrally symmetric), so there are one-electron states, arranged in shells, characterized by the principal quantum number n and the quantum number l of the angular momentum (electron configuration). In a closed shell the moments of the electrons cancel out. In an unfilled shell the spin S is the greatest and the angular momentum L is the greatest, for the lowest-energy state (Hund's rule). For heavy atoms, the relativistic effects are important, and the electronic states are characterized by the total angular momentum **j**.

The magnetic moment of the nucleus can also be written as $\overrightarrow{\mu} = g\mu_0\mathbf{I}$, where g is a nuclear Lande factor and **I** is the nuclear angular momentum; the constant g cannot be computed in general. Due to the spin-spin interaction, the spins of the nucleons are not conserved, neither are their total orbital momentum, in general. The formula $\overrightarrow{\mu} = g\mu_0\mathbf{I}$ implies the average over the nucleon motion; **I** is also called "nuclear spin", as if the nucleus would be an elementary particle. The magnetic moment of the nucleus is produced by the nucleons outside the closed shells (the magnetic moments of the nucleons in closed shells cancel out). In general, we have for nucleons $\overrightarrow{\mu}/\mu_0 = g_l\mathbf{l} + g_s\mathbf{s}$, where **l** is the orbital angular momentum and **s** is the spin. For protons $g_l = 1$ and $g_s = 5.58$, for neutrons $g_l = 0$ and $g_s = -3.82$. We can write

$$g_j\mathbf{j} = g_l\mathbf{l} + g_s\mathbf{s} = \frac{1}{2}(g_l + g_s)\mathbf{j} + \frac{1}{2}(g_l - g_s)(\mathbf{l} - \mathbf{s}) \tag{8.33}$$

and multiply by $\mathbf{j} = \mathbf{l} + \mathbf{s}$ to get

$$g_j = g_l \pm \frac{g_s - g_l}{2l + 1}\ ,\ j = l \pm 1/2 \tag{8.34}$$

(and $s = 1/2$). These formulae are useful for one or two nucleons outside a closed shell (with appreciable discrepancies with respect to the experimental values of the magnetic moments); for more nucleons outside a closed shell we should known the nuclear wavefunction. In addition, the spin-orbit interaction (which is of the first order in v/c, in contrast with atoms, because the nuclear forces depend on the spin) includes the velocity in the angular momentum, and, therefore, it includes the vector potential in the presence of an electromagnetic field; it is easy to see that it leads to an additional magnetic moment of the nucleons.

The electronic energy levels in the atom are affected by the nuclear mass (isotope shift) and by the finite extension of the nucleus (especially the s-electrons). The electric field of the nuclear quadrupole and the nuclear magnetic dipole give the hyperfine interaction, involving especially the s-electrons (contact hyperfine interaction); the main contribution, which can be written as $\sim \mathbf{IJ}$, where $\mathbf{I}$ is the nuclear angular momentum and $\mathbf{J}$ is the electronic angular momentum, comes from the magnetic moment; the quadrupole contribution implies also $(\mathbf{IJ})^2$; both imply the total angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$. The magnetic interaction of an s-electron affects also the nuclear energy levels.

Usually, molecules have a vanishing electronic spin; they have also a vanishing electronic orbital moment (in their ground-state; we say that the moments are quenched). Consequently, the hyperfine splitting of the electronic levels is due to the quadrupole interaction of the nucleus with the electrons (for nuclei with spin $I \neq 0$, $1/2$). This interaction is averaged over electronic states and over molecular rotations. If the spins of the nuclei are $1/2$, the nuclear quadrupole is zero; then, the main contribution to the molecular hyperfine splitting comes from the direct interaction between the magnetic moments of the nuclei. For molecules containing heavy nuclei the relativistic effects are important; for instance, there exists an indirect interaction between nuclear magnetic moments in the second-order of the perturbation theory mediated by electrons. There is also an interaction (leading to a hyperfine splitting) between the nuclear magnetic moments and the magnetic field of the rotating molecule; indeed, a rotating molecule gives rise to a current density $\mathbf{j} = \rho \overrightarrow{\Omega} \times \mathbf{r}$, where ρ is the charge density and $\overrightarrow{\Omega}$ is the angular velocity; this current generates a magnetic field and the nuclear magnetic moment has a certain energy in this field, which is the interaction energy of the hyperfine splitting (after averaging over molecular states).

With the interaction energy $H_{int} = -\overrightarrow{\mu}\mathbf{H}$ and the general dependence $\overrightarrow{\mu} = \gamma\hbar\mathbf{J}$ of the magnetic moment $\overrightarrow{\mu}$ on the angular momentum $\mathbf{J}$, taking into acount the commutation relations $[J_i, J_j] = i\varepsilon_{ijk}J_k$, the equation of motion $i\hbar\dot{\overrightarrow{\mu}} = [\overrightarrow{\mu}, \mathcal{H}]$ leads to the Larmor equation

$$\dot{\overrightarrow{\mu}} = \gamma\overrightarrow{\mu} \times \mathbf{H} \ , \tag{8.35}$$

as in the classical motion (γ is the gyromagnetic factor). $\overrightarrow{\mu} \times \mathbf{H}$ is the torque of the forces acting upon the angular momentum (and the magnetic moment). For a uniform magnetic field we can take the vector potential $A_x = -Hy/2$ and $A_y = A_z = 0$; we can see that the motion along the y-axis is that of a harmonic oscillator with frequency $\omega_c = |q|\,H/mc$, which is twice the Larmor frequency Ω; this is the cyclotron frequency; the corresponding energy levels are known as Landau levels. For an electron in a magnetic field $H = 1Ts$ we get $\omega_c = 1.6 \times 10^{11}Hz$ and an energy $\hbar\omega_c = 10^{-4}eV \simeq 1K$ ($1eV = 1.16 \times 10^4 K$) (twice the energy of its magnetic moment in that field).

It is worth noting that a (microscopic) charge distribution can generate an electric field according to its multipole expansion; in general, an estimation of this field for atoms, molecules, etc is q/a^2, where q is an effective charge and a is a distance of the order of atomic distances. The magnetic field includes the factor v/c, where v stands for the velocity of the charges; usually, $v/c \ll 1$. For instance, the (dipolar) magnetic field $\sim \overrightarrow{\mu}/a^3$ of a magnetic moment $\mu = \mu_B$ is $\simeq 10^4 Gs = 1Ts$ at a distance 1Å (this is a rather high magnetic field). For comparison, an electron charge at the same distance (or an electronic dipole) yields an electric field $\simeq 10^6 statvolt/cm$ ("atomic fields").

Paramagnetic moments in matter may arise from atoms, molecules (radicals) or lattice defects with an odd number of electrons, which have a non-vanishing spin; another source is provided by atoms or ions with partly filled shells (*e.g.*, transition elements, rare-earth and actinide elements); a few compounds with an even number of electrons may also exhibit paramagnetism, like, for instance, molecular oxygen; the spins of the conduction electrons in metals can be partially aligned by an external magnetic field, leading to Pauli's paramagnetism.[2] The conduction electrons in metals exhibit also the Landau diamagnetism.[3] The nuclear spins provide also paramagnetic moments, etc. In general, the magnetic moments in condensed matter are assumed to be averaged over the quantum states of the atomic constituents which generate them (and, usually, distributed continuously); the same holds also for spins. This way, we get classical vectors, which, in an external magnetic field, obey the Larmor equation of motion (8.35); we have densities of spins and magnetic moments (the latter is magnetization), which may vary in space and time. This picture is sufficient in many usual situations, where we measure the quantum averages, slightly modified in time and space by forces like those produced by external fields.

8.3 Nuclear magnetic resonance

Let us consider the motion of a magnetic moment $\overrightarrow{\mu}$ in a constant (static) and uniform magnetic field $\mathbf{H}_0$ directed along the z-axis (the longitudinal field) and an oscillating magnetic field $\mathbf{H}(t) = \mathbf{H}\cos\omega t$, directed along the x-axis (the transverse field), where ω is the oscillation frequency. The interaction hamiltonian can be written as

$$H_{int} = -\overrightarrow{\mu}(H_0\mathbf{e}_z + H(t)\mathbf{e}_x) \ , \tag{8.36}$$

where $\mathbf{e}_{x,z}$ are the corresponding unit vectors. The Larmor equation $\dot{\overrightarrow{\mu}} = \gamma\overrightarrow{\mu} \times [H_0\mathbf{e}_z + H(t)\mathbf{e}_x]$ reads

$$\begin{gathered}\dot{\mu}_x = \gamma\mu_y H_0 \ , \\ \dot{\mu}_y = -\gamma\mu_x H_0 + \gamma\mu_z H\cos\omega t \ , \\ \dot{\mu}_z = -\gamma\mu_y H\cos\omega t \ , \end{gathered} \tag{8.37}$$

where γ is the gyromagnetic factor.

The magnetic moment in the equations written above is a quantum-mechanical operator; it is related by the quantum-mechanical operator

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[2] W. Pauli, "Uber Gasentartung und Paramagnetismus", Z. Phys. **41** 81 (1927).

[3] L. Landau, "Diamagnetismus der Metalle", Z. Phys. **64** 629 (1930).

of the angular momentum $\mathbf{J}$ (spin) by $\overrightarrow{\mu} = g\mu_B\mathbf{J} = \gamma\hbar\mathbf{J}$, where g is a Lande factor, μ_B is a Bohr magneton (atomic or nuclear) and γ is a gyromagnetic factor; the magnetic moment of a particle, or assembly of particles, is given by $\mu = g\mu_B J = \gamma\hbar J$ (it is convenient to use a suffix for this magnetic moment, and write, for instance, $\mu_p = g\mu_B J = \gamma\hbar J$, where the suffix p stands for "particle", in order to distinguish it from the magnitude $[(\overrightarrow{\mu})^2]^{1/2}$ of the operator $\overrightarrow{\mu}$). Apart from eigenvalues of operators in eigenstates (μ_p corresponds to the highest eigenvalue of the component J_z), we measure also mean (average) values over quantum states, statistical ensembles, etc. In the absence of the field $\mathbf{H}$, the interaction $-\overrightarrow{\mu}\mathbf{H}_0 = -\mu_z H_0 = -\gamma\hbar J_z H_0$ splits the degenerate level according to $-\gamma\hbar m_z H_0$, where $m_z = -J, -J+1, ...J$ is the quantum number of the component J_z; it is convenient to introduce the frequency $\omega_0 = \gamma H_0$ and write the energy levels as $-\hbar\omega_0 m_z$. The states labelled by m_z are eigenstates of the operator J_z and μ_z; for each of these states J_z and μ_z are constant, while $\mu_{x,y}$ (and $J_{x,y}$) are undetermined; the mean value of $\mu_{x,y}$ (and $J_{x,y}$) over any state m_z is vanishing. The interaction $-\overrightarrow{\mu}\mathbf{H}(t) = -\gamma\hbar J_x H(t)$ produces transitions between the states m_z and $m_z \pm 1$, so it mixes up such states; consequently, we measure mean (average, expectation) values of the operators $\overrightarrow{\mu} = (\mu_x, \mu_y, \mu_z)$.

We can take the average of the magnetic moment over the quantum motion in equations (8.37) and get meaningful equations, since these equations are linear; this means that we can replace the operator $\overrightarrow{\mu} = \gamma\hbar\mathbf{J}$, where $\mathbf{J}$ is the operator of the angular momentum, by its average, denoted $\overrightarrow{\mu_{av}}$ and given by

$$\overrightarrow{\mu_{av}} = \sum_{\sigma\sigma'} \int d\mathbf{r}\psi^*_{\sigma'}(\overrightarrow{\mu})_{\sigma'\sigma}\psi_\sigma \quad , \tag{8.38}$$

where ψ_σ is the spinor corresponding to the angular momentum $\mathbf{J}$; $\overrightarrow{\mu_{av}}$ is now a classical variable which can be measured. It is this quantity which is often viewed as the magnetic moment, especially for assemblies of particles (a similar average can be introduced for the angular momentum, so we can preserve the equation $\overrightarrow{\mu_{av}} = \gamma\hbar\mathbf{J}_{av}$); we note that equations (8.38) define also a density of magnetic moment (magnetization). For a sample of condensed matter $\overrightarrow{\mu_{av}}$ can carry a position label $\mathbf{r}_i$, denoting the position of the i-th particle with this magnetic moment; in a course-graining average, specific to the continuum models of matter, the label $\mathbf{r}_i$, may become the continuous, local position $\mathbf{r}$, so that the average magnetic moment $\overline{\overrightarrow{\mu_{av}}}$ may be a function $\overline{\overrightarrow{\mu_{av}}}(t, \mathbf{r})$ of the time t and position $\mathbf{r}$. Moreover, the measurable quantities in condensed matter are statistical averages, so that we may assume that we have a local thermodynamic equilibrium and $\overline{\overrightarrow{\mu_{av}}}(t, \mathbf{r})$ is also averaged over such a statistical distribution, leading to $\overline{\overline{\overrightarrow{\mu_{av}}}}$. If we are not interested in the spatial variations (which may imply diffusion of the moments), we may leave aside the $\mathbf{r}$-dependence; for simplification we may also leave aside the average bars and the suffix av, and write simply $\overrightarrow{\mu}$ for this classical quantity; in fact, it is more convenient to use the magnetization $\mathbf{M}$ (the magnetic moment of the unit volume, accordingly averaged), which obeys the equations of motion

$$\dot{M}_x = \gamma M_y H_0 \ ,$$

$$\dot{M}_y = -\gamma M_x H_0 + \gamma M_z H \cos \omega t \ , \tag{8.39}$$

$$\dot{M}_z = -\gamma M_y H \cos \omega t \ ,$$

derived from equations (8.38) by the succession of averages described above (quantum-mechanical, coarse-graining, statistical). We consider here the particular situation of magnetic moments associated with atomic nuclei, but the procedure described above is more general and can also be applied to other magnetic moments.

At thermal equilibrium the statistical average of the magnetization is zero; applying the magnetic field $\mathbf{H}_0$ an interaction $-\overrightarrow{\mu}\mathbf{H}_0$ appears, which restores the thermal equilibrium with a non-zero average magnetic moment directed along the longitudinal field $\mathbf{H}_0$. Since the interaction energy μH_0 is much smaller than the temperature T, we may use the distribution $\sim e^{\overrightarrow{\mu}\mathbf{H}_0/T}$ of the classical statistics; we get the statistical average of the magnetic moment $\overline{\mu_z} = \mu^2 H_0/3T$ and the longitudinal magnetization $M_0 = n\overline{\mu}_z = n\mu^2 H_0/3T$, where n is the density of particles; the transverse components of the magnetization are vanishing ($M_{x,y} = 0$); here μ is the "magnetic moment of the particle" ($\mu = \gamma\hbar J$). This is known as the Curie-Langevin-Debye law.[4] The relaxation of the longitudinal magnetization is governed by

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[4] P. Curie, "Lois experimentales du magnetisme. Proprietes magnetiques des

the kinetic equation

$$\frac{dM_z}{dt} = \alpha_1(M_0 - M_z) \ , \tag{8.40}$$

where α_1 is a (longitudinal) damping coefficient; the solution is $M_z = M_0(1 - e^{-\alpha_1 t})$, for zero initial magnetization. The released energy goes to the environment, for instance to the solid lattice. Indeed, a change in magnetization gives rise to an electric field which acts upon the neighbouring ions and generates vibrations (phonons). Therefore, during the relaxation of the magnetization a phonon can be created, or a phonon can be inelastically scattered (phonon Raman scattering), or an electron (in metals) can be inelastically scattered, or various other processes may occur, by which the magnetic energy is released to the environment. This is why α_1 is also called a spin-latice relaxation coefficient. In general, it depends on the temperature; usually, an uncertainty in energy is associated with T; for phonons we should note that their number goes like T^3 and their energy goes like T^4 , so that for Raman scattering we may have $\alpha_1 \sim T^7$; for other processes we may have other temperature-dependence laws.

The average transverse magnetization is vanishing; if, by external means, we take the transverse magnetization out of equilibrium ($M_{x,y} \neq 0$ initially), it will relax according to

$$\frac{dM_x}{dt} = -\alpha_2 M_x \ , \ \frac{dM_y}{dt} = -\alpha_2 M_y \ , \tag{8.41}$$

where α_2 is a transverse damping coefficient. The solution is $M_{x,y} = M_{x,y0}e^{-\alpha_2 t}$. This relaxation does not imply an energy flow.

The damping coefficients (which give rise to relaxation times) must

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corps a diverses temperatures", Ann. Chim. Phys. **5** 289 (1895); P. Langevin, "Sur la theorie du magnetisme", J. Physique **4** 678 (1905); P. Langevin, "Magnetism et theorie des electrons", Ann. Chim. Phys. **5** 70 (1905); P. Debye, "Einige Resultate einer kinetischen Theorie der Isolatoren", Phys. Z. **13** 97 (1912).

be included in equations (8.39) which become

$$\begin{aligned} \dot{M}_x &= \gamma M_y H_0 - \alpha_2 M_x \ , \\ \dot{M}_y &= -\gamma M_x H_0 + \gamma M_z H \cos\omega t - \alpha_2 M_y \ , \\ \dot{M}_z &= -\gamma M_y H \cos\omega t - \alpha_1 (M_z - M_0) \ ; \end{aligned} \tag{8.42}$$

for small values of the field H we may put approximately $M_z \simeq M_0$ in these equations and neglect the time-dependence of the longitudinal component M_z of the magnetization; equations (8.42) can be approximated by

$$\begin{aligned} \dot{M}_x &\simeq \gamma M_y H_0 - \alpha_2 M_x \ , \\ \dot{M}_y &\simeq -\gamma M_x H_0 + \gamma M_0 H \cos\omega t - \alpha_2 M_y \ , \end{aligned} \tag{8.43}$$

or

$$\begin{aligned} \dot{M}_x &\simeq \omega_0 M_y - \alpha_2 M_x \ , \\ \dot{M}_y &\simeq -\omega_0 M_x + \omega_m H \cos\omega t - \alpha_2 M_y \ , \end{aligned} \tag{8.44}$$

where $\omega_0 = \gamma H_0$ and $\omega_m = \gamma M_0$. These equations can also be transformed into

$$\begin{aligned} \ddot{M}_x + \omega_0^2 M_x + \alpha_2 \dot{M}_x &= \omega_0 \omega_m H \cos\omega t \ , \\ \ddot{M}_y + \omega_0^2 M_y + \alpha_2 \dot{M}_y &= -\omega \omega_m H \sin\omega t \ \ , \end{aligned} \tag{8.45}$$

for $\alpha_2 \ll \omega_0, \omega_m$, which are equations of motion of damped harmonic oscillators. They are equivalent with the original equations (8.44) providing we redefine the small damping parameter α_2. The solution of equations (8.44) consists of free damped oscillations and forced damped oscillations. The free oscillations are given by

$$\begin{aligned} M_x &= (A_x \cos\omega_0 t + B_x \sin\omega_0 t) e^{-\alpha_2 t} \ , \\ M_y &= (-A_x \sin\omega_0 t + B_x \cos\omega_0 t) e^{-\alpha_2 t} \ \ , \end{aligned} \tag{8.46}$$

where A_x and B_x are constants (they are determined from the initial conditions, for instance $M_{x,y}(t=0) = 0$). The particular solution is given by

$$\begin{aligned} M_x &= a\cos\omega t + b\sin\omega t\ , \\ M_y &= \tfrac{-a\omega+b\alpha_2}{\omega_0}\sin\omega t + \tfrac{b\omega+a\alpha_2}{\omega_0}\cos\omega t\ \ , \end{aligned} \tag{8.47}$$

where

$$\begin{aligned} a &= -\omega_0\omega_m H\tfrac{\omega^2-\omega_0^2-\alpha_2^2}{(\omega^2-\omega_0^2-\alpha_2^2)^2+4\omega^2\alpha_2^2}\ , \\ b &= \omega_0\omega_m H\tfrac{2\omega\alpha_2}{(\omega^2-\omega_0^2-\alpha_2^2)^2+4\omega^2\alpha_2^2}\ . \end{aligned} \tag{8.48}$$

We can simplify these solutions by assuming $\alpha_2 \ll \omega_0, \omega_m$ and ω close to ω_0. We get

$$M_x \simeq a\cos\omega t + b\sin\omega t\ ,\ M_y \simeq -a\sin\omega t + b\cos\omega t\ \ , \tag{8.49}$$

where

$$a \simeq -\tfrac{1}{2}\omega_m H\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha_2^2}\ ,\ b \simeq \tfrac{1}{2}\omega_m H\tfrac{\alpha_2}{(\omega-\omega_0)^2+\alpha_2^2}\ . \tag{8.50}$$

These solutions are obtained also from the oscillator equations (8.45) with $\alpha_2 \rightarrow \alpha_2/2$ in equations (8.50). From equations (8.47) we can see that the magnetization performs a Larmor precession about the z-axis with frequency ω (the frequency of the external field); the transverse magnetization rotates with constant magnitude $M_x^2 + M_y^2 = a^2 + b^2 \simeq (\omega_m H/2\alpha_2)^2$. The power absorbed from the field and dissipated by the motion of the transverse magnetization can be obtained from equations (8.45), through

$$\tfrac{d}{dt}\left(\tfrac{1}{2}\dot{M}_x^2 + \tfrac{1}{2}\omega_0^2 M_x^2\right) + \alpha_2\dot{M}_x^2 = \omega_0\omega_m H\dot{M}_x\cos\omega t\ , \tag{8.51}$$

We get

$$P = \overline{H\dot{M}_x\cos\omega t} = \frac{1}{2}Hb\omega = \frac{1}{4}\omega_m H^2\frac{\omega\alpha_2}{(\omega-\omega_0)^2+\alpha_2^2}\ ; \tag{8.52}$$

or

$$P = \frac{\pi}{4}\omega_m\omega_0 H^2\delta(\omega-\omega_0)\ ,\ \alpha_2 \rightarrow 0\ (\alpha_2 \ll \omega_0)\ . \tag{8.53}$$

These are typical solutions of damped harmonic oscillators exhibiting resonance for $\omega = \omega_0$. This is the typical solution of the magnetic resonance.[5] Equations (8.42) and (8.43) are called Bloch equations.[6] It is worth noting that the absorbed power computed above implies the particular solution of the harmonic oscillators which is valid for long times. For short times (as, for instance, for a finite, short duration of the external field $H(t)$ (a pulse) the general solution must be used, which involves also the free oscillations (and the initial conditions).

The results given above apply to the nuclear magnetic resonance (NMR), which implies the magnetic moments of the atomic nuclei. The nuclear magnetic moments are measured usually in nuclear Bohr magnetons. The nuclear Bohr magneton is $\mu_0 = |e| \hbar/2M_p c$, where $e = -4.8 \times 10^{-10} esu$ ($statcoulomb$, $e = -1.6 \times 10^{-19} C$) is the electron charge ($|e|$ is the proton charge), $M_p = 1.67 \times 10^{-24} g$ is the proton mass, $\hbar \simeq 10^{-27} erg \cdot s$ is Planck's constant and $c = 3 \times 10^{-10} cm/s$ is the speed of light in vacuum. The nuclear Bohr magneton is $\mu_0 \simeq 5 \times 19^{-24} erg/Gs$. The nuclear magnetic moments (averaged over the nucleon motion) are written as $\overrightarrow{\mu} = g\mu_0 \mathbf{I}$, where g is called the Lande (gyromagnetic) factor and $\mathbf{I}$ is the nuclear spin (angular momentum in $\hbar$ units); g can be positive or negative; the magnetic moment of the proton is $\mu_p = 2.79\mu_0 \simeq 1.4 \times 10^{-23} erg/Gs$ and the magnetic moment of the neutron is $\mu_n = -1.91\mu_0 \simeq -0.96 \times 10^{-23} erg/Gs$. The nuclear magnetic moments vary between $-2\mu_0$ and $6\mu_0$ (and the nuclear spin may go up to 9/2 or higher). It is also convenient to write the magnetic moments as $\overrightarrow{\mu} = \gamma\hbar\mathbf{I}$, where γ $(= g\mu_0/\hbar)$ is also called the gyromagnetic factor (coefficient). For proton $\gamma \simeq 2.7 \times 10^4 s^{-1} Gs^{-1}$ $(I = 1/2)$; $\overrightarrow{\mu} = \gamma\hbar\mathbf{I}$ includes the angular moment $\mathbf{J} = \hbar\mathbf{I}$.

In an external magnetic field $\mathbf{H}_0$ the magnetic moment acquires the Zeeman energy $U = -\overrightarrow{\mu}\mathbf{H}_0 = -\gamma\hbar\mathbf{I}\mathbf{H}_0$; we can see that the spin tends to align itself along the magnetic field; for instance, if initially the spins are distributed equally among the states $m_z = \pm 1/2$ for spin 1/2, where m_z is the quantum number of the component I_z in the presence of an external field H_0 oriented along the z-axis the level $m_z = 1/2$ will be more populated, being lower in energy (for g, $\gamma > 0$). At thermal

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[5] E. M. Purcell, H. C. Torrey, R. V. Pound, "Resonance absorption by nuclear magnetic moments in a solid", Phys. Rev. **69** 37 (1946); F. Bloch, W. W. Hansen and M.Packard, "Nuclear induction", Phys. Rev. **69** 127 (1946); F. Bloch, W. W. Hansen and M. Packard, "The nuclear induction experiment", Phys. Rev. **70** 474 (1946).

[6] F. Bloch, "Nuclear induction", Phys. Rev. **70** 460 (1946).

equilibrium the ratio of the two populations is $N_{1/2}/N_{-1/2} = e^{\beta\gamma\hbar H_0}$, where $\beta = 1/T$ is the inverse of the temperature. The frequency $\omega_0 = \gamma H_0$ (usually positive) for proton and $H_0 = 1Ts$ is $\omega_0 = 2.7 \times 10^8 Hz$ or $\nu_0 = \omega_0/2\pi = 4.3 \times 10^7 Hz$.

The Larmor equations discussed above are classical equations of motion. With energy $-\overrightarrow{\mu}\mathbf{H}$, where $\mathbf{H}$ is an external magnetic field, $\overrightarrow{\mu} = \gamma\hbar\mathbf{I}$ and the commutation relations $[I_i, I_j] = i\varepsilon_{ijk}I_k$ for the spin operators, the quantum-mechanical equations of motion for $\mathbf{I}$ and for $\overrightarrow{\mu}$ (and magnetization $\mathbf{M}$) are the same as the classical Larmor equations. For the constant field $\mathbf{H}_0$ these equations of motion are equivalent to the diagonalization of the energy $-\overrightarrow{\mu}\mathbf{H}_0$; the energy levels, which are usually degenerate, are split by the external magnetic field according to $-\gamma\hbar H_0 m_z = -\hbar\omega_0 m_z$. The external time-dependent field $H_x(t) = H\cos\omega t$, with an interaction hamiltionian $H_{int}(t) = -\gamma\hbar I_x H\cos\omega t$, produces quantum transitions between states m_z and $m_z \pm 1$, according to the selection rules for I_x. The states m_z are separated by energy $\hbar\omega_0$ and are thermally populated. We can see that the resonance frequency $\omega_0 = \gamma H_0$ occurring in equations (8.44) and (8.45) is the same as the frequency difference between two neighbouring energy levels.

The amplitude of transition from the quantum state n, originally prepared with the quantum probability 1, to the state k, under the action of an interaction $H_{int}(t) = H_{int}\cos\omega t$, in the first-order of the perturbation theory, is given by

$$c_k = \frac{1}{2\hbar}(H_{int})_{kn}\frac{e^{i(-\omega+\omega_{kn})t+\alpha t}}{\omega - \omega_{kn} + i\alpha} \ , \tag{8.54}$$

where $\omega_{kn} = (E_k - E_n)/\hbar$ is the frequency difference between the states k and n with energies E_k and E_n, and the interaction is introduced adiabatically ($\alpha \to 0^+$). The transition probability is $|c_k|^2$ and the transition rate (number of transitions per unit time) is

$$\begin{aligned} \frac{\partial|c_k|^2}{\partial t} &= \frac{1}{2\hbar^2}\left|(H_{int})_{kn}\right|^2\frac{\alpha}{(\omega-\omega_{kn})^2+\alpha^2} \to \\ &\to \frac{1}{2\hbar^2}\left|(H_{int})_{kn}\right|^2\delta(\omega - \omega_{kn}) \ , \ \alpha \to 0^+ \ . \end{aligned} \tag{8.55}$$

We apply these formulae to the transitions $m_z \to m_z \pm 1$ caused by the hamiltonian $H_{int}(t) = -\gamma\hbar I_x H\cos\omega t$; each of these transitions proceeds with the absorption or emission of the quanta of energy $\hbar\omega_0$; these transitions release and absorb energy, and we are interested in the net energy absorption rate per unit time.

In the presence of the longitudinal field $\mathbf{H}_0$ the energy levels are given by $-\gamma\hbar H_0 m_z = -\hbar\omega_0 m_z$; the lowest energy level has $m_z = I$ and the highest energy level has $m_z = -I$. The energy absorption proceeds from m_z to $m_z - 1$, where $m_z = I,\ I-1, ... -I+1$, with the rate

$$\frac{\partial \left|c_{m_z-1}\right|^2}{\partial t} = \frac{1}{2}\gamma^2 H^2 \left|(I_x)_{m_z-1,m_z}\right|^2 \frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ ; \tag{8.56}$$

the energy emission implies transitions from m_z to $m_z + 1$, where $m_z = I-1,\ I-2,\ ... -I$; the rate of these transitions is given by

$$\frac{\partial \left|c_{m_z+1}\right|^2}{\partial t} = \frac{1}{2}\gamma^2 H^2 \left|(I_x)_{m_z+1,m_z}\right|^2 \frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ ; \tag{8.57}$$

the matrix elements of the spin component I_x are

$$\begin{aligned} (I_x)_{m_z-1,m_z} &= \tfrac{1}{2}[(I+m_z)(I-m_z+1)]^{1/2} \ , \\ (I_x)_{m_z+1,m_z} &= \tfrac{1}{2}[(I-m_z)(I+m_z+1)]^{1/2} \ . \end{aligned} \tag{8.58}$$

The transition rates must be weighted by the statistical distribution $e^{\beta\hbar\omega_0 m_z} / \sum_{m_z} e^{\beta\hbar\omega_0 m_z}$, so that the net transition rate is given by

$$\begin{aligned} R = \overline{\tfrac{\partial\left|c_{m_z-1}\right|^2}{\partial t}} - \overline{\tfrac{\partial\left|c_{m_z+1}\right|^2}{\partial t}} = \\ = \tfrac{1}{2}\gamma^2 H^2 \overline{\left|I_x\right|^2} \tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ \ , \end{aligned} \tag{8.59}$$

where

$$\begin{gathered}
\overline{|I_x|^2} = [\textstyle\sum_{m_z=I}^{-I+1} |(I_x)_{m_z-1,m_z}|^2 - \\
- \textstyle\sum_{m_z=I-1}^{-I} |(I_x)_{m_z+1,m_z}|^2] e^{\beta\hbar\omega_0 m_z} / \\
/ \textstyle\sum_{m_z=I}^{-I} e^{\beta\hbar\omega_0 m_z} = \\
= \tfrac{1}{4}[\textstyle\sum_{m_z=I}^{-I+1}(I^2+I+m_z-m_z^2)- \\
- \textstyle\sum_{m_z=I-1}^{-I}(I^2+I-m_z-m_z^2)] e^{\beta\hbar\omega_0 m_z} / \\
/ \textstyle\sum_{m_z=I}^{-I} e^{\beta\hbar\omega_0 m_z}
\end{gathered} \tag{8.60}$$

(here, the net emission rate is equal with the net absorption rate, R in equation (8.59) being, in fact, $|R|$); the rearrangement of the summations in equation (8.60) leads to

$$\overline{|I_x|^2} = \frac{1}{2}\sum_{m_z-I}^{I} m_z e^{\beta\hbar\omega_0 m_z} / \sum_{m_z=-I}^{I} e^{\beta\hbar\omega_0 m_z} = \frac{1}{2}\overline{m_z} \ , \tag{8.61}$$

where $\overline{m_z}$ is the thermal average of the quantum number m_z. For $\beta\hbar\omega_0 \ll 1$ we get $\overline{m_z} = \hbar\omega_0 I(I+1)/3T$ (and $\overline{m_z^2} = I(I+1)/3$); we note that the average magnetic moment directed along the z-axis is $\gamma\hbar\overline{m_z} = \gamma^2\hbar^2 H_0 I(I+1)/3T$ while the same average calculated with the classical statistics is $\mu^2 H_0/3T = \gamma^2\hbar^2 H_0 I^2/3T$ (as given above); in the quantum-mechanical statistics I^2 is replaced by $I(I+1)$, as expected. Inserting $\overline{|I_x|^2}$ given by equation (8.61) in equation (8.59) we get the net absorption rate

$$R = \frac{1}{4}\gamma^2 H^2 \overline{m_z} \frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \tag{8.62}$$

and the power absorbed per unit volume

$$P = n\hbar\omega_0 R = \frac{1}{4} n\hbar\omega_0 \gamma^2 H^2 \overline{m_z} \frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ , \tag{8.63}$$

or

$$\begin{gathered}
P = \tfrac{1}{4}\gamma\omega_0 M_0 H^2 \tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} = \\
\tfrac{1}{4}\omega_m \omega_0 H^2 \tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ ,
\end{gathered} \tag{8.64}$$

since $n\gamma\hbar\overline{m_z}$ is the magnetization M_0 along the z-axis (and $\omega_m = \gamma M_0$). This equation should be compared with the equation (8.52) which gives the absorbed power per unit volume within the classical treatment; we can see that they are the same (near the resonance, with $\alpha = \alpha_2$; up to I^2 replaced by $I(I+1)$ in magnetization and ω_m). We note that the perturbation is applied here adiabatically (for a long time), which warrants the attaining of the thermal equilibrium; for short pulses, the equilibrium might not be attained, and the thermal average is not warranted.

8.4 Emitted field

The absorbed power given by equation (8.52) or (8.64), exhibiting a resonance at $\omega = \omega_0$, can be used for identifying the resonance phenomenon. Similarly, the field generated by the induced magnetization can also be used.

A magnetization $\mathbf{M}$ induces a current density $\mathbf{j} = c \cdot curl\mathbf{M}$, which, in turn, gives rise to a vector potential

$$\begin{gathered}\mathbf{A}(\mathbf{r},t) = \frac{1}{c}\int d\mathbf{r}'\frac{\mathbf{j}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|} = \\ = \int d\mathbf{r}'\frac{curl'\mathbf{M}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|} \ ,\end{gathered} \tag{8.65}$$

or

$$\mathbf{A}(\mathbf{r},t) = \int d\mathbf{r}'\frac{\mathbf{M}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)\times(\mathbf{r}-\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|^3} \ ; \tag{8.66}$$

in the quasi-static limit we may use $\mathbf{M}(\mathbf{r}',t)$ instead of $\mathbf{M}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)$; for $r \gg r'$ we may also take approximately

$$\mathbf{A}(\mathbf{r},t) = -v\mathbf{M}\times grad\frac{1}{r} \ , \tag{8.67}$$

where v is the volume of the magnetized body. We can see that it is the surface contribution which gives rise to this vector potential, since the magnetization is uniform inside the body. Since $div\mathbf{A} = v\mathbf{M}curl \cdot grad(1/r) = 0$, we have a vanishing scalar potential $\Phi = 0$, in accordance with the fact that the magnetization current $\mathbf{j}$ has not an associated charge density. Similarly, the electric field $\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}$ can be neglected in the quasi-static limit; we are left with the magnetic field

$$\mathbf{H}_m = curl\mathbf{A} = 4\pi v\mathbf{M}\delta(\mathbf{r}) + v\frac{3\mathbf{r}(\mathbf{M}\mathbf{r}) - \mathbf{M}r^2}{r^5} \ , \tag{8.68}$$

which is a dipolar field, as expected. We can see that this field exhibits resonance through the transverse magnetization $M_{x,y}$ given by equation (8.49).

The magnetic field given by equation (8.68) induces an electromotive force E_{em} in a coil placed in the neighbourhood of the magnetized body, according to Faraday's law

$$curl\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}_m}{\partial t} \ ; \tag{8.69}$$

for the flux of the component $H_{m,y}$ through the area S placed at the distance d we get the electromotive force

$$E_{em} \simeq -\frac{2v}{cd^3}S\frac{\partial M_y}{\partial t} = \frac{vS}{cd^3}\omega_0\omega_m H\frac{\Delta\omega\cos\omega t - \alpha_2\sin\omega t}{(\Delta\omega)^2 + \alpha_2^2} \ , \tag{8.70}$$

where $\Delta\omega = \omega - \omega_0$. It is worth noting the change of the phase $\tan\delta = \alpha_2/\Delta\omega$ on passing through the resonance frequency $\omega = \omega_0$.

8.5 Line width

The damping coefficient α_2 in the resonance formulae gives the resonance line width $\Delta\omega \simeq \alpha_2$. The coefficient α_2 originates mainly in residual interactions. For instance, a magnetic moment μ produces a dipolar magnetic field $B_i \sim \mu/r^3$ at the distance r (an internal magnetic field, *i.e.* a magnetic induction). For protons $\mu = 1.4 \times 10^{-23} erg/Gs$; for $r = 2\text{Å}$ we get $B_i \simeq 2Gs$. This field corresponds to a frequency $\alpha_2 = \gamma B_i \simeq 5 \times 10^4 Hz$. Comparing it with $\omega_0 = 10MHz$, we can see that the resonance line is very sharp.

The magnetic moments may feel a field B_i (and a damping coefficient α_2) during a time τ; thereafter, being in motion, a magnetic moment feels a field $-B_i$ during a time $\overline{\tau}$, such that, over iregular successions of time intervals τ and $\overline{\tau}$, the magnetic moment feels a zero average field (fluctuating field). Obviously, the effective field B_i and the damping coefficient α_2 are reduced by the factor $\alpha_2\tau$, where τ is the average relaxation time. Indeed, if in a "random walking" the phase is $\delta\Phi = \sum_{i=1}^{n} \delta\varphi_i$, then $(\delta\Phi)^2 = n(\delta\varphi)^2 = n(\gamma B_i\tau)^2$ and the reduced damping coefficient is $\alpha_2^{'} = (\delta\Phi)^2/n\tau = (\gamma B_i)^2\tau = \alpha_2(\alpha_2\tau)$. The reduction of the line width due to the motion of the magnetic moments (the diffusion of the magnetic moments)[7] is known as the motional narrowing.[8] The effect increases with increasing temperature and is more visible in liquids. For instance, the relaxation time of the rotational motion of water molecules is $\simeq 10^{-10}s$; for $\alpha_2 = 10^5Hz$ we have $\alpha_2^{'} = 1Hz$, which is an appreciable reduction.

The motional narrowing is due to interactions, not to collisions. For instance, a paramagnet has an exchange interaction J between the electron spins of neighbouring atoms; then $\hbar/J$ acts as a "relaxation" time τ, and the damping coefficient α_2 is reduced by the factor $\alpha_2\tau = \alpha_2\hbar/J$. This is known as the "exchange narrowing".

It is worth noting the role played by the relaxation (damping, friction, loss, dissipation) coefficient α_2 in the Bloch equations and, equivalently, in the associated equations of motion of the harmonic oscillator. According to equation (8.51) of the harmonic oscillator, $H(t)\dot{M}_x$ is the energy spent by the external field $H(t)$ (directed along the x-axis) per unit time and unit volume to produce the magnetization (it corresponds to the mechanical work done per unit time by an external force upon a harmonic oscillator); according to equation (8.51), its average is equal to $\alpha_2\dot{M}_x^2/\omega_0\omega_m$, *i.e.* it is lost by processes governed by the damping coefficient α_2; for instance, internal magnetic interactions, which eventually lead to heat. According to equation (8.59), the energy absorption process consists of quantum transitions which absorb and release energy, with different amplitudes (rates), such that we have a net absorption, identical with that corresponding to the harmonic oscillator. It is worth noting that the energy of the magnetic field generated by the induced magnetization in the quasi-

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[7] H. C. Torrey, "Bloch equations with diffusion terms", Phys. Rev. **104** 563 (1956).

[8] N. Bloembergen, E. M. Purcell and R. V. Pound, "Relaxation effects in nuclear magnetic resonance absorption", Phys. Rev. **73** 679 (1948).

static approximation does not enter the energy balance; it is a static energy, like, for instance, the electrostatic energy of a charge; if the energy radiated by the electromagnetic field generated by the induced magnetization is taken into account (for high frequencies), then the equations of the relativistic quantum fields must be considered.

It is also worth noting that dissipation, governed by the relaxation coefficient α_2, is essential for maintaining the thermal equilibrium in the absorption and emission processes; if the dissipation is low, the energy pumped from the outside may generate an inversion of population and an amplified emission of coherent radiation, *i.e.* a maser or a laser.

8.6 Hyperfine splitting

The electronic energy levels in atoms (ions) are split by the fine interaction originating in relativistic effects. The aditional interaction of the electrons with the nucleus is the hyperfine interaction. It originates in the magnetic field generated by the electron and acting upon the nucleus, and in the electron motion, on one side, and, on the other, in the magnetic field (and electric field) generated by the nucleus and acting upon the electrons. The magnetic field of the electron is produced by the electronic orbital and spin currents. The orbital currents give a weak field, because they are away from the nucleus; but the spin current for zero orbital momentum (s state) is located just on the nucleus; this is the contact hyperfine interaction.

An electron is localized over its Compton length $\lambda = \hbar/mc$ ($3.8 \times 10^{-11} cm$); it produces a magnetic moment $\mu_B = \frac{|e|}{2c} c\lambda = \frac{|e|\hbar}{2mc}$, which is the Bohr magneton. The current is $I = |e|\, c/\lambda$; it produces a magnetic field $H = I/c\lambda = |e|/\lambda^2$; the nucleus sees the fraction $|\psi(0)|^2 \lambda^3$ of the electron, where ψ is the electron wavefunction; the effective magnetic field is $H = |e| |\psi(0)|^2 \lambda \simeq \mu_B |\psi(0)|^2$. The corresponding Zeeman energy is $U = -\mu H = -\mu\mu_B |\psi(0)|^2$ or, since the magnetic moment of the nucleus is $\mu = \gamma\hbar I$ and the electron field is oriented with respect to the spin S, $U \simeq -\gamma\hbar\mu_B |\psi(0)|^2 \mathbf{IS}$, where $\mathbf{I}$ is the nuclear spin and $\mathbf{S}$ is the electron spin; we can see that $\mu_B |\psi(0)|^2$ is a magnetic field, $\gamma\mu_B |\psi(0)|^2$ is a frequency and $a = \gamma\hbar\mu_B |\psi(0)|^2$ is an energy; the contact hyperfine interaction is written as $U = -a\mathbf{IS}$. For hydrogen, for instance, $a \simeq 500Gs$, corresponding to $\simeq 1420MHz$ ($|\gamma|\, a/2\pi$, where $\gamma = -1.8 \times 10^7 s^{-1} Gs^{-1}$ is the gyromagnetic factor of the electron). This is seen in the radiofrequency line of the interstellar (atomic) hydrogen.

The fine splitting corresponds to $S_z = \pm 1/2$; the hyperfine interaction splits each of the two $S_z = \pm 1/2$ levels into other I_z levels; for instance, for $I = 1/2$, we have the levels $S_z = 1/2$, $I = \pm 1/2$ and $S_z = -1/2$, $I_z = \pm 1/2$.

A missing negative ion in alkali halides may leave behind a trapped electron; this is a colour center (F center); the electron interacts hyperfinely with the neighbouring ions, leading to many split levels; the corresponding transitions can be seen in magnetic resonance, which, this time, is called paramagnetic resonance (or electron spin resonance). Similarly, a donor atom, like phosphorus in silicon, exhibits a paramagnetic electron, whose spin levels are split by the hyperfine interaction with the surrounding atoms. The transitions can be seen in spin (paramagnetic) resonance (together with motional narrowing).

In metals, the conduction electrons can give rise to a hyperfine interaction $-aI_z\overline{S}_z$, so that, the nuclear momentum sees an energy $-\gamma\hbar H_0 I_z - a\overline{S}_z I_z$, where H_0 is the external field and S_z is the electron spin component oriented along the z-axis; the average value $\overline{S}_z$ is related to the external field by Pauli spin magnetization $M_z = gN\mu_B\overline{S}_z = \chi_s H_0$, where N is the number of electrons; it follows the Zeeman energy $-\gamma\hbar H_0 I_z - a\overline{S}_z I_z = -\gamma\hbar(1 + a\chi_s/g\gamma\hbar N\mu_B)I_z H_0$; we can see that the external field suffers a shift $\Delta H_0/H_0 = a\chi_s/g\gamma\hbar N\mu_B$ due to the hyperfine coupling of the nuclear momentum with the spin of the conduction electrons. This is known as the Knight shift.[9] The interaction of the nuclear spin with induced electron orbital moment gives rise to another frequency shift, known as chemical shift.[10]

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[9] C. W. Townes, C. Herring and W. D. Knight, "The effect of electronic paramagnetism on nuclear magnetic resonance frequencies in metals", Phys. Rev. **77** 852 (1950).

[10] N. F. Ramsey, "Magnetic shielding of nuclei", Phys. Rev. **78** 699 (1950); "Chemical effects in nuclear magnetic resonance and in diamagnetic susceptibility", Phys. Rev. **86** 243 (1952).

8.7 Ferromagnetic resonance

The magnetization of a ferromagnet can be aligned by a static external field and a transverse (usually large) magnetization can be induced by an external radiofrequency (microwaves) field to precess about the aligned magnetization. Very often, magnons are generated before reaching a regular precession. The exchange interaction may narrow appreciably the resonance line; the (de-) magnetization factors should be taken into account, since the magnetization is large.[11]

The exchange interaction between spins should be included in the Bloch equations, especially in thin ferromagnetic films; this interaction acts as a local field which implies the spatial derivatives of the magnetization, so it is convenient to use spatial Fourier transforms; the wavevector is related to the thickness of the film.[12]

Similarly, magnetic resonance can be seen in antiferromagnets, or in other magnetic structures;[13] in all cases the local fields must be carefully estimated.

8.8 Quasi-classical dynamics

The relevant quantities in condensed matter are average (mean) values taken over quantum states, statistical assemblies, or coarse-graining averages; such quantities are the only measurable ones. In the equations of motion (8.37) of the quantum-mechanical operator of the magnetic moment in the presence of an external magnetic field $(H_0\mathbf{e}_z + H(t)\mathbf{e}_x)$ it is posible to take such averages, since these equations are linear and self-contained; this way, we get the Bloch equations (8.42)-(8.44), which are classical equations of motion. They lead to the same description of the magnetic resonance as the quantum-transitions treatment.

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[11] C. Kittel, "Interpretation of anomalous Larmor frequencies in ferromagnetic resonance experiment", Phys. Rev. **71** 270 (1947); "On the theory of ferromagnetic resonance absorption", Phys. Rev. **73** 155 (1948).

[12] C. Kittel, "Excitation of spin waves in a ferromagnet by a uniform rf field", Phys. Rev. **110** 1295 (1958).

[13] C. Kittel, "Theory of antiferromagnetic resonance", Phys. Rev. **82** 565 (1951).

It may happen that the structure of the quantum states of the magnetic moment (spin) is not governed by an external field, as H_0 in the case of the NMR, but it is produced by local interactions of the magnetic moments with their environment. For instance, the hyperfine interaction acts in the case of paramagnetic (spin) resonance, the quadrupole interaction determines the nuclear quadrupole resonance (NQR), etc. In such cases the direct application of the averages technique is not useful in the equations of motion of the magnetic moment, since these equations depend also on external degrees of freedom, or they include a non-linear dependence. We are left, of course, with the quantum transitions approach to such magnetic resonance cases. However, the quantum nature of the condensed matter has certain particularities, which may allow a quasi-classical description.

Indeed, in normal condensed matter the wavefunctions and energy levels have a limited validity, due, on one side, to the large number of states densely distributed in energy, to the natural uncertainties arising from internal, residual interactions and, on the other side, to the inevitable interaction with the external world, which makes practically impossible the preparation of a pure quantum state. In fact, mixed states described by the density matrix, or thermodynamic states described by the statistical matrix are appropriate for condensed matter, exhibiting, to a large extent, a classical behaviour. These particularities provide also the basis for a quasi-classical dynamics in some cases in condensed matter. (This is true for usual conditions, which define a "normal" condensed matter. At low temperatures, we may encounter quantum states for condensed matter, like superfluidity, superconductivity, ferromagnetism, etc).

Let us consider a sample of condensed matter consisting of atomic constituents (not necessarily identical), like atoms, ions, molecules, spins, magnetic moments, etc (at rest, as in solids, or in motion as in liquids, gases, etc). As independent entities, each of these atomic constituents has its own (quantum) dynamics, defined by stationary states and energy levels. Some of these states may be degenerate, as, for instance, the spin states associated with various spatial orientations of the spin (the spatial degeneracy). The local interaction occurring in condensed matter, between these atomic constituents, or between them and their environment lead to changes in these quantum states, or to generation of new quantum states, as, for instance, those occurring by the removal of the degeneracies; such interactions split (and shift) the energy levels, with respect to the quantum number m. Let us consider a collection of N such "quatum systems" labelled by $i = 1, 2...N$, each with a set of quantum states labelled by quantum numbers n_i and energy ε_{n_i}, such as the total energy of the collection is $E_n = \varepsilon_{n_1} + \varepsilon_{n_2} + ... + \varepsilon_{n_N}$; it is convenient to denote the states of the collection by $n = (n_1, n_2, ...n_N)$. Now we see that another energy $E_{n'}$ is obtained by changing at least by a unity at least one of the quantum numbers n_i, for instance $E_{n'} = \varepsilon_{n_1} + ... + \varepsilon_{n'_i} + ... + \varepsilon_{n_N}$, where $n'_i = n_i \pm 1$. Such a change implies a small difference in energy, $E_{n'} - E_n$ in comparison with the energies $E_{n,n'}$, providing $N \gg 1$. If the dynamics is such as the change in energy proceeds in time Δt, then $E_{n'} - E_n$ is of the order $\hbar/\Delta t$, where $\hbar$ is Planck's constant. This indicates a change in the mechanical action of the order $\hbar$, which is much smaller that the mechanical action associated to the whole set of N systems. Consequently, we may adopt a quasi-classical description for the dynamics of the assembly of N systems. Moreover, we may take such assemblies in the vicinity of any position in the sample, and take the average of the physical quantities over such coarse-graining structures; the number N of systems in each assembly is much larger than unity, but still sufficiently small at the macroscopic scale as to allow the definition of a coarse-graining averaged model (possibly continuous) for the macroscopic sample. The physical quantities defined in this manner are classical quantities which obey a (quasi-) classical dynamics.

As it is well known, the equation of motion for an operator O reads $\dot{O} = \frac{i}{\hbar}[H, O]$, or $\dot{O}_{mn} = \frac{i}{\hbar}(E_m - E_n)O_{mn} = i\omega_{mn}O_{mn}$, where H is the hamiltonian, E_n, E_m are the energies of the states n and, respectively, m and $\omega_{mn} = (E_m - E_n)/\hbar$ is the frequency of transition between the states n and m. In the quasi-classical approximation the quantum states are sufficiently dense to approximate the frequency ω_{mn} by $\omega_{mn} \simeq -s(\partial E_m/\partial m)_m = -\omega_s$, where $n = m + s$ and E_m depends slightly on m; this amounts to a quasi-classical motion which implies a mechanical action much greater than $\hbar$. Similarly, for a set of quantum states sufficiently dense the matrix elements $O_{mn} = O_{m,m+s}$ depend slightly on s for small s, and vanish rapidly for greater s, so that we may write $O_{mn} = O_{m,m+s} \simeq O_s$; in fact, O_s is the temporal Fourier transform of O, corresponding to the frequency ω_s;[14] we may drop out the label s of the O_s, and we may add an external force, as represented by a hamiltonian h, in general time-dependent; the equation of motion becomes $\dot{O} = -i\omega_s O + (\partial O^{cl}/\partial t)_{cl;h}$, where the last term means the time derivative of the classical counterpart O^{cl} of O, as given by h, according to the classical motion. With $O = O^{(1)} + iO^{(2)}$, we get $\dot{O}^{(1)} = \omega_s O^{(2)} + (\partial O^{cl}/\partial t)_{cl;h}$, $\dot{O}^{(2)} = -\omega_s O^{(1)}$ (since the classical quantity $(\partial O^{cl}/\partial t)_{cl;h}$ is real); we get $\ddot{O}^{(1)} + \omega_s^2 O^{(1)} = (\partial/\partial t)(\partial O^{cl}/\partial t)_{cl;h}$. Here $O^{(1)}$ is that part of the classical quantity O which depend on the time through h; since h is usually a smal perturbation, $O^{(1)}$ may be neglected in O^{cl} (if present). Leaving aside the superscript (1) in $O^{(1)}$ we can write the quasi-classical equation of motion[15]

$$\ddot{O} + \omega_s^2 O = (\partial/\partial t)(\partial O^{cl}/\partial t)_{cl;h} \; ; \tag{8.71}$$

this is the equation of motion of a classical harmonic oscillator subjected to the action of a generalized classical force $f =$ $= -(\partial/\partial t)(\partial O^{cl}/\partial t)_{cl;h}$; its eigenfrequency ω_s is the quantum transition frequency ω_{mn} in the quasi-classical approximation. Since the quasi-classical approximation is valid for a wavepacket,[16] we may also introduce a lifetime α^{-1} given by a damping term $\alpha\dot{O}$ in equation (8.71) (for convenience we take $2\alpha\dot{O}$). The quasi-classical approximation is valid for a slow time dependence.[17]

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[14] The average of O with the wavefunction $\psi = \sum_n c_n \varphi_n e^{-i\omega_n t}$ is $\overline{O} = \sum_{mn} c_m^* c_n O_{mn} e^{i\omega_{mn} t} = \sum_{ms} c_m^* c_{m+s} O_{m,m+s} e^{-i\omega_s t}$, which is approximately $\overline{O} \simeq \sum_m |c_m|^2 \sum_s O_s e^{-i\omega_s t} \simeq \sum_s O_s e^{-i\omega_s t}$; $O_s(t) = O_s e^{-i\omega_s t}$ is the time-dependent operator in the quasi-classical equation of motion (8.71).

[15] The general solution for $O^{(1)}$ from the homogeneous version of equation (8.71) is $O^{(1)} = A\cos(\omega_s t + \delta)$, where A is amplitude and δ is a phase, both undetermined; from $\dot{O}^{(2)} = -\omega_s O^{(1)}$, we get $O^{(2)} = -A\sin(\omega_s t + \delta)$, and $O = O^{(1)} + iO^{(2)} = Ae^{-i(\omega_s t + \delta)}$, as expected; the latter ($\sim e^{-i\omega_s t}$, or $e^{i\omega_s t}$) is the quantum version (in the quasi-classical approximation), while the former ($\sim \cos\omega_s t$, or $\sin\omega_s t$) is the classical version of the same quantity.

[16] P. Debye, "Wellenmechanik und Korespondenzprinzip", Phys. Z. **28** 170 (1927); C. G. Darwin, "Free motion in the Wave Mechanics", Proc. Roy. Soc. London **A117** 258 (1927).

[17] Harmonic-oscillator equations in the dispersion theory marked the beginning of the Quantum Mechnaics: H. A. Kramers and W. Heisenberg, "Uber die

For a standard dynamics of a particle with the coordinate q, momentum p and mass m, we have $\dot{q} = -i\omega_s q + p/m$, $\dot{q}^{(1)} = \omega_s q^{(2)} + p/m$, $\dot{q}^{(2)} = -\omega_s q^{(1)}$ and $\ddot{q}^{(1)} = -\omega_s^2 q^{(1)} - (1/m)\partial h/\partial q$, where we note the occurrence of the force $\partial h/\partial q$ produced by h.

If the perturbation hamiltonian is given by $h = -\overrightarrow{\mu}\mathbf{H}\cos\omega t$, where $\overrightarrow{\mu}$ is the (quasi-) classical magnetic moment (obtained by the corrresponding coarse-graining average) the quasi-classical dynamics for a frequency $\omega_s = \omega_0$ (which is a non-standard dynamics; there is no classical hamiltonian) is governed by the quasi-classical equations of motion

$$\dot{\overrightarrow{\mu}} = -i\omega_0\overrightarrow{\mu} + \gamma\overrightarrow{\mu^{cl}} \times \mathbf{H}\cos\omega t \ , \tag{8.72}$$

where γ is the gyromagnetic factor; in this equation $\overrightarrow{\mu}$ is the magnetic moment generated by the hamiltonian h (magnetic field $\mathbf{H}\cos\omega t$, particular solution) and $\overrightarrow{\mu^{cl}}$ may have a non-vanishing part $\overrightarrow{\mu_0}$ generated by the statistical distribution over the states whose energies are denoted $\hbar\omega(m)$ ($\hbar\omega_0$ is one of the differences $\hbar\omega(m^{'}) - \hbar\omega(m)$, according to the selection rules); these $\overrightarrow{\mu_0}$ contributions are retained in $\overrightarrow{\mu^{cl}}$. Equations (8.72) for the real part of the moment $\overrightarrow{\mu}$ become

$$\ddot{\overrightarrow{\mu}} + \omega_0^2\overrightarrow{\mu} = -\gamma\omega\overrightarrow{\mu_0} \times \mathbf{H}\sin\omega t \ . \tag{8.73}$$

We may assume that the thermal average of the magnetic moment is vanishing in the absence of the interaction,

$$\overline{\overrightarrow{\mu_0}} = \sum\overrightarrow{\mu_0}e^{-\beta H}/\sum e^{-\beta H} \ , \tag{8.74}$$

where $\beta = 1/T$ is the inverse of the temperature T. In the presence of the interaction which produces the energy levels $\hbar\omega(m)$ the mean value of the magnetic moment is

$$\overline{\overrightarrow{\mu_0}} = \sum\overrightarrow{\mu_0}e^{-\beta H-\beta\hbar\omega(m)}/\sum e^{-\beta H-\beta\hbar\omega(m)} \simeq -\beta\hbar\overline{\overrightarrow{\mu_0}\omega(m)} \ , \tag{8.75}$$

for $\beta\hbar\omega(m) \ll 1$; it is differences of the type $\hbar\omega(m^{'}) - \hbar\omega(m)$ which matters in this mean value, so we may write conveniently $\overline{\overrightarrow{\mu_0}\omega(m)} =$

Streuung von Strahlen durch Atome", Z. Phys. **31** 681 (1925); W. Heisenberg, "Uber quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen", Z. Phys. **33** 879 (1925).

$\mathbf{c}\mu\omega_0$, where $\mathbf{c}$ is an undetermined numerical vectorial coefficient directed along the mean magnetization (magnetic moment $\overrightarrow{\mu_0}$) and μ is the magnetic moment. Now, equations (8.73) can be written for magnetization (including damping) as

$$\ddot{\mathbf{M}}+\omega_0^2\mathbf{M}+2\alpha\dot{\mathbf{M}}=\omega\omega_m\mathbf{c}\times\mathbf{H}\sin\omega t \ \ , \tag{8.76}$$

where $\omega_m=\gamma n\mu(\hbar\omega_0/T)$, n being the density of magnetic moments; $\mathbf{M}_0=n\beta\hbar\mu\omega_0\mathbf{c}=(\omega_m/\gamma)\mathbf{c}$ is a static magnetization. We can see that the situation is very much similar with the NMR ; in fact, the classical equations (8.76) apply also to the NMR. We note also the occurrence of the vector $\mathbf{c}$, which indicates the anisotropy of the magnetization. The (particular) solution of equations (8.76) is

$$\mathbf{M}=\mathbf{c}\times\mathbf{H}(a\sin\omega t+b\cos\omega t) \ \ , \tag{8.77}$$

where

$$a=-\frac{1}{2}\omega_m\frac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha^2} \ , \ b=-\frac{1}{2}\omega_m\frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \tag{8.78}$$

(for ω near the resonance frequency ω_0); the absorbed (mean) power (per unit volume) is given by

$$\begin{split}P=\overline{(\mathbf{c}\times\mathbf{H})\dot{\mathbf{M}}\sin\omega t}=-\tfrac{1}{2}\omega_0 b(\mathbf{c}\times\mathbf{H})^2=\\=\tfrac{1}{4}\omega_m\omega_0(\mathbf{c}\times\mathbf{H})^2\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ .\end{split} \tag{8.79}$$

The magnetization induced by the external field $\mathbf{H}\cos\omega t$ performs a rotation about $\mathbf{H}$ in the plane perpendicular to $\mathbf{H}$ and $\mathbf{c}$ with the angular frequency ω. The power computed by means of the quantum transitions of the interaction hamiltonian $H_{int}(t)=-\overrightarrow{\mu}\mathbf{H}\cos\omega t$ ($H_{int}=-\overrightarrow{\mu}\mathbf{H}$) coincides with the absorbed power given by equation (8.79), providing the numerical vector $\mathbf{c}$ is determined from the matrix elements of the magnetic moment $\overrightarrow{\mu}$ (the thermal average of the transition rate being taken into account). We emphasize again that the considerations made above assume the thermal equilibrium, which requires times longer than the damping (relaxation) times; for short pulses of the external field the magnetization suffers a sudden zenithal oscillation and precession; the mean value can be computed by means of the perturbation theory; it is of the order $n\mu$ multiplied by a reduction factor $|H_{int}|/\hbar\Delta\omega \simeq \gamma H/\Delta\omega$, where $\Delta\omega$ is the bandwidth generated by the pulse (the inverse of the duration of the pulse); this estimation may be taken as M_0 in the damped free-oscillation solution of the harmonic oscillator equation.

8.9 Electric dipole and quadrupole moments

With usual notations the scalar electromagnetic potential is given by Kirchhoff's solution

$$\Phi(\mathbf{r},t) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}', t - |\mathbf{r}-\mathbf{r}'|/c)}{|\mathbf{r}-\mathbf{r}'|} \ , \tag{8.80}$$

where ρ is the charge density (and c denotes the speed of light); it is a particular solution of the wave equation

$$\frac{1}{c^2}\frac{\partial^2\Phi}{\partial t^2} - \Delta\Phi = 4\pi\rho \ . \tag{8.81}$$

In matter charges perform a finite motion, so we can average equation (8.81) over this motion and get the static equation

$$\Delta\Phi = -4\pi\rho \tag{8.82}$$

and the Coulomb potential

$$\Phi(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ ; \tag{8.83}$$

in this limit the electric field is given by

$$\mathbf{E} = -grad\Phi = \int d\mathbf{r}' \frac{\rho(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \ . \tag{8.84}$$

Similar results are obtained in the quasi-static limit, where the wavelengths are much larger than the relevant distances.

Let us consider a classical point charge q placed at $\mathbf{r}_0$; the potential becomes

$$\Phi = \frac{q}{|\mathbf{r}-\mathbf{r}_0|} = \frac{q}{r} + \frac{q\mathbf{r}_0\mathbf{r}}{r^3} + \frac{1}{2}qx_{0i}x_{0j}\frac{3x_ix_j - r^2\delta_{ij}}{r^5} + ... \ , \tag{8.85}$$

where we have expanded in powers of x_{0i} ($r \gg r_0$) (and summation over repeated indices is included). We may also sum over several charges (the extension to continuous charge distributions is straightforward). The first term $\Phi_0 = q/r$ is the Coulomb law, the second term

$$\Phi_1 = \frac{q\mathbf{r}_0\mathbf{r}}{r^3} = \frac{\mathbf{dr}}{r^3} \ , \ \mathbf{d} = q\mathbf{r}_0 \tag{8.86}$$

is the dipole contribution, the third term

$$\Phi_2 = \frac{1}{2}qx_{0i}x_{0j}\frac{3x_ix_j - r^2\delta_{ij}}{r^5} \tag{8.87}$$

is the quadrupole contribution; $\mathbf{d} = q\mathbf{r}_0$ is the dipole moment, its electric field is

$$\mathbf{E}_1 = -grad\frac{\mathbf{dr}}{r^3} = \frac{3(\mathbf{dr})\mathbf{r} - r^2\mathbf{d}}{r^5} \ . \tag{8.88}$$

Since

$$\Delta\frac{1}{r} = \delta_{ij}\frac{3x_ix_j - r^2\delta_{ij}}{r^5} = 0 \ , \tag{8.89}$$

we can write the quadrupole contribution as

$$\begin{aligned} \Phi_2 &= \tfrac{1}{6}q(3x_{0i}x_{0j} - r_0^2\delta_{ij})\tfrac{3x_ix_j - r^2\delta_{ij}}{r^5} = \\ &= \tfrac{1}{2}q(3x_{0i}x_{0j} - r_0^2\delta_{ij})\tfrac{x_ix_j}{r^5} = \tfrac{1}{2}D_{ij}\tfrac{x_ix_j}{r^5} \ , \end{aligned} \tag{8.90}$$

where

$$D_{ij} = q(3x_{0i}x_{0j} - r_0^2\delta_{ij}) \tag{8.91}$$

is the quadrupole moment; it is a traceless tensor with five independent components. The quadrupole electric field is given by

$$E_{2i} = \frac{3}{2}D_{ij}\frac{x_j}{r^5} \ . \tag{8.92}$$

The quadrupole moment can be brought to its principal axes; since it is traceless, only two diagonal components are independent. If the charge distribution is symmetric around the z-axis, we have

$$D_{xx} = D_{yy} = -\frac{1}{2} D_{zz} \tag{8.93}$$

and

$$\Phi_2 = \frac{1}{4r^3} D (3\cos^2\theta - 1) = \frac{1}{2r^3} D P_2(\cos\theta) \ , \tag{8.94}$$

where θ is the angle between $\mathbf{r}$ and the z-axis, $D = D_{zz}$ and P_2 is the Legendre polynomial of the 2nd order.

If the total charge is zero, the dipole moment does not depend on the origin of coordinates; if the total charge and the dipole moment are zero, the quadrupole moment does not depend on the origin of coordinates.

In general, we have the expansion

$$\begin{gathered} \tfrac{1}{|\mathbf{r}-\mathbf{r}_0|} = \textstyle\sum_{l=0}^{\infty} \tfrac{r_0^l}{r^{l+1}} P_l(\cos\Theta) = \\ = \textstyle\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \tfrac{r_0^l}{r^{l+1}} \tfrac{4\pi}{2l+1} Y_{lm}(\theta_0, \varphi_0) Y^*_{lm}(\theta, \varphi) \end{gathered} \tag{8.95}$$

in spherical functions, which allows the representation

$$\Phi = \sum_{lm} \sqrt{\frac{4\pi}{2l+1}} \frac{1}{r^{l+1}} Q_{lm} Y^*_{lm}(\theta, \varphi) \ , \tag{8.96}$$

where

$$Q_{lm} = \sqrt{\frac{4\pi}{2l+1}} \sum_a q_a r_a^l Y_{lm}(\theta_a, \varphi_a) \tag{8.97}$$

is the electric moment of the 2^l-th order; it includes summation over all charges a. We have

$$\begin{gathered} Q_{00} = \textstyle\sum_a q_a \ , \ Q_{10} = i \sum_a q_a r_a \cos\theta_a = i d_z \ , \\ Q_{1\pm1} = \mp \tfrac{i}{\sqrt{2}} \textstyle\sum_a q_a r_a \sin\theta_a e^{\pm i\varphi_a} = \mp \tfrac{i}{\sqrt{2}} (d_x \pm i d_y) \end{gathered} \tag{8.98}$$

and

$$Q_{20} = \tfrac{1}{2}\sum_a q_a r_a^2 (1 - 3\cos^2\theta_a) = -\tfrac{1}{2} D_{zz} \ ,$$

$$Q_{2\pm1} = \pm\sqrt{\tfrac{3}{2}}\sum_a q_a r_a^2 \cos\theta_a \sin\theta_a e^{\pm i\varphi_a} =$$

$$= \pm\tfrac{1}{\sqrt{6}}(D_{xz} \pm iD_{yz}) \ , \tag{8.99}$$

$$Q_{2\pm2} = -\tfrac{1}{2}\sqrt{\tfrac{3}{2}}\sum_a q_a r_a^2 \sin^2\theta_a e^{\pm 2i\varphi_a} =$$

$$= -\tfrac{1}{2\sqrt{6}}(D_{xx} - D_{yy} \pm 2iD_{xy}) \ .$$

Let us assume that a charge distribution is placed in an external field with scalar potential Φ; the energy of the charge distribution in this external field is given by

$$U = \sum_a q_a \Phi(\mathbf{r}_a) \ . \tag{8.100}$$

We may expand $\Phi(\mathbf{r}_a)$ in powers of the coordinates x_{ai},

$$U = U_0 + U_1 + U_2 + \ , \tag{8.101}$$

where

$$U_0 = \Phi_0 \sum_a q_a \ \ , \tag{8.102}$$

$$U_1 = grad\Phi_0 \sum_a q_a \mathbf{r}_a = -\mathbf{d}\mathbf{E}_0 \tag{8.103}$$

and U_2 is the quadrupole contribution. The suffix 0 denotes the origin (around which the distribution is placed), $\mathbf{d}$ is the dipole moment and $\mathbf{E}_0$ is the electric field at the origin. Up to the first-order approximation the force acting upon the charge distribution is given by

$$\mathbf{F} = \mathbf{E}_0 \sum_a q_a + (\mathbf{d}grad)\ \mathbf{E}|_0 + ... \tag{8.104}$$

and the torque is given by

$$\mathbf{K} = \sum_a q_a \mathbf{r}_a \times \mathbf{E}_0 = \mathbf{d} \times \mathbf{E}_0 \ . \tag{8.105}$$

The rotation of a rigid dipole $d = ql$ under the action of the torque of forces given by equation (8.105) implies the motion of the angular momentum $L = mvl$, $d\mathbf{L}/dt = \mathbf{K} = \mathbf{d} \times \mathbf{E}_0$. If we leave aside the azimuthal motion, the equation of motion is $ml^2\ddot{\theta} = -qlE_0 \sin\theta$, where θ is the angle between $\mathbf{d}$ and $\mathbf{E}_0$; for small angles θ and a constant field, this is the equation of motion of a harmonic oscillator with frequency $\omega = \sqrt{qE_0/ml} = \sqrt{dE_0/I}$, where $I = ml^2$ is the moment of inertia; the quantum counterpart reads $I\omega^2 = \omega L = dE_0$ $(L = I\omega)$ and $\omega = dE/\hbar$, where $\hbar$ is Planck's constant; such a frequency is known as the Rabi frequency.[18]

The energy of a dipole in the field generated by another dipole is

$$U = -\mathbf{d}_1\mathbf{E}_2 = \frac{(\mathbf{d}_1\mathbf{d}_2)r^2 - 3(\mathbf{d}_1\mathbf{r})(\mathbf{d}_2\mathbf{r})}{r^5} \ , \tag{8.106}$$

where we have used the dipole field given by equation (8.88). Similarly, for a charge q in the field of a dipole we have the energy

$$U = q\frac{\mathbf{dr}}{r^3} \ . \tag{8.107}$$

The quadrupole contribution to the interaction energy is

$$\begin{aligned} U_2 = \tfrac{1}{2}\sum\nolimits_a q_a x_{ai} x_{aj} \tfrac{\partial^2\Phi_0}{\partial x_i \partial x_j} = \tfrac{1}{2}\sum\nolimits_a q_a (x_{ai}x_{aj} - \\ -\tfrac{1}{3}\delta_{ij} r_a^2) \tfrac{\partial^2\Phi_0}{\partial x_i \partial x_j} = \tfrac{1}{6} D_{ij} \tfrac{\partial^2\Phi_0}{\partial x_i \partial x_j} \ . \end{aligned} \tag{8.108}$$

In general, since

$$\Phi(\mathbf{r}_a) = \sum_{lm} r^l \sqrt{\frac{4\pi}{2l+1}} a_{lm} Y_{lm}(\theta_a, \varphi_a) \tag{8.109}$$

we get

$$U = \sum_a q_a \Phi(\mathbf{r}_a) = \sum_{lm} a_{lm} Q_{lm} \ , \tag{8.110}$$

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[18] I. I. Rabi, "On the process of space quantization", Phys. Rev. **49** 324 (1936); I. I. Rabi, "Space quantization in a gyrating magnetic field", Phys. Rev. **51** 652 (1937).

where Q_{lm} is the moment given by equation (8.97) and a_{lm} are the coefficients of the expansion of the potential in spherical harmonics.

The wavefunctions may have a definite parity; then, the average of the dipole momentum over such a wavefunction is zero. Atoms in stationary states have not a dipole electric moment (except for excited hydrogen, or hydrogen-like excited atoms). The dipole moment has non-zero matrix elements only between states of different parity. Usually, in molecules this is not true, the molecules may have a nonvanishing dipole electric moment (polar molecules).

The quadrupole moment associated with the electrons in atom should be averaged over the electron motion. The resulting quantity can be expressed in terms of the total angular momentum **J** of the electrons (the only vector available for the atom); it is easy to see that we should have

$$Q_{ij} = \frac{3Q}{2J(2J-1)}(J_i J_j + J_j J_i - \frac{2}{3}\delta_{ij}J^2) \ , \tag{8.111}$$

where the distinction between D_{ij} and Q_{ij} is superfluous (as a result of the averaging) and the pre-factor in equation (8.111) has been chosen for convenience: we have

$$Q_{zz} = \frac{3Q}{J(2J-1)}[M^2 - \frac{1}{3}J(J+1)] \ , \tag{8.112}$$

where M is the quantum number of J_z, and $Q_{zz}(M = J) = Q$ (maximum value). In addition, we can see that $Q_{ij} = 0$ for $J = 0$ or $J = 1/2$, as expected. If the spin-orbit interaction can be neglected, a similar representation holds for Q_{ij} in terms of the angular momentum **L** of the electrons.

The moments described above are permanent electric moments. In the presence of an external elctric field $\mathbf{E}_0$ we can compute the perturbation-theory contribution to the energy of an atom (Stark effect), for an interaction energy $-\mathbf{d}\mathbf{E}_0$. Usually, since the diagonal matrix elements of **d** are zero we have a contribution $\mathcal{E} = -(1/2)\alpha_{ij}E_{01}E_{0j}$ of the second-order of the perturbation theory (for hydrogen there is a linear contribution), so we have an induced dipole moment $d_i = -\partial\mathcal{E}/\partial E_{0i} = \alpha_{ij}E_{0j}$; α_{ij} is called the polarizability tensor. Typical values of atomic (or molecular) polarizabilities are of the order of the volume of the charge distribution. It is worth noting that we can also compute the contributions of the interaction energy $(1/6)Q_{ij}\partial^2\Phi_0/\partial x_i\partial x_j$, where Φ_0 is the scalar potential of the external field (and the derivatives are taken at the origin, where the charge distribution is placed), by means of the perturbation theory; then, we can have contributions linear in the external field (its spatial derivatives).

In general, two neutral charge distributions interact mainly by their dipolar electric fields, which go like $1/r^3$; the main contribution to energy arises in the second-order of the perturbation theory (and is negative), where we get an energy $\Delta E \sim -1/r^6$ and an attractive force $F \sim -1/r^7$; this is known as the van der Waals-London force; the van der Waals energy is of the order of $0.1-0.01eV$ at distances a few times larger than atomic (molecular) distances (at short distances the atoms repel each other). A quadrupole-quadrupole interaction gives an energy $\Delta E \sim 1/r^5$ (in the first order of the perturbation theory). The dipole energy may also occur in the secular equation for two identical atoms, leading to an energy $\Delta E \sim 1/r^3$. Usually, it is of interest the average over all orientations of the angular momenta, so that the van der Waals formula holds (averaging over all orientations results in vanishing all moments; we are left with the second order of the perturbation theory for dipoles as the main contribution). It is worth noting the interaction of an ion, with electric field $\sim 1/r^2$, and the quadrupole of an atom: the energy is $\sim 1/r^3$, which, however, is vanishing by averaging over all directions of the total angular moment; the next-order contribution is a second-order peturbation with respect to the dipole moment, which goes like $1/r^4$; it can be written as $-(1/2)\alpha q^2/r^4$, where α is the polarizability of the atom; this gives an attractive force (which explains the attraction of an electron by neutral atoms, with binding energy in the $1eV$-range; though in fields which go like $-1/r^3$ (or $-1/r^4$) the number of bound states is finite, and it may even be zero).

In general, the vanishing of inter-atomic (molecular) forces at large distances means that they decrease exponentially, since the quantum-mechanical atomic (molecular) charge distribution decreases exponentially at large distances. At large distances we must include the effect of retardation (radiation), which (for dipolar interaction) gives an energy $\Delta E \sim -1/r^7$ and an attractive force $\sim -1/r^8$; this is known as the Casimir force.

In general, the electric and magnetic moments of the nucleus are averaged over nuclear wavefunctions. In stationary states the nuclear dipole momentum is zero, due to the parity conservation. Since the total nuclear charge is non-zero (and since we are interested, in general, in intrinsic nuclear properties) we should eliminate the contribution of the center of mass by replacing the nucleon coordinates $\mathbf{r}_i$ by $\mathbf{r}_i - \mathbf{R}$ and the nucleon momenta $\mathbf{p}_i$ by $\mathbf{p}_i - \mathbf{P}/A$, where $\mathbf{R} = (1/A)(\sum_p \mathbf{r}_p + \sum_n \mathbf{r}_n)$ is the position of the center of mass (summation over protons p and neutrons n) and $\mathbf{P} = AM\mathbf{V}$ is the momentum of the center of mass (M is the nucleon mass and $\mathbf{V}$ is the velocity of the center of mass). In particular cases, like the quadrupole moment, we may use the representation in terms of the total angular momentum, denoted by **I,** which avoids this point (since the nuclear forces depend on spin, the total spin **S** is not conserved - except its magnitude).

Usually, molecules have a vanishing electronic spin; they have also a vanishing electronic orbital moment (in their ground-state). Consequently, their hyperfine splitting of the electronic levels is due to the quadrupole interaction of the nucleus with the electrons (for nuclei with spin $I \neq 0, 1/2$). This interaction is averaged over electronic states and over molecular rotations.

Consider identical nuclear spins I in condensed matter. Usually, in a symmetric environment, the quantum states are degenerate with respect to the quantum number m of the z-component of the spin; I^2 and one component, say, I_z are usually conserved quantities. Consider a local interaction, generated by the environment, usually an electric one. The charge distribution in the nucleus is affected by such an interaction, according to a multipole expansion. In the ground state the nuclear dipoles are vanishing; the next-order interaction is a quadrupole one. If Φ is the electric potential we have, at the position of the nucleus, an interaction

$$\begin{aligned} V = \sum_a q_a \Phi(\mathbf{r}_a) = \sum_a q_a \Phi + \sum_{ai} q_a x_{ai} \frac{\partial \Phi}{\partial x_{ai}} + \\ + \frac{1}{2} \sum_{aij} q_a x_{ai} x_{aj} \frac{\partial^2 \Phi}{\partial x_{ai} \partial x_{aj}} + \dots \ , \end{aligned} \tag{8.113}$$

where x_{ai} are the coordinates of the position vector $\mathbf{r}_a$ of the (proton) charge q_a. The first term in equation (8.113) is the monopole interaction, the second term is the dipole interaction, the third term is the quadrupole interaction; the quadrupole interaction can also be written as

$$\begin{aligned} V_2 &= \tfrac{1}{6}\textstyle\sum_{aij} q_a(3x_{ai}x_{aj} - r_a^2\delta_{ij})\tfrac{\partial^2\Phi}{\partial x_{ai}\partial x_{aj}} = \\ &= -\tfrac{1}{6}\textstyle\sum_{aij} q_a(3x_{ai}x_{aj} - r_a^2\delta_{ij})\tfrac{\partial E_{ai}}{\partial x_{aj}} \ , \end{aligned} \tag{8.114}$$

where $\mathbf{E}_a$ is the electric field acting upon the a-th proton; the derivatives are taken at the position of the nucleus, which is placed at the origin, so that $V_{ij} = \partial E_{ai}/\partial x_{aj}$ do no depend on a; in equation (8.114) the Laplace equation $\Delta\Phi = 0$ has been used; the symmetric tensor

$$D_{ij} = \sum_a q_a(3x_{ai}x_{aj} - r_a^2\delta_{ij}) \tag{8.115}$$

of rank two and vanishing trace is the electric quadrupole moment. If we average over the proton coordinates we get

$$D_{ij} \rightarrow Q_{ij} = \frac{3Q}{2I(2I-1)}(I_iI_j + I_jI_i - \frac{2}{3}I^2\delta_{ij}) \ , \tag{8.116}$$

where I_i is the spin components; the pre-factor in equation (8.116) is chosen such as

$$Q_{zz} = \frac{Q}{I(2I-1)}(3I_z^2 - I^2) = \frac{Q}{I(2I-1)}[3m^2 - I(I+1)] \tag{8.117}$$

and

$$Q_{zz}(m = I) = Q = \sum_a q_a(3z_a^2 - r_a^2) \ , \tag{8.118}$$

where the summation is performed over all coordinates in the quantum state $m = I$ and average is taken over the motion; we can see that the quadrupole moment is zero for spin $I = 0$ and spin $I = 1/2$.

The quadrupole interaction

$$V_2 = \frac{1}{6}\sum_{ij} Q_{ij}V_{ij} \ , \ V_{ij} = \frac{\partial^2\Phi}{\partial x_{ai}\partial x_{aj}} \tag{8.119}$$

removes the degeneracy with respect to the quantum number m, partially or totally. This interaction can also be written as

$$\begin{gathered}V_2=\tfrac{Q}{2I(2I-1)}[(I_x^2-\tfrac{1}{3}I^2)V_{xx}+(I_y^2-\tfrac{1}{3}I^2)V_{yy}+\\+(I_z^2-\tfrac{1}{3}I^2)V_{zz}+\\+(I_xI_y+I_yI_x)V_{xy}+(I_yI_z+I_zI_y)V_{yz}+\\+(I_xI_z+I_zI_x)V_{xz}]\ .\end{gathered}\tag{8.120}$$

By a suitable rotation of the spin $\mathbf{I}$ we can diagonalize the matrix V_{ij} and the quadratic form V_2, which can be written as $V_2=v_xI_x^2+v_yI_y^2+v_zI_z^2$ (up to a constant), with $v_x+v_y+v_z=0$. We can see that for axial symmetry $v_x=v_y$ the interaction is proportional to I_z^2.

8.10 Nuclear quadrupole resonance

The nuclear magnetic moments in solids are affected by the interaction with the surrounding ions, which generate high gradients of electric field. Consequently, a quadrupole interaction V_2 of the form given by equation (8.119) acts on the nuclear magnetic moments. This interaction splits the degeneracy of the energy levels (and shifts the energy levels), such that transitions between such levels may be induced by an external time-dependent magnetic field (the energy levels can depend on the temperature). These transitions have a resonance character, and are known as the nuclear quadrupole resonance (NQR).[19] The resonance frequencies are in the radiofrequency range. The NQR does not appear for nuclear spins $I=0$, $1/2$, which give a vanishing quadrupole moment. The average of the quadrupole interaction with respect to the molecular motion leads to a very weak effective inter-

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[19] W. A. Nierenberg, N. F. Ramsey and S. B. Brody, "Measurements of Nuc1ear Quadrupole Moment Interactions", Phys. Rev. **70** 773 (1946); W. A. Nierenberg and N. F. Ramsey, "The radiofrequency spectra of sodium halides", Phys. Rev. **72** 1075 (1947); H.-G. Dehmelt and H. Kruger, "Kernquadrupolfrequenzen in festen dichlorathylen", Naturwiss. **37** 111 (1950); R. V. Pound, "Nuclear electric quadrupole interactions in crystals", Phys. Rev. **79** 685 (1950).

action in liquids, so that the NQR is not observed in liquids (nor in gases, where the interaction is very weak).

If we estimate the electrostatic energy as Ze^2/r_a, where e is the electron charge, Ze is the nucleus charge and r_a ($10^{-8}cm$) is an atomic scale distance, then the quadrupole interaction is of the order $(Ze^2/r_a)(r_n/r_a)^2$, where r_n is the nuclear radius; for $r_n = 10^{-12}cm$, we get a factor $(r_n/r_a)^2 = 10^{-8}$ for the quadrupole interaction, in comparison with the atomic interaction (the atomic interaction is $Ze^2/r_a \simeq 10^{-11}erg$, corresponding to an ultraviolet frequency $\simeq 10^{15}s^{-1}$; the frequencies associated with the quadrupole interaction are of the order 10^7s^{-1}).

Within the quasi-classical approximation the equations of motion of the magnetization near a given resonance frequency ω_0 are given by equations (8.76), with the solutions (8.77), (8.78) and the absorbed power given by equation (8.79). The numerical vector $\mathbf{c}$ in these equations can be determined from the matrix elements of the magnetic moments with interaction, or by comparing the absorbed power calculated within the quasi-classical approximation with the absorbed power calculated by means of the quantum transition rates.

The quadrupole interaction V_2 exhibits, in general, an anisotropy; its diagonalization, which leads to eigenfreqencies denoted by ω_s in the quasi-classical approximation, defines an ellipsoid (the principal axes of the quadratic form); the external radiofrequency field $\mathbf{H}$ may have an arbitrary orientation with respect to these axes, as expressed by the vectorial product $\mathbf{c} \times \mathbf{H}$ in equation (8.77). If the sample is an amorphous solid, or it is impurified, or it is a powder, etc, an average must be taken over the orientations of the sample, as given by $\overline{\sin^2\theta}$ in the equation for the absorbed power, where θ is the angle between $\mathbf{H}$ and $\mathbf{c}$.

An external, uniform magnetic field H_0 can be applied in NQR experiments; it produces the energy levels $\hbar\omega(m) = \gamma\hbar m H_0$, where m is the quantum number of the z-component of the spin; the spectroscopic line has frequency γH_0 (selection rules $\Delta m = \pm 1$). If the quadrupole interaction is small it can be treated as a perturbation. Making use of $I_\pm = I_x \pm iI_y$ and $I^2 = I_+I_- + I_z^2 - I_z = I_-I_+ + I_z^2 + I_z$ in equation

(8.120), with the matrix elements

$$(I_\pm)_{m\pm1,m} = [(I \mp m)(I \pm m + 1)]^{1/2} \ , \tag{8.121}$$

we get the diagonal term

$$\overline{V}_2 = \frac{Q}{2I(2I-1)}\left[V_{zz} - \frac{1}{2}(V_{xx} + V_{yy})\right] I_z^2 \tag{8.122}$$

(up to a constant), which leads to energy corrections $\sim m^2$. These corrections to the energy levels lead to new spectroscopic lines (a splitting of multiplicity $2I$; for I odd the lines $m = \pm 1/2$ are not affected by V_2); the selection rules $\Delta m = \pm 1$ are enlarged now to higher values of Δm; however, the corresponding lines have a very small intensity.

8.11 Spin echo

The resonance exhibited by the absorbed power in the exciting circuit which produce the external radiofrequency magnetic field can be used to identify magnetic resonances; this is called the continuous wave procedure. The detection of the magnetic field emitted by the sample in magnetic resonance, either by the same exciting coil or by a second, receiving coil, can provide another means for identifying resonances.

Let us asume that at the initial moment $t = 0$ we create a pulse of high radiofrequency magnetic field of duration t_w and (resonance) frequency ω_0; this duration is much longer than the wave period ω_0^{-1}, but shorter than the relaxation (damping) time α^{-1}; $\omega_0^{-1} \ll t_w \ll \alpha^{-1}$ (usually t_w is of the order of a few microseconds, while α^{-1} is of the order $10^{-5} - 10^{-4} s^{-1}$). The role of such a pulse is to generate ("transverse") magnetization (which precesses about the direction of the "longitudinal" magnetization); due to its short duration, the pulse generates also a bandwidth $\Delta\omega$ around ω_0, such as $\Delta\omega \cdot t_w \simeq \pi/2$. Inside the pulse, *i.e.* for $0 < t < t_w$, the solution of the equations of motion for the magnetization (harmonic-oscillator equations) is the general solution of the homogeneous equations plus the particular solution, determined by the initial conditions at $t = 0$. Outside the pulse the solution is the damped free-oscillations solution of the form

$A\cos(\omega_0 t+\delta)e^{-\alpha t}$, where A is the amplitude and δ is a phase, determined from the "initial" conditions at $t=t_w$; this is also called the free-induction solution. Now, let us assume that we create another, identical pulse at time $t=\tau$, much longer than any relevant time ($\tau \gg \alpha^{-1} \gg t_w \gg \omega_0^{-1}$). The solution inside the second pulse ($\tau < t < \tau + t_w$) consists also of the general solution of the homogeneous equation plus the particular solution; the difference is now that the initial magnetization for $t=\tau$ is $A\cos(\omega_0\tau+\delta)e^{-\alpha\tau}$. The pulse enhances this magnetization, so that, at time $t=\tau+t_w$ we have a magnetization of the form $A\cos\omega_0\tau$ (the phase δ may be omitted). This magnetization is the initial condition for the decaying solution which follows the application of the second pulse, *i.e.* for $t>\tau+t_w$; it reads $A\cos\omega_0\tau\cos\omega_0(t-\tau)e^{-\alpha(t-\tau)}$ (where we omitted the small time t_w). It is easy to see that this solution contains a contribution $\sim e^{i\omega_0(t-2\tau)}$, which, integrated over the bandwidth, leads to $\sin[\Delta\omega(t-2\tau)]/(t-2\tau)$; this response exhibits a maximum value for $t=2\tau$; it is called the "spin echo"; its bandwidth is of the order $\Delta\omega\cdot t_w=\pi/2$.[20] The procedure can be repeated with a succession of pulses, which may produce several echoes.

The detection of the signal proceeds by the induced voltage given by $E_{em}=(1/c)S\partial(H_m/\partial t)$, where H_m is the emitted field and S is the cross-sectional area of the receiving coil; the emitted field is approximately $H_m\simeq M(v/d^3)$, where M is the magnetization, v is the sample volume and d is the distance of the receiving coil from the sample; for the echo, the average magnetization is of the from $M\simeq A\sin[\Delta\omega(t-2\tau)]/\Delta\omega(t-2\tau)$, and its time derivative is $\simeq A(\Delta\omega)^2 t_w$; collecting all these data we get the induced voltage $E_{em}\simeq(vS/cd^3)A(\Delta\omega)^2 t_w$, where A is the amplitude of the signal (magnetization) in the free-induction solution $A\cos(\omega_0 t+\delta)e^{-\alpha t}$. Further on, we estimate the amplitude A.

For the NMR the general solution is of the form

$$M=(B\cos\omega_0 t+C\sin\omega_0 t)e^{-\alpha t}+a\cos\omega t+b\sin\omega t \qquad (8.123)$$

for both components of the transverse magnetization, where the coefficients B and C are determined from the initial conditions $M(t=$

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[20] E. L. Hahn, "Spin echoes", Phys. Rev. **80** 580 (1950).

$0) = 0$, $\dot{M}(t = 0) = 0$ and a, b are given by equations (8.50); ω_0 is the eigenfrequency of the oscillator (resonance frequency) and ω is the frequency of the external field $H\cos\omega t$ (directed along the x-axis); α_2 in equations (8.50) is denoted here by α; we get $B + a = 0$, $C\omega_0 + b\omega \simeq 0$ and

$$M = a(\cos\omega t - e^{-\alpha t}\cos\omega_0 t) + b(\sin\omega t - \frac{\omega}{\omega_0}e^{-\alpha t}\sin\omega_0 t) \quad (8.124)$$

valid for $0 < t < t_w$ (inside the first pulse); the amplitude A of the free-induction solution is given by $M(t_w)$, which is approximately $A \simeq b\alpha t_w \sin\omega_0 t_w$, where $b = \omega_m H/2\alpha$, $\omega_m = \gamma M_0$, $M_0 = n\mu^2 H_0/3T$ (it is preferable to have $\omega_0 t_w = (2n+1)\pi/2$, for any integer n). Here, M_0 is the longitudinal magnetization, H_0 is the longitudinal magnetic field and T is the temperature (n being the concentration of the magnetic moments μ). Putting together all these results we get an average induced voltage $E_{em} \simeq (vS/cd^3)\omega_m H(\Delta\omega \cdot t_w)^2 \sin\omega_0 t_w \simeq (vS/cd^3)\omega_m H \sin(\omega_0/\Delta\omega)$.

For the NQR the magnetization is given by (equations (8.77), (8.78))

$$\mathbf{M} = (\mathbf{B}\cos\omega_0 t + \mathbf{C}\sin\omega_0 t)e^{-\alpha t} + \mathbf{f}(a\cos\omega t + b\sin\omega t) \ , \quad (8.125)$$

where $\mathbf{f} = \mathbf{c} \times \mathbf{H}$, with the initial conditions $\mathbf{M}(t = 0) = \mathbf{M}_0$, $\dot{\mathbf{M}}(t = 0) = 0$, $\mathbf{M}_0 = n\hbar\mu\omega_0\mathbf{c}/T = \omega_m\mathbf{c}/\gamma$ (equation (8.75)); we get

$$\begin{gathered}\mathbf{M} = \mathbf{M}_0 e^{-\alpha t}\cos\omega_0 t + \mathbf{f}a(\cos\omega t - e^{-\alpha t}\cos\omega_0 t) + \\ +\mathbf{f}b(\sin\omega t - \tfrac{\omega}{\omega_0}e^{-\alpha t}\sin\omega_0 t)\end{gathered} \quad (8.126)$$

and the amplitude

$$A \simeq M_0\cos\omega_0 t_w + fb\alpha t_w \sin\omega t_w \ ; \quad (8.127)$$

the average induced voltage is

$$\begin{gathered}E_{em} \simeq (vS/cd^3) \mid \mathbf{M}_0\Delta\omega\cos(\omega_0/\Delta\omega) + \\ +(\mathbf{c} \times \mathbf{H})\omega_m \sin(\omega_0/\Delta\omega) \mid \ .\end{gathered} \quad (8.128)$$

These values for the induced voltage are all affected by the decaying factor $e^{-\alpha \cdot 2\tau}$.

It is worth noting that we have assumed here the thermal equilibrium in deriving the magnetization $\mathbf{M}_0$ for the NQR, which implies the thermal reduction factor $\hbar\omega_0/T$; in fact, the assumption $\alpha t_w \ll 1$ indicates that the thermal equilibrium might not be attained; in that case, the magnetization $\mathbf{M}_0$ is governed by the transition rates for short times, and, usually, it is higher than the thermally averaged magnetization; the estimation for the mean value of M_0 gives $n\mu$ multiplied by the reduction factor $|H_{int}| / \hbar\Delta\omega = \gamma H/\Delta\omega$.

9 "Exact" solutions

9.1 A general case

Consider two magnetic fields $\mathbf{H}_0 = (H_0 \sin\alpha,\ 0,\ H_0 \cos\alpha)$ and $\mathbf{H}(t) = (H \cos\omega t,\ 0,\ 0)$, and their hamiltonian of interaction

$$\begin{aligned} H_{int} &= \gamma\hbar\mathbf{J}[\mathbf{H}_0 + \mathbf{H}(t)] = \\ &= \gamma\hbar[J_x(H_0 \sin\alpha + H\cos\omega t) + J_z H_0 \cos\alpha] \ , \end{aligned} \tag{9.1}$$

with a spin $\mathbf{J}$ (γ is a gyromagnetic factor). The field $\mathbf{H}_0$ is constant and oriented along an axis which makes the angle α with the z-axis, while the field $\mathbf{H}(t)$ is a time-dependent field which oscillates with frequency ω along the x-axis. Equation (9.1) gives a time-dependent hamiltonian whose eigenfunctions and eigenvalues depend on the time. In order to solve the equation

$$H_{int}\varphi = E\varphi \ , \tag{9.2}$$

we need the formulae

$$\begin{aligned} e^{i\theta J_y} J_x e^{-i\theta J_y} &= J_x \cos\theta + J_z \sin\theta \ , \\ e^{i\theta J_y} J_z e^{-i\theta J_y} &= J_z \cos\theta - J_x \sin\theta \ ; \end{aligned} \tag{9.3}$$

they are established easily by denoting $C_x = e^{i\theta J_y} J_x e^{-i\theta J_y}$, $C_z = e^{i\theta J_y} J_z e^{-i\theta J_y}$ and noticing that

$$\frac{\partial C_x}{\partial\theta} = C_z \ , \ \frac{\partial C_z}{\partial\theta} = -C_x \ , \tag{9.4}$$

by making use of the commutation relations $[I_i, I_j] = i\varepsilon_{ijk}I_k$ (ε_{ijk} is the completely antisymmetric symbol of rank 3); θ is a parameter (similar rotation relations hold for $e^{i\theta J_x} J_{y,z} e^{-i\theta J_x}$ and $e^{i\theta J_z} J_{x,y} e^{-i\theta J_z}$).

Making use of the transformation $e^{i\theta J_y} H_{int} e^{-i\theta J_y}$ with

$$\tan\theta = \tan\alpha + \frac{H}{H_0\cos\alpha}\cos\omega t \ , \tag{9.5}$$

we get the energy levels

$$E_m = m\lambda \ , \ \lambda = \gamma\hbar(H_0^2 + 2H_0 H\sin\alpha\cos\omega t + \\ + H^2\cos^2\omega t)^{1/2} \ , \ -j \leq m \leq j \tag{9.6}$$

and the eigenfunctions

$$\varphi_m = e^{-i\theta J_y}\varphi_m^0 \ , \tag{9.7}$$

where φ_m^0 are the eigenfunctions of J_z, $J_z\varphi_m^0 = m\varphi_m^0$; it is assumed that $H_0\cos\alpha \neq 0$.

The solution Φ of the Schrodinger equation

$$i\hbar\frac{\partial\Phi}{\partial t} = H_{int}\Phi \tag{9.8}$$

is of the form

$$\Phi = \sum_m C_m(t) e^{-\frac{i}{\hbar}\int^t dt' E_m}\varphi_m = \\ = \sum_m C_m(t) e^{-\frac{i}{\hbar}\int^t dt' E_m - i\theta J_y}\varphi_m^0 \ ; \tag{9.9}$$

the coefficients C_m satisfy the equation

$$\dot{C}_m + \tfrac{1}{2}[(j-m)(j+m+1)]^{1/2}\dot{\theta}C_{m+1}e^{-i\int^t dt'\omega_0} - \\ -\tfrac{1}{2}[(j+m)(j-m+1)]^{1/2}\dot{\theta}C_{m-1}e^{i\int^t dt'\omega_0} = 0 \ , \tag{9.10}$$

where $\omega_0 = \lambda/\hbar$ and the elements of matrix

$$(\varphi_m^0, J_y\varphi_{m'}^0) = \tfrac{i}{2}[(j-m)(j+m+1)]^{1/2}\delta_{m',m+1} - \\ -\tfrac{i}{2}[(j+m)(j-m+1)]^{1/2}\delta_{m',m-1} \tag{9.11}$$

of J_y has been used.

In order to make further progress we consider $j = 1/2$, *i.e.* $\mathbf{J} = \frac{1}{2}\overrightarrow{\sigma}$, where $\overrightarrow{\sigma}$ are the Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \ , \ \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \ , \ \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ ; \quad (9.12)$$

equations (9.10) become

$$\dot{C}_{1/2} = \frac{1}{2}\dot{\theta} C_{-1/2} e^{i\int^t dt' \omega_0} \ , \ \dot{C}_{-1/2} = -\frac{1}{2}\dot{\theta} C_{1/2} e^{-i\int^t dt' \omega_0} \ , \quad (9.13)$$

or

$$\dot{C} = AC \ , \ C = \begin{pmatrix} C_{1/2} \\ C_{-1/2} \end{pmatrix} \ ,$$
$$A = \begin{pmatrix} 0 & \frac{1}{2}\dot{\theta} e^{i\int^t dt' \omega_0} \\ -\frac{1}{2}\dot{\theta} e^{-i\int^t dt' \omega_0} & 0 \end{pmatrix} \ . \quad (9.14)$$

The solution is

$$C(t) = e^M C(t_0) \ , \quad (9.15)$$

where

$$M = \begin{pmatrix} 0 & s \\ -s^* & 0 \end{pmatrix} \ , \ s = \frac{1}{2}\int_{t_0}^{t} dt' \dot{\theta}(t') e^{i\int_{t_0}^{t'} dt'' \omega_0(t'')} \ , \quad (9.16)$$

where t_0 is the initial moment of time (for $t_0 = -\infty$ a corresponding convergence factor should be inserted in the integrals). The matrix M has the property $M^2 = -|s|^2$, so we have

$$e^M = \cos|s| + \frac{\sin|s|}{|s|} M \quad (9.17)$$

and

$$C_{1/2} = \cos|s| \, C_{1/2}(t_0) + \tfrac{s}{|s|} \sin|s| \, C_{-1/2}(t_0) \ ,$$
$$C_{-1/2} = -\tfrac{s^*}{|s|} \sin|s| \, C_{1/2}(t_0) + \cos|s| \, C_{-1/2}(t_0) \ . \quad (9.18)$$

The wavefunction Φ given by equation (9.9) becomes

$$\begin{gathered}\Phi = (C_{1/2}\cos\tfrac{\theta}{2}e^{-\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} - \\ -C_{-1/2}\sin\tfrac{\theta}{2}e^{\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0})\varphi^0_{1/2} + \\ +(C_{1/2}\sin\tfrac{\theta}{2}e^{-\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} + \\ +C_{-1/2}\cos\tfrac{\theta}{2}e^{\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0})\varphi^0_{-1/2} \quad ,\end{gathered} \tag{9.19}$$

where we have used

$$e^{-\frac{i}{2}\theta\sigma_y} = \cos\frac{\theta}{2} - i\sigma_y\sin\frac{\theta}{2} \ . \tag{9.20}$$

If the spin is in the state $\varphi^0_{-1/2}$ at t_0 ($C_{-1/2}(t_0) = 1$, $C_{1/2}(t_0) = 0$), the probabilities of transitions $W(m, -1/2)$ are

$$\begin{gathered}W(1/2, -1/2) =\mid \tfrac{s}{|s|}\sin|s|\cos\tfrac{\theta}{2}e^{-\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} - \\ -\cos|s|\sin\tfrac{\theta}{2}e^{\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} \mid^2 \quad , \\ W(-1/2, -1/2) =\mid \tfrac{s}{|s|}\sin|s|\sin\tfrac{\theta}{2}e^{-\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} + \\ +\cos|s|\cos\tfrac{\theta}{2}e^{\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} \mid^2 \quad .\end{gathered} \tag{9.21}$$

Similarly, if the spin is in the state $\varphi^0_{1/2}$ at t_0 ($C_{1/2}(t_0) = 1$, $C_{-1/2}(t_0) = 0$), the probabilities of transitions $W(m, 1/2)$ are

$$\begin{gathered}W(1/2, 1/2) =\mid \cos|s|\cos\tfrac{\theta}{2}e^{-\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} + \\ +\tfrac{s^*}{|s|}\sin|s|\sin\tfrac{\theta}{2}e^{\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} \mid^2 \quad , \\ W(-1/2, 1/2) =\mid \cos|s|\sin\tfrac{\theta}{2}e^{-\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} - \\ -\tfrac{s^*}{|s|}\sin|s|\cos\tfrac{\theta}{2}e^{\frac{i}{2}\int_{t_0}^{t}dt^{'}\omega_0} \mid^2 \quad .\end{gathered} \tag{9.22}$$

We can check that the matrix given by equation (9.18) is a unitary matrix and the probability is conserved.

For spin $j = 1$ the spin matrices are

$$J_x = \tfrac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \ , \ J_y = \tfrac{i}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \ , \qquad J_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \ . \tag{9.23}$$

The Schrodinger equation for the wavefunction given by equation (9.9) leads to

$$\dot{C}_1 = -\tfrac{\dot{\theta}}{\sqrt{2}} C_0 e^{i\int^t dt' \omega_0} \ , \ \dot{C}_{-1} = \tfrac{\dot{\theta}}{\sqrt{2}} C_0 e^{-i\int^t dt' \omega_0} \ , \qquad \dot{C}_0 = \tfrac{\dot{\theta}}{\sqrt{2}} C_1 e^{-i\int^t dt' \omega_0} - \tfrac{\dot{\theta}}{\sqrt{2}} C_{-1} e^{i\int^t dt' \omega_0} \ . \tag{9.24}$$

The solution of this system of equations is

$$\begin{pmatrix} C_1(t) \\ C_0(t) \\ C_{-1}(t) \end{pmatrix} = e^M \begin{pmatrix} C_1(t_0) \\ C_0(t_0) \\ C_{-1}(t_0) \end{pmatrix} \ , \tag{9.25}$$

where

$$M = \tfrac{1}{\sqrt{2}} \begin{pmatrix} 0 & -s^* & 0 \\ s & 0 & -s^* \\ 0 & s & 0 \end{pmatrix} \ , \qquad s = \int_{t_0}^t dt' \dot{\theta}(t') e^{-i\int_0^{t'} dt'' \omega_0(t'')} \ . \tag{9.26}$$

Making use of the properties

$$M^3 = -\left|s\right|^2 M \ , \ M^4 = -\left|s\right|^2 M^2 \ , \tag{9.27}$$

we get

$$e^M = 1 + \frac{\sin\left|s\right|}{\left|s\right|} M + 2\frac{\sin^2\frac{\left|s\right|}{2}}{\left|s\right|^2} M^2 \ , \tag{9.28}$$

which gives the coefficients $C_m(t)$ as functions of the initial coefficients $C_m(t_0)$. In order to compute the transition amplitudes we need also

$$e^{-i\theta J_y} = 1 - iJ_y \sin\theta + J_y^2 \cos\theta \ . \tag{9.29}$$

Similar calculations can be performed for spin $j = 3/2$ (and, in principle, for any spin j), though they are complicated.[1]

9.2 Right angles. Nuclear magnetic resonance

Consider the particular case $\alpha = 0$, corresponding to the field $\mathbf{H}_0$ directed along the z-axis (and the field $\mathbf{H}(t)$ directed along the x-axis). In addition, we assume $H \ll H_0$. It is easy to see that this case corresponds to the nuclear magnetic resonance.

Making use of equations (9.5) and (9.6), we have

$$\theta \simeq \frac{H}{H_0} \cos\omega t \ , \ \omega_0 \simeq \gamma H_0 \ . \tag{9.30}$$

We introduce adiabatically the fields from $t_0 = -\infty$; for $j = 1/2$, according to equation (9.16) we get

$$s \simeq \frac{\gamma H \omega}{4\omega_0} \left[\frac{e^{i(\omega+\omega_0)+\varepsilon t}}{\omega_0 + \omega - i\varepsilon} - \frac{e^{-i(\omega-\omega_0)+\varepsilon t}}{\omega_0 - \omega - i\varepsilon} \right] e^{i\omega_0/\varepsilon} \quad , \tag{9.31}$$

or, for ω near ω_0,

$$s \simeq -\frac{\gamma H \omega}{4\omega_0} \frac{e^{-i(\omega-\omega_0)+\varepsilon t}}{\omega_0 - \omega - i\varepsilon} e^{i\omega_0/\varepsilon} \ . \tag{9.32}$$

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[1] See, for instance, J. Schwinger, "On nonadiabatic processes in inhomogeneous fields", Phys. Rev. **51** 648 (1937); a constant magnetic field precessing with a constant angular velocity treated in Schwinger's paper is easier than the problem treated here; in general, according to Majorana, a spin j can be viewed as $2j$ spins 1/2 (see K. A. Milton, ed., *A Quantum Legacy, Seminal Papers of Julian Schwinger*, World Scientific, Singapore (2000)).

On the other hand, within the present approximation, the probability of the$-1/2 \to 1/2$ transiton is

$$W(1/2,-1/2) \simeq |s|^2 = \left(\frac{\gamma H}{4}\right)^2 \frac{e^{2\varepsilon t}}{(\omega_0-\omega)^2+\varepsilon^2} \ , \tag{9.33}$$

according to equation (9.21), where a time average has been taken. The (mean) absorbed power is

$$P = \frac{\pi}{4}\hbar\omega_0\gamma^2 H^2 \cdot \frac{1}{2} \cdot \delta(\omega_0-\omega) \ , \tag{9.34}$$

which coincides with perturbation-theoretical calculations for the magnetic resonance with an average spin $j = 1/2$.

For $\alpha \neq 0$ (and $H \ll H_0$) the angle θ is

$$\theta \simeq \alpha + \frac{H}{H_0}\cos\alpha\cos\omega t \tag{9.35}$$

and the frequency ω_0 is

$$\omega_0 \simeq \gamma H_0 + \gamma H \sin\alpha\cos\omega t \ ; \tag{9.36}$$

for spin $J = 1/2$ the relevant s is given by

$$s \simeq -\frac{H\omega}{4H_0}\cos\alpha\frac{e^{-i(\omega-\omega_0)+\varepsilon t}}{\omega_0-\omega-i\varepsilon}e^{i\omega_0/\varepsilon} \ . \tag{9.37}$$

In computing the probabilities we may neglect the oscillating terms occurring in θ, because they give vanishing time averages; we get, for instance,

$$\begin{gathered} W(1/2,-1/2) \simeq \sin^2\tfrac{\alpha}{2} + \left(\tfrac{H\omega}{4H_0}\right)^2 \cdot \\ \cdot\cos^2\alpha\sin^2\tfrac{\alpha}{2}\tfrac{e^{2\varepsilon t}}{(\omega_0-\omega)^2+\varepsilon^2} \ , \end{gathered} \tag{9.38}$$

where $\omega_0 \simeq \gamma H_0$. We can see that the first term ($\sin^2\frac{\alpha}{2}$) in equation (9.38) is the probability in the rotated frame in the absence of the interaction.

9.3 Nuclear quadrupole resonance

The nuclear spin is affected by the hyperfine interaction with the spins of the conduction electrons in metals; this interaction is an external (static) field interaction and manifests itself as a shift in the external static field, called the Knight shift. Similarly, the nuclear spin may be affected by the hyperfine interaction with the orbital momentum of the electronic environment; this is another shift in the static external field, called the chemical shift. An electron trapped in a vacancy, or the electronic spin of an impurity may feel the hyperfine interaction with the nuclear spins of the environment; this interaction manifests itself as a static external field acting upon the electronic spin in the electronic spin resonance (paramagnetic resonance). The nuclear spin may be affected by the quadrupole interaction with its electronic environment; the quadrupole interaction has five parameters (a traceless symmetric tensor of rank two); each spectral line is parametrized by two parameters (the strength and the frequency); we can use the magnitude and the direction of a fictitious static magnetic field (with respect to the direction of the radiofrequency field) to parametrize each spectral line.

Let us assume an interaction hamiltonian given by

$$\begin{gathered} H_{int} = H_{int}^0 + V(t) \ , \ H_{int}^0 = \gamma\hbar H_0 (J_x \sin\alpha + J_z \cos\alpha) \ , \\ V(t) = \gamma\hbar H J_x \cos\omega t \ . \end{gathered} \tag{9.39}$$

The eigenfunctions of H_{int}^0 are $\varphi_m = e^{-i\alpha J_y}\varphi_m^0$, with energies $E_m = m\gamma\hbar H_0 = m\hbar\omega_0$, where φ_m^0 are the eigenfunctions of the component J_z, $J_z\varphi_m^0 = m\varphi_m^0$, m integers or half-integers in the range $-j \leq m \leq j$ and $\omega_0 = \gamma H_0$. The Schrodinger equation

$$i\hbar\frac{\partial\Phi}{\partial t} = [H_{int}^0 + V(t)]\Phi \tag{9.40}$$

leads to

$$\Phi = \sum C_m e^{-\frac{i}{\hbar}E_m t}\varphi_m \tag{9.41}$$

and

$$\begin{gathered}
i\hbar\dot{C}_m = \textstyle\sum_{m'} C_{m'} e^{\frac{i}{\hbar}(E_m - E_{m'})t}\,(\varphi_m, V(t)\varphi_{m'}) = \\
= \gamma\hbar H m \sin\alpha\cos\omega t \cdot C_m + \\
+\gamma\hbar H \cos\alpha\cos\omega t \cdot \\
\cdot \textstyle\sum_{m'} C_{m'} e^{\frac{i}{\hbar}(E_m - E_{m'})t}\,(\varphi_m, J_x\varphi_{m'}) \ \ ;
\end{gathered} \tag{9.42}$$

the matrix elements of J_x are

$$\begin{gathered}
(\varphi_m, J_x\varphi_{m'}) = (\varphi^0_m, e^{i\alpha J_y} J_x e^{-i\alpha J_y}\varphi^0_{m'}) = \\
= \cos\alpha(\varphi^0_m, J_x\varphi^0_{m'}) + m\sin\alpha\delta_{mm'} \ \ ,
\end{gathered} \tag{9.43}$$

where

$$\begin{gathered}
(\varphi^0_m, J_x\varphi^0_{m'}) = \tfrac{1}{2}[(j+m)(j-m+1)]^{1/2}\delta_{m',m-1} + \\
+\tfrac{1}{2}[(j-m)(j+m+1)]^{1/2}\delta_{m',m+1} \ .
\end{gathered} \tag{9.44}$$

Equation (9.42) becomes

$$\begin{gathered}
i\dot{C}_m = \gamma H m \sin\alpha\cos\omega t \cdot C_m + \\
+\tfrac{1}{2}\gamma H[(j+m)(j-m+1)]^{1/2}\cos\alpha\cos\omega t e^{i\omega_0 t}C_{m-1} + \\
+\tfrac{1}{2}\gamma H[(j-m)(j+m+1)]^{1/2}\cos\alpha\cos\omega t e^{-i\omega_0 t}C_{m+1} + \ \ .
\end{gathered} \tag{9.45}$$

Usually H is small in comparison with H_0, so we may adopt a perturbation scheme in the first order; we get the transition amplitudes

$$\begin{gathered}
(\varphi_{m+1}, \Phi) = C_{m+1} e^{-\frac{i}{\hbar}E_{m+1}t} \ \ , \\
C_{m+1} = \tfrac{1}{4}\gamma H[(j-m)(j+m+1)]^{1/2}\cos\alpha \tfrac{e^{-i(\omega-\omega_0)t+\varepsilon t}}{\omega-\omega_0+i\varepsilon}
\end{gathered} \tag{9.46}$$

for $m \to m+1$ and

$$\begin{gathered}
(\varphi_{m-1}, \Phi) = C_{m-1} e^{-\frac{i}{\hbar}E_{m-1}t} \ \ , \\
C_{m-1} = \tfrac{1}{4}\gamma H[(j+m)(j-m+1)]^{1/2}\cos\alpha \tfrac{e^{-i(\omega-\omega_0)t+\varepsilon t}}{\omega-\omega_0+i\varepsilon}
\end{gathered} \tag{9.47}$$

(with $\varepsilon \to 0^+$). We get the absorbed net mean power

$$\begin{aligned} P = \hbar\omega_0 \left(\tfrac{\partial |C_{m-1}|^2}{\partial t} - \tfrac{\partial |C_{m+1}|^2}{\partial t} \right) = \\ = \tfrac{1}{4}\hbar\omega_0\gamma^2 H^2 \overline{m} \cos^2\alpha \tfrac{\varepsilon}{(\omega_0-\omega)^2+\varepsilon^2} \ \ , \end{aligned} \tag{9.48}$$

which coincides with the result for the nuclear quadrupole resonance; we note that $\gamma\hbar\overline{m}$ is a mean magnetic moment (where the thermal weights can be included) and $n(\gamma\hbar\overline{m})$ is a magnetic field, where n is the density of spins.

9.4 Parametric interaction

The evolution equation

$$i\hbar\frac{\partial\Phi}{\partial t} = H^0_{int}\Phi \tag{9.49}$$

with the hamiltonian $H^0_{int} = \gamma\hbar H_0(J_x \sin\alpha + J_z \cos\alpha)$ gives $\Phi = e^{-\frac{i}{\hbar}H^0_{int}t}\Phi_0$, where Φ is a static wavefunction prepared at the initial moment $t = 0$. We can transfer the time dependence upon the operators, by, for instance,

$$\widetilde{J}_x = e^{\frac{i}{\hbar}H^0_{int}t} J_x e^{-\frac{i}{\hbar}H^0_{int}t} \ \ , \tag{9.50}$$

and preserve the static wavefunction Φ_0 (this is the well-known Heisenberg representation); we get

$$\begin{aligned} \dot{\widetilde{J}}_x = -\omega_0 \cos\alpha \widetilde{J}_y \ , \ \dot{\widetilde{J}}_z = \omega_0 \sin\alpha \widetilde{J}_y \ , \\ \dot{\widetilde{J}}_y = -\omega_0 \sin\alpha \widetilde{J}_z + \omega_0 \cos\alpha \widetilde{J}_x \ \ ,. \end{aligned} \tag{9.51}$$

where $\omega = \gamma H_0$. This system of equations is solved by

$$\begin{pmatrix} \widetilde{J}_x \\ \\ \widetilde{J}_y \\ \\ \widetilde{J}_z \end{pmatrix} = e^M \begin{pmatrix} J_x \\ \\ J_y \\ \\ J_z \end{pmatrix} \ , \tag{9.52}$$

$$M = \omega_0 t \begin{pmatrix} 0 & -\cos\alpha & 0 \\ \cos\alpha & 0 & -\sin\alpha \\ 0 & \sin\alpha & 0 \end{pmatrix} \ ,$$

or

$$\begin{gathered} \widetilde{J}_x = (\sin^2\alpha + \cos\omega_0 t\cos^2\alpha) J_x - \sin\omega_0 t\cos\alpha \cdot J_y + \\ +(1-\cos\omega_0 t)\cos\alpha\sin\alpha \cdot J_z \ , \\ \widetilde{J}_y = \sin\omega_0 t\cos\alpha \cdot J_x + \cos\omega_0 t \cdot J_y - \sin\omega_0 t\sin\alpha \cdot J_z \ , \\ \widetilde{J}_z = (1-\cos\omega_0 t)\cos\alpha\sin\alpha \cdot J_x + \sin\omega_0 t\sin\alpha \cdot J_y + \\ +(\cos^2\alpha + \cos\omega_0 t\sin^2\alpha) J_z \ , \end{gathered} \tag{9.53}$$

since

$$e^M = 1 + \frac{\sin\omega_0 t}{\omega_0 t} M + \frac{1-\cos\omega_0 t}{(\omega_0 t)^2} M^2 \ . \tag{9.54}$$

We apply now the interaction

$$\widetilde{V}(t) = \gamma\hbar H\cos\omega t \cdot \widetilde{J}_x \ ; \tag{9.55}$$

the wavefunction may remain static (Φ_0), while the operators change according to

$$\begin{gathered} \widetilde{\widetilde{J}}_x = e^{\frac{i}{\hbar}\int^t dt' \widetilde{V}(t')} \widetilde{J}_x e^{-\frac{i}{\hbar}\int^t dt' \widetilde{V}(t')} \simeq \\ \simeq \widetilde{J}_x + \tfrac{i}{\hbar}[\int^t dt' \widetilde{V}(t'), \widetilde{J}_x] \ , \end{gathered} \tag{9.56}$$

where we limit ourselves to the first order of the perturbation theory; this is the well-known interaction representation. The equations of motion read

$$\dot{\widetilde{\widetilde{J}}}_x = \dot{\widetilde{J}}_x + \tfrac{i}{\hbar}[\int^t dt^{'} \widetilde{V}(t^{'}), \dot{\widetilde{J}}_x] \ ,$$

$$\dot{\widetilde{\widetilde{J}}}_y = \dot{\widetilde{J}}_y - \gamma H \cos\omega t \cdot \widetilde{J}_z + \tfrac{i}{\hbar}[\int^t dt^{'} \widetilde{V}(t^{'}), \dot{\widetilde{J}}_y] \ , \tag{9.57}$$

$$\dot{\widetilde{\widetilde{J}}}_z = \dot{\widetilde{J}}_z + \gamma H \cos\omega t \cdot \widetilde{J}_y + \tfrac{i}{\hbar}[\int^t dt^{'} \widetilde{V}(t^{'}), \dot{\widetilde{J}}_z] \ .$$

We may approximate $\widetilde{\mathbf{J}}$ by its expectation value in the state Φ_0, which may be taken as an eigenstate φ_m^0 of the component J_z; in this case the commutators in equations (9.57) are vanishing. On the other hand, we may average over oscillations with combined frequencies $\omega_0 \pm \omega$; in addition, we note that $\widetilde{\mathbf{J}}$ oscillates with frequency ω_0. so that equations (9.57) become

$$\ddot{J}_x + \omega_0^2 J_x = 0 \ , \ \ddot{J}_z + \omega_0^2 J_z = 0 \ ,$$

$$\ddot{J}_y + \omega_0^2 J_y = \gamma H \omega m \sin\omega t \cos^2\alpha \cdot m \ \ , \tag{9.58}$$

where we denoted the averages by $\mathbf{J}$. The value m corresponds to the z-axis; we may use instead its projection along the direction of the field $\mathbf{H}_0$, $m^{'} = m\cos\alpha$; we use the same notation m for this value. These approximations are called parametric interaction, since they depend on the parameter m.

The particular solution for J_y is given by

$$J_y = a\cos\omega t + b\sin\omega t \ \ , \tag{9.59}$$

where

$$a \simeq -\tfrac{1}{2}\gamma H m \cos\alpha \tfrac{\varepsilon}{(\omega-\omega_0)^2+\varepsilon^2} \ \ ,$$

$$b = -\tfrac{1}{2}\gamma H m \cos\alpha \tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\varepsilon^2} \ \ . \tag{9.60}$$

The absorbed mean power is

$$P = \gamma H \hbar \overline{\dot{J}_y \cos\alpha \sin\omega t} = -\tfrac{1}{2}\gamma H \hbar \omega a \cos\alpha =$$

$$= \tfrac{1}{4}\hbar\omega_0 \gamma^2 H^2 m \cos^2\alpha \tfrac{\varepsilon}{(\omega-\omega_0)^2+\varepsilon^2} \ \ , \tag{9.61}$$

which coincides with equation (9.48) ($m = \overline{m}$).

9.5 Spectral line

9.5.1 Introduction

Magnetic resonance research focuses on the parametrization of the energy levels, which provides information about the magnetic moments and the electronic and magnetic structure of the local molecular environment. The spectral line of the response receives comparatively little attention, it being given by well-known transition probabilities in the first-order of the perturbation theory. However, it provides direct access to measurable quantities, like the absorbed power or the emitted magnetic field, which require the calculation of the magnetization.

As it is well known, in typical experiments of magnetic resonance we consider two energy levels separated by a frequency ω_0, populate the upper level by means of electromagnetic radiation with frequency $\omega \simeq \omega_0$ and detect the response. The excitation is peformed by a time-dependent magnetic field $\mathbf{H} = \mathbf{H}_1 \cos \omega t$, where $\mathbf{H}_1$ is the amplitude and t denotes the time. In the standard treatment $\mathbf{H}$ is viewed as a small perturbation to the free hamiltonian, whose energy levels are not changed by perturbation, in the first order of the perturbation theory. The response is provided either by the absorbed power or by free-induction decay, including various versions of the latter, like the spin echo procedure. In free-induction decay the dis-excitation processes are spontaneous statistical processes, and the response, which is governed by the loss (damping) parameter, is spontaneous emission of incoherent radiation. It exhibits the characteristic shape of a spectral line.

We present here a different approach to magnetic resonance, where the time-dependent interaction, introduced adiabatically in a long time, changes the free energy levels and generates oscillations in magnetization.[2] Since we are interested in one spectral line at one time, it is sufficient to consider a two-level magnetic system.[3] The continuous emission of radiation is a stimulated, coherent emission, which

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[2] M. Apostol, "Spectral line of stimulated emission in magnetic resonance", Int. J. Adv. Res. Phys. Sci. **4** 36 (2017) (J. Theor. Phys. **276** (2017)).

[3] The quantum-mechanical structure of the radiation interacting with a two-level system has been considered by E. T. Jaynes and F. W. Cummings, "Compar-

enhances the response. We examine here to what extent the response signal is enhanced by stimulated emission in realistic situations. The calculations are based on Schwinger's treatment of Rabi's problem,[4] and are performed up to second-order powers of the coupling constant.

9.5.2 Zeeman splitting and transverse excitation

We assume a free hamiltonian

$$\mathcal{H}_0 = \frac{1}{2}\hbar\omega_0 J_z \quad , \tag{9.62}$$

where $\hbar$ is Planck's constant and J_z is the z-component of the Pauli matrices $\mathbf{J} = (J_x,\, J_y,\, J_z)$; the frequency $\omega_0 = 2\gamma H_0$ can be viewed as being due to the Zeeman splitting caused by a static magnetic field H_0, applied along the negative z-axis, γ being a gyromagnetic factor. We consider an interaction hamiltonian

$$\mathcal{H}_i = -\hbar\gamma H J_x e^{\alpha t} \quad , \tag{9.63}$$

where $H = H_1 \cos\omega t$; we assume that frequency ω is close to the frequency ω_0; the interaction is introduced adiabatically through the factor $e^{\alpha t}$, $\alpha \to 0^+$. This factor may account for the energy loss; it corresponds to the transverse relaxation time in nuclear magnetic resonance, where the Bloch approximation scheme, which disentangles the transverse components from the longitudinal component of the magnetization, allows the introduction of a second, longitudinal, relaxation time. It is convenient to introduce the coupling parameter $g = g_0 e^{\alpha t} \cos\omega t$, $g_0 = 2\gamma H_1/\omega_0$ and write the interaction hamiltonian as

$$\mathcal{H}_i = -\frac{1}{2}\hbar\omega_0 g J_x \ ; \tag{9.64}$$

we assume $g_0 \ll 1$. The two hamiltonians $\mathcal{H}_{0,i}$ given by equations (9.62) and (9.63) describe a typical nuclear magnetic resonance for a two-level magnetic system.

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ison of quantum and semiclassical radiation theories with application to the beam maser", Proceedings of the IEEE **51** 89 (1963).

[4] I. I. Rabi, "On the process of space quantization", Phys. Rev. **49** 324 (1936); I. I. Rabi, "Space quantization in a gyrating magnetic field", Phys. Rev. **51** 652 (1937); J. Schwinger, "On nonadiabatic processes in inhomogeneous fields", Phys. Rev. **51** 648 (1937).

The eigenvalues of the full hamiltonian $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_i$ are $E_{1,2}=\pm\frac{1}{2}\hbar\omega_0\lambda$, $\lambda=\sqrt{1+g^2}$ (Rabi frequencies), and the eigenvectors, up to second-order powers of the coupling constant g, are

$$\begin{gathered}\psi_1=a\varphi_{1/2}-b\varphi_{-1/2}\ ,\ \psi_2=b\varphi_{1/2}+a\varphi_{-1/2}\ , \\ a=1-g^2/8\ ,\ b=g/2\ ;\end{gathered} \tag{9.65}$$

noteworthy, these eigenvectors (which are orthonormal) depend on the time through the coupling constant g. The wavefunction is a superposition of the form

$$\psi(t)=C_1(t)e^{-\frac{i\omega_0}{2}\int^t dt^{'}\lambda(t^{'})}\psi_1(t)+C_2(t)e^{\frac{i\omega_0}{2}\int^t dt^{'}\lambda(t^{'})}\psi_2(t)\ \ , \tag{9.66}$$

where $\lambda=\sqrt{1+g^2}\simeq 1+g^2/2$ and $C_{1,2}(t)$ are time-dependent coefficients to be determined. The lower limit of the time integration in equation (9.66) is $-\infty$ for the interacting term in λ (the term $g^2/2$) and an arbitrary time for the free term; this contribution of the free term is a constant phase factor which may be included in $\psi_{1,2}$, such that we recover the non-interacting temporal phase factors $e^{\mp\frac{i}{2}\omega_0 t}$ in the limit $g\rightarrow 0$. The Schrodinger equation $i\hbar\partial\psi/\partial t=\mathcal{H}\psi$ leads to

$$\dot{C}_1+\tfrac{1}{2}\dot{g}e^{i\omega_0 t}C_2=0\ ,\ \dot{C}_2-\tfrac{1}{2}\dot{g}e^{-i\omega_0 t}C_1=0\ ; \tag{9.67}$$

such systems of coupled equations for the coefficients of the wavefunction have been introduced by Schwinger in his solution to Rabi problem.[5] The solution of the system of equations (9.67) is

$$\begin{gathered}C_1=\left(1-\tfrac{1}{2}\left|A\right|^2\right)C_1^0-AC_2^0\ , \\ C_2=A^*C_1^0+\left(1-\tfrac{1}{2}\left|A\right|^2\right)C_2^0\ \ ,\end{gathered} \tag{9.68}$$

where

$$A=\frac{1}{2}\int_{-\infty}^t dt^{'}\dot{g}e^{i\omega_0 t^{'}} \tag{9.69}$$

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[5] J. Schwinger, "On nonadiabatic processes in inhomogeneous fields", Phys. Rev. **51** 648 (1937); in this paper the system of equations (9.67) is solved for a gyrating magnetic field, where the coefficients $C_{1,2}$ reduce to constants.

and $C^0_{1,2}$ are the initial values of the coefficients $C_{1,2}$ at time $t \to -\infty$. For $\Delta\omega = \mid \omega - \omega_0 \mid \ll \alpha \ll \omega_0$ the leading term in equation (9.69) is

$$A \simeq -\frac{i}{4} g_0 \omega_0 \frac{\alpha}{(\Delta\omega)^2 + \alpha^2} \to -\frac{i\pi}{4} g_0 \omega_0 \delta(\Delta\omega) \ , \ \ \alpha \to 0 \tag{9.70}$$

(where δ is the Dirac delta function). We assume a thermal equilibrium for the initial states, such that the initial populations of the energy levels are given by

$$\begin{gathered} w^0_1 = \left| C^0_1 \right|^2 = \tfrac{1}{2}(1-p) \ , \ \ w^0_2 = \left| C^0_2 \right|^2 = \tfrac{1}{2}(1+p) \ , \\ p = \tanh(\beta\hbar\omega_0/2) \ \ , \end{gathered} \tag{9.71}$$

β being the inverse of the temperature; since the frequency ω_0 is in the radio-frequency range, we may use $p \simeq \beta\hbar\omega_0/2 \ll 1$ for a wide range of temperatures. The populations of the two states after introducing the interaction are

$$w_{1,2} = \left| (\psi_{1,2}(t), \psi(t)) \right|^2 = \left| C_{1,2}(t) \right|^2 \simeq w^0_{1,2} \pm \tfrac{1}{16} \tfrac{p g_0^2 \omega_0^2}{(\Delta\omega)^2 + \alpha^2} \ ; \tag{9.72}$$

we can see that the upper level acquires a net over-population due to the interaction. If we keep the factor $e^{\alpha t}$ in A (equation (9.70)), we can compute the transition rate, which is identical with the result of the first-order perturbation calculation. The leading contributions to the mean value $\overline{\mathbf{J}} = (\psi(t), \mathbf{J}\psi(t))$ of the angular momentum $\mathbf{J}$ in the state $\psi(t)$ are

$$\begin{gathered} \overline{J}_x \simeq \tfrac{1}{2} p g_0 \omega_0 \tfrac{\alpha}{(\Delta\omega)^2 + \alpha^2} \sin\omega_0 t \ , \\ \overline{J}_y \simeq -\tfrac{1}{2} p g_0 \omega_0 \tfrac{\alpha}{(\Delta\omega)^2 + \alpha^2} \cos\omega_0 t \ , \\ \overline{J}_z \simeq \tfrac{1}{8} \tfrac{p g_0^2 \omega_0^2}{(\Delta\omega)^2 + \alpha^2} \ ; \end{gathered} \tag{9.73}$$

these results are identical with those obtained by solving the Bloch equations of motion for magnetization.

The interaction induces a magnetic moment $\mathbf{m} = \hbar\gamma\overline{\mathbf{J}}$ and a magnetization $\mathbf{M} = n\mathbf{m}$, where n is the concentration of the two-level systems in the sample. The current density $\mathbf{j}_m = c \cdot curl\mathbf{M}$ (where c denotes the speed of light in vacuum) generates a dipolar magnetic field

$$\mathbf{H}_m \simeq v\frac{3\mathbf{r}(\mathbf{rM}) - r^2\mathbf{M}}{r^5} \tag{9.74}$$

at the position $\mathbf{r}$ from the sample, where v is the sample volume. We can see that this response is proportional to the number $N = vn$ of two-level systems in the sample and oscillates with the resonance frequency ω_0 ($\omega \simeq \omega_0$). The mean power absorbed (and dissipated) per unit volume is

$$P = \overline{\mathbf{H}\dot{\mathbf{M}}} = \frac{1}{8}pg_0^2 n\hbar\omega_0^3 \frac{\alpha}{(\Delta\omega)^2 + \alpha^2} \ ; \tag{9.75}$$

it exhibits the characteristic shape of a spectral line, as $M_{x,y} = n\hbar\gamma\overline{J}_{x.y}$ and $\mathbf{H}_m$ do.

9.5.3 Arbitrary orientation

In electron spin resonance (paramagnetic resonance) or the nuclear quadrupole resonance the ω_0-splitting is produced by the local molecular environment, which may have an arbitrary orientation. Therefore, we assume a free hamiltonian

$$\mathcal{H}_0 = \frac{1}{2}\hbar\omega_0\mathbf{nJ} \ \ , \tag{9.76}$$

where $\mathbf{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ is the unit vector defined by the angles θ, φ of the spherical coordinates; if the orientation is random, we may average over these angles. The eigenvalues of $\mathcal{H}_0$ are $\pm\hbar\omega_0/2$ and the eigenvectors are given by the 1/2-spin rotation matrix

$$\begin{aligned} \varphi_1^0 &= \cos\tfrac{\theta}{2} \cdot \varphi_{1/2} + e^{i\varphi}\sin\tfrac{\theta}{2} \cdot \varphi_{-1/2} \ \ , \\ \varphi_2^0 &= -\sin\tfrac{\theta}{2} \cdot \varphi_{1/2} + e^{i\varphi}\cos\tfrac{\theta}{2} \cdot \varphi_{-1/2} \ \ , \end{aligned} \tag{9.77}$$

where $\varphi_{\pm 1/2}$ are the eigenvectors of J_z ($J_z\varphi_{\pm 1/2} = \pm\varphi_{\pm 1/2}$). The interaction hamiltonian

$$\mathcal{H}_i = -\hbar\gamma H J_z e^{\alpha t} = -\frac{1}{2}\hbar\omega_0 g J_z \tag{9.78}$$

is provided by a magnetic field $H = H_1 \cos \omega t$ directed along the z-axis.

The full hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_i$ can be diagonalized straightforwardly; its eigenvalues are $E_{1,2} = \pm \frac{1}{2} \hbar \omega_0 \lambda$,

$$\lambda = \sqrt{1 - 2g\cos\theta + g^2} \simeq 1 - g\cos\theta + \frac{1}{2} g^2 \sin^2\theta \tag{9.79}$$

(Rabi frequencies), and its eigenvectors are given by

$$\begin{aligned} \psi_1 &= \cos\tfrac{\theta}{2}\left[1 - g\sin^2\tfrac{\theta}{2} + g^2\sin^2\tfrac{\theta}{2}\left(1 - \tfrac{5}{2}\cos^2\tfrac{\theta}{2}\right)\right]\varphi_{1/2} + \\ &+ e^{i\varphi}\sin\tfrac{\theta}{2}\left[1 + g\cos^2\tfrac{\theta}{2} + g^2\cos^2\tfrac{\theta}{2}\left(1 - \tfrac{5}{2}\sin^2\tfrac{\theta}{2}\right)\right]\varphi_{-1/2} \ , \\ \psi_2 &= -\sin\tfrac{\theta}{2}\left[1 + g\cos^2\tfrac{\theta}{2} + g^2\cos^2\tfrac{\theta}{2}\left(1 - \tfrac{5}{2}\sin^2\tfrac{\theta}{2}\right)\right]\varphi_{1/2} + \\ &+ e^{i\varphi}\cos\tfrac{\theta}{2}\left[1 - g\sin^2\tfrac{\theta}{2} + g^2\sin^2\tfrac{\theta}{2}\left(1 - \tfrac{5}{2}\cos^2\tfrac{\theta}{2}\right)\right]\varphi_{-1/2} \ , \end{aligned} \tag{9.80}$$

where contributions up to the g^2-order are included. Also, it is useful to give the interacting eigenvectors $\psi_{1,2}$ in terms of the free (non-interacting) eigenvectors $\varphi^0_{1,2}$,

$$\psi_1 = a\varphi^0_1 + b\varphi^0_2 \ , \ \psi_2 = -b\varphi^0_1 + a\varphi^0_2 \ , \tag{9.81}$$

where

$$a = 1 - \tfrac{1}{8} g^2 \sin^2\theta \ , \ b = \tfrac{1}{2} g \sin\theta \left(1 + g\cos\theta\right) \ . \tag{9.82}$$

The time-dependent interacting wavefunction has the same form as in equation (9.66); the Schrodinger equation $i\hbar\partial\psi/\partial t = \mathcal{H}\psi$ leads to Schwinger's system of equations

$$\begin{aligned} &\dot{C}_1 - \dot{g}\sin\theta\left(\tfrac{1}{2} + g\cos\theta\right)e^{i\omega_0\int^t dt^{'}\lambda(t^{'})}C_2 = 0 \ , \\ &\dot{C}_2 + \dot{g}\sin\theta\left(\tfrac{1}{2} + g\cos\theta\right)e^{-i\omega_0\int^t dt^{'}\lambda(t^{'})}C_1 = 0 \ . \end{aligned} \tag{9.83}$$

In estimating the time integrals $\int^t dt^{'}\lambda(t^{'})$ we encounter terms corresponding to transitions $\omega = 0, \pm\omega_0/2, \pm\omega_0$; limiting ourselves to $\omega \simeq \omega_0$, the system of equations (9.83) becomes

$$\dot{C}_1 + \beta C_2 = 0 \ , \ \dot{C}_2 - \beta^* C_1 = 0 \ , \tag{9.84}$$

where

$$\beta = \frac{i}{4} g_0 \sin\theta \cdot (\omega + i\alpha) e^{-i(\omega-\omega_0)t+\alpha t} \quad . \tag{9.85}$$

The solution of this system of equations is

$$\begin{aligned} C_1 &= \left(1 - \tfrac{1}{2}\left|A\right|^2\right) C_1^0 + A C_2^0 \ , \\ C_2 &= -A^* C_1^0 + \left(1 - \tfrac{1}{2}\left|A\right|^2\right) C_2^0 \ , \end{aligned} \tag{9.86}$$

where

$$A = -\frac{i}{4} g_0 \omega_0 \sin\theta \frac{\alpha}{(\Delta\omega)^2 + \alpha^2} \quad . \tag{9.87}$$

We use $C_{1,2}^0 = \sqrt{(1 \mp p)/2}$, where p is given by equation (9.71), corresponding to thermal equilibrium. The populations of the two states are

$$w_{1,2} \simeq w_{1,2}^0 \pm \tfrac{1}{16} \sin^2\theta \tfrac{p g_0^2 \omega_0^2}{(\Delta\omega)^2 + \alpha^2} \tag{9.88}$$

and the leading contributions to the mean value of the angular momentum in the state $\psi(t)$ are

$$\begin{aligned} &\overline{J}_+ = \overline{J}_x + i\overline{J}_y \simeq 2p\left|A\right|(i - g\cos\theta\sin\omega_0 t)e^{-i(\widetilde{\omega}_0 - \varphi)t} - \\ &-2p\left|A\right|(1+\cos\theta)(\sin\widetilde{\omega}_0 t - g_0\cos\theta\sin\omega_0 t\cos\widetilde{\omega}_0 t)e^{i\varphi} + \\ &+2p\left|A\right| g\sin^2\theta\sin\widetilde{\omega}_0 t + 2p\left|A\right|^2\sin\theta\cdot e^{i\varphi} \ , \end{aligned} \tag{9.89}$$

and

$$\begin{aligned} &\overline{J}_z \simeq 2p\left|A\right|\sin\theta\,(\sin\widetilde{\omega}_0 t - g_0\cos\theta\sin\omega_0 t\cos\widetilde{\omega}_0 t) + \\ &+p\left|A\right| g\sin 2\theta\sin\widetilde{\omega}_0 t + 2p\left|A\right|^2\cos\theta \ , \end{aligned} \tag{9.90}$$

where $\widetilde{\omega}_0 = \omega_0(1 + \frac{1}{4}g_0^2\sin^2\theta)$ and $\overline{J}_- = \overline{J}_x - i\overline{J}_y == \overline{J}_+^*$. We may use ω_0 instead of $\widetilde{\omega}_0$ in the above equations, leave aside the time-independent contributions and the terms oscillating with frequency

$2\omega_0$, and get

$$\begin{aligned}\overline{J}_x &\simeq 2p\left|A\right|[\sin(\omega_0 t-\varphi)-\tfrac{1}{4}g_0\cos\theta\sin(\omega_0 t+\varphi)-\\ &\quad -(1+\cos\theta)\sin\omega_0 t\cos\varphi]\ ,\\ \overline{J}_y &\simeq 2p\left|A\right|[\cos(\omega_0 t-\varphi)+\tfrac{1}{4}g_0\cos\theta\cos(\omega_0 t+\varphi)-\\ &\quad -(1+\cos\theta)\sin\omega_0 t\sin\varphi]\ ,\\ \overline{J}_z &\simeq 2p\left|A\right|\sin\theta\sin\omega_0 t\ ;\end{aligned} \tag{9.91}$$

the mean power absorbed per unit volume is

$$P=\overline{\mathbf{H}\dot{\mathbf{M}}}=\frac{1}{8}pg_0^2n\hbar\omega_0^3\sin^2\theta\frac{\alpha}{(\Delta\omega)^2+\alpha^2}\ . \tag{9.92}$$

If we take the average over angles φ and θ, we get $\overline{J}_{x,y}=0$ and

$$\overline{J}_z=\frac{1}{3}pg_0\omega_0\frac{\alpha}{(\Delta\omega)^2+\alpha^2}\sin\omega_0 t\ . \tag{9.93}$$

Making use of these results, we can compute immediately the emitted field, which exhibits the coherent character of a stimulated emission.

9.5.4 Conclusion

In conclusion, we have solved the Schrodinger equation for a two-level magnetic system subject to a time-dependent external magnetic field with arbitrary orientation up to the second order in the coupling constant. The mean power absorbed per unit volume and the emitted radiation have been estimated. It is shown that the emitted radiation has the character of a coherent radiation, stimulated by the driving external field, due to the continuous oscillations of the magnetization.

As it is well-known, the coherent response increases the signal by a factor of the order $\sqrt{N}$, where N is the number of the two-level systems in the sample. However, in realistic situations important decoherence factors appear, which reduce appreciably this enhancement. First, we have used in the discussion above quantum-mechanical wavefunctions, while the sample was supposed to be at thermal equilibrium. The thermal bath is an important decoherence factor. For instance, at room temperature the energy levels are affected by an uncertainty of the order $T = 300K \simeq 4 \times 10^{-14} erg$, which is much higher than the two-level separation energy $\hbar\omega_0 \simeq 10^{-21} erg$ for $\omega_0 = 1MHz$. On the other hand, the magnetic momenta may be ordered along a distance of the order $1\mu m$, which further reduces the number of coherent two-level systems. All these reduction factors apply to the number N of two-level systems in the sample.

10 Concluding Chapter

10.1 Summary and introduction

The Heisenberg time-dependence of quantum-mechanical operators is analyzed within the quasi-classical approximation, where the quanta of action $\hbar$ (Planck's constant) is much smaller than the relevant amounts of mechanical action. It is shown that such a circumstance can provide an approximation by harmonic oscillators to some quantum-mechanical systems, especially in condensed matter. The accuracy of the approximation is assessed by estimating the mean power absorbed from an external time-dependent force; this power exhibits, both classically and quantum-mechanically, a typical resonance behavior. It is shown that the mean power obtained by means of the harmonic-oscillator approximation is the variation with respect to the quantum number of the total mean power. In most simple cases the difference between the exact result and the approximate one resides in a numerical factor. A few examples are given for simple quantum-mechanical systems (rigid planar and spatial rotator endowed with an electric dipole moment under the action of an electric field), as well as the nuclear magnetic and quadrupole resonances.

It is well known that the quasi-classical approximation works in Quantum Mechanics whenever the quanta of action $\hbar$ (Planck's constant) is much smaller than the relevant amounts of mechanical action; this implies high quantum numbers. The energy levels of the hydrogen atom become dense for high values of the quantum number and can be approximated by the energy provided by the Classical Mechanics. This is the well-known Bohr's principle of correspondence.[1] When the de Broglie's wavelength is much smaller than the relevant spatial

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[1] N. Bohr, "On the quantum theorie of line-spectra", Kgl. Danske Vidensk. Selsk. Skr., nat.-math. Afd. 8 Raekke IV, 1 (1918-1922); N. Bohr, "Uber die Serienspektra der Elemente", Z.Phys. **2** 423 (1920); N. Bohr, "Uber die Anwendung

dimensions and does not vary too much, then the wavefunction may be approximated by a quasi-plane wave and the motion may have a trajectory, very much alike the geometrical-optics approximation for waves. This is known as the quasi-classical approximation (or the Jeffrey-Wentzel-Kramers-Brillouin - JWKB - approximation).[2] A superposition of such plane waves gives a wavepacket which simulates spatial localization (classical limit).[3] In the quasi-classical limit $\hbar \rightarrow 0$ the quantum-mechanical commutator reproduces the corresponding classical Poisson brackets.[4]

Another, less known, aspect of the quasi-classical approximation is described here; it arises from the Heisenberg's time-dependence of the quantum-mechanical operators.[5] It leads to an approximation by classical harmonic oscillators of some quantum-mechanical systems, especially in condensed matter; such an approximation may be called a quasi-classical dynamics.

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der Quantentheorie auf die Atombau I: Grundpostulate der Quantentheorie", Z. Phys. **13** 117 (1923).

[2] H. Jeffreys, "On certain approximate solutions of linear differential equations of the second order", Proc. Roy. Soc. London **23** 428 (1924); G. Wentzel, "Eine Verallgemeinerung der Quantenbedingungen fur die Zwecke der Quantenmechanik ", Z. Phys. **38** 518 (1926); H. A. Kramers, "Wellenmechanik und halbzahlige Quantisierung ", Z. Phys. **39** 828 (1926); L. Brillouin, "La mecanique ondulatoire de Schrodinger: une methode generale de resolution par approximations successives ", C. R. Acad. Sci. Paris **183** 24 (1926); L. Brillouin, "Remarques sur la Mecanique Ondulatoire", J. Physique **7** 353 (1926); W. Pauli, *General Principles of Quantum Mechanics*, Springer, Berlin (1980); L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 3, *Quantum Mechanics*, Elsevier, Oxford (1991).

[3] P. Debye, "Wellenmechanik und Korrespondenzprinzip", Phys. Z. **28** 170 (1927); C. G. Darwin, "Free motion in the Wave Mechanics", Proc Roy. Soc. London **A117** 258 (1927).

[4] P. A. M. Dirac, "The fundamental equations of Quantum Mechanics", Proc. Roy. Soc. **A109** 642 (1926).

[5] W. Heisenberg, "Uber Quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen", Z. Phys. **33** 879 (1925); W. Heisenberg, *The Physical Principles of the Quantum Theory*, Dover, NY (1949).

10.2 Quasi-classical dynamics. Quantum systems

Let O be a dynamical variable of a quantum-mechanical motion governed by a hamiltonian H (independent of time); its equation of motion is $\dot{O} = (i/\hbar)[H, O]$, or $\dot{O}_{mn} = (i/\hbar)(E_m - E_n)O_{mn}$, where O_{mn} are the matrix elements for the states m, n with energies E_m, E_n; we assume $O_{mn} \neq 0$ for $m \neq n$. For large values of the energy levels E_m and the quantum number m the energy levels are "densely distributed", in the sense that $\Delta E_m/E_m = (E_m - E_n)/E_m \ll 1$ for any finite difference $\Delta E_m = E_m - E_n$; according to Bohr's correspondence principle, in this case we are approaching the (quasi-) classical limit. Moreover, under the same conditions, the matrix elements O_{mn} depend weakly on m and may fall abruptly to zero with increasing $|m - n|$ (due to the rapid oscillations of the wavefunctions with large quantum numbers); according to the equation of motion, the matrix elements O_{mn} are approximated by the Fourier components O_{n-m} of the classical quantity $O(\mathrm{t})$. We write $n = m+s, \omega_n = E_n/\hbar = \omega_{m+s} = \omega_m + s(\partial\omega_m/\partial m) + ...$ and $O_{mn} = O_{m,m+s} \simeq O_s$ for small values of s (in comparison with m, $s \ll m$). For a superposition $\psi = \sum_m c_m \varphi_m e^{-i\omega_m t}$ of wavefunctions $\varphi_m e^{-i\omega_m t}$, the mean value of the variable O is

$$\begin{gathered} \overline{O} = \sum_{mn} c_m^* c_n O_{mn} e^{i(\omega_m - \omega_n)t} \simeq \\ \simeq \sum_{ms} c_m^* c_m O_s e^{-is(\partial\omega_m/\partial m)t} \simeq \sum_s O_s e^{-i\omega_s t} \quad , \end{gathered} \tag{10.1}$$

which is the Fourier transform of the classical quantity $O(t)$ with frequencies $\omega_s = s(\partial\omega_m/\partial m)$. The equation of motion for one component reads

$$\dot{O}_s = -i\omega_s O_s \quad , \tag{10.2}$$

for a fixed m.

The nature and meaning of this equation require a few clarifications. First, we note the approximate character of the equation (10.2), as a result of the approximations involved in deriving equation (10.1). Equation (10.2) is an approximation for the classical equation of motion of the classical quantity O. Indeed, on one hand it retains partially the quantum-mechanical character of the motion through

$\omega_s = (E_{m+s} - E_m)/\hbar$ and the presence of m in O_s (not written explicitly); on the other hand, it refers to a motion which changes the energy ($E_m \neq E_{m+s}$), while the classical motion proceeds with the conservation of the energy. For such reasons, we call equation (10.2) the quasi-classical equation of motion. For instance, writing $O_s = O_s^{(1)} + iO_s^{(2)}$, we have $\dot{O}_s^{(1)} = \omega_s O_s^{(2)}$, $\dot{O}_s^{(2)} = -\omega_s O^{(1)}$ and $\ddot{O}_s^{(1)} = -\omega_s^2 O_s^{(1)}$, $\ddot{O}_s^{(2)} = -\omega_s^2 O_s^{(2)}$; the classical quantity is either $O_s^{(1)}$ or $O_s^{(2)}$ (O is a real quantity); the classical equations of motion can be represented as $\dot{O}_s^{(1)} = \partial H/\partial P$, $\dot{P} = -\partial H/\partial O_s^{(1)}$, $\ddot{O}_s^{(1)} = (\partial/\partial t)(\partial H/\partial P)$, where P is a generalized momentum and $(\partial/\partial t)(\partial H/\partial P)$ acts as a generalized force (and similar equations for $O_s^{(2)}$); in general, the generalized force $(\partial/\partial t)(\partial H/\partial P)$ differs from the harmonic-oscillator force $-\omega_s^2 O_s^{(1)}$. For the particular case of a harmonic oscillator with eigenfrequency ω_0 the quasi-classical equation of motion is formally the same as the classical equation of motion, but the former assumes in addition $\hbar\omega_0 = E_{m+1} - E_m$, *i.e.* the quantum-mechanical condition for the quantization of the energy. The quantum-mechanical motion governed by the commutator with the hamiltonian is equivalent in the (quasi-) classical limit $\hbar \rightarrow 0$ with the classical motion governed by the Poisson brackets, though the quasi-classical motion is associated with the quantum jumps (change of energy), while the classical motion refers to a given orbit (which implies the energy conservation). In the classical limit $\hbar \rightarrow 0$ the quantum jumps disappear and we are left with a classical motion; but the classical equation of motion is not necessarily the equation of motion of a harmonic oscillator. It is a remarkable property of the Quantum Mechanics that the quantum-mechanical motion of any dynamical variable can be approximated, within certain limitations as those pointed out here, by a harmonic-oscillator motion in the quasi-classical limit, as indicated by equation (10.2).

The quasi-classical equation of motion (10.2) implies that the motion is governed by a harmonic-oscillator effective hamiltonian

$$H_{eff} = \frac{1}{2M}P_s^2 + \frac{1}{2}M\omega_s^2 O_s^2 \ , \tag{10.3}$$

where P_s is the canonical-conjugate momentum for the "coordinate" O_s and M is a "mass" parameter.

In the presence of a time-dependent, external interaction given by a hamiltonian $H_{int}(t) = h\cos\omega t$, the change in time of the quantity O_s acquires a new contribution, which we write as $\dot{O}^{cl}$; equation (10.2) becomes

$$\dot{O}_s = -i\omega_s O_s + \dot{O}^{cl} \ ; \tag{10.4}$$

the new term $\dot{O}^{cl}$ denotes that part of the time derivative of the classical quantity O, denoted O^{cl}, which arises from the external interaction. At this moment, we may drop out the suffix s in equation (10.4) and denote $\omega_0 = \omega_s$. With $O = O^{(1)} + iO^{(2)}$ we get from equation (10.4) $\dot{O}^{(1)} = \omega_0 O^{(2)} + \dot{O}^{cl}$, $\dot{O}^{(2)} = -\omega_0 O^{(1)}$ and

$$\ddot{O}^{(1)} + \omega_0^2 O^{(1)} = [(\partial/\partial t)\dot{O}^{cl}]_{int} \ ; \tag{10.5}$$

the suffix *int* in equation (10.5) indicates that we retain only the contribution of the external interaction. Equation (10.5) is the equation of motion of a harmonic oscillator under the action of a generalized force $[(\partial/\partial t)\dot{O}^{cl}]_{int}$; a similar equation is obtained for $O^{(2)}$; we may drop out the labels (1), (2) and write simply

$$\ddot{O} + \omega_0^2 O = [(\partial/\partial t)\dot{O}^{cl}]_{int} \ . \tag{10.6}$$

We are interested in the particular solution of equation (10.6), which is generated by the interaction. Within the quasi-classical dynamics the interaction produces small effects, so that we may denote δO the particular solution of equation (10.6); it is the variation of the quantity O for small changes $s \ll m$ in the quantum numbers m; equation (10.6) becomes

$$\delta\ddot{O} + \omega_0^2 \delta O = [(\partial/\partial t)\dot{O}^{cl}]_{int} \ ; \tag{10.7}$$

if present in the *rhs* of this equation, δO should be neglected there, in order to preserve the perturbation character of the interaction. A damping term can be introduced in equation (10.7) (the coefficient α), which becomes

$$\delta\ddot{O} + \omega_0^2 \delta O + 2\alpha\delta\dot{O} = (\partial/\partial t)(\dot{O}^{cl})_{int} \ \ , \tag{10.8}$$

where $\alpha \to 0^+$; multiplying by $\delta\dot{O}$ we get a conservation law,

$$\frac{d}{dt}\left(\frac{1}{2}(\delta\dot{O})^2 + \frac{1}{2}\omega_0^2(\delta O)^2\right) + 2\alpha(\delta\dot{O})^2 = \delta\dot{O}[(\partial/\partial t)\dot{O}^{cl}]_{int} \ \ , \tag{10.9}$$

which is related to the energy conservation.

The calculation of the generalized force $[(\partial/\partial t)\dot{O}^{cl}]_{int}$ is carried out by means of the Poisson brackets. For the classical dynamics of the variable O we have $\dot{O}=\{O,H_{eff}\}+\{O,H_{int}\}$ and

$$\begin{gathered}(\partial/\partial t)\dot{O}=\{\{O,H_{eff}\},H_{eff}\}+\{\{O,H_{eff}\},H_{int}\}+\\ +\{\{O,H_{int}\},H_{eff}\}+\{\{O,H_{int}\},H_{int}\}\ ;\end{gathered} \tag{10.10}$$

the first term in the *rhs* of equation (10.10) must be left aside since it does not contain the interaction; similarly, the last term in equation (10.10) must be left aside, since we limit ourselves to the first order of the perturbation theory in H_{int}; therefore, we get

$$(\partial/\partial t)(\dot{O}^{cl})_{int}=\{\{O,H_{eff}\},H_{int}\}+\{\{O,H_{int}\},H_{eff}\} \tag{10.11}$$

for the generalized force appearing in equation (10.7). We note that the effective hamiltonian H_{eff} is used in equation (10.11), and not the classical counterpart of the original hamiltonian H, in order to preserve the consistency of the quasi-classical approximation. For special forms of the interaction hamiltonian the generalized force given by equation (10.11) may contain O and P generated by H_{eff} (or expressions containing such O and P); let us denote them by O_0 and P_0. The classical behaviour of these quantities implies undetermined constants (arising from initial conditions), besides a time dependence. If the external interaction proceeds at a slower time scale than the the motion of these quantities, we may take the time average of the classical O_0 and P_0. In condensed matter at thermal equilibrium O_0 and P_0 can be determined by their thermal averages. Also, we may approximately take for O_0 and P_0 the mean values for the quantum state m. All these procedures introduce an additional approximate character in the solution of the quasi-classical equation (10.8). It is also worth stressing the fact that there might be cases (like the motion of the magnetization in condensed matter) where we have equations of motion but not necessarily a (classical) hamiltonian formalism; in that case the time derivative $\partial/\partial t$ in equation (10.7) retains only its basic meaning, that of a derivative with respect to the time.

Assuming that h depends only on O in $H_{int}(t)=h\cos\omega t$ and using the hamiltonian given by equation (10.3) we get

$\dot{O}^{cl} = P/M$ and

$$\begin{aligned}[(\partial/\partial t)\dot{O}^{cl}]_{int} = (\dot{P}/M)_{int} = -(\partial H_{int}/\partial O)/M = \\ = -(1/M)(\partial h/\partial O)\cos\omega t \ ;\end{aligned} \tag{10.12}$$

equation (10.8) becomes

$$\delta\ddot{O} + \omega_0^2 \delta O + 2\alpha\delta\dot{O} = -\frac{1}{M}\cdot\frac{\partial h}{\partial O}\cos\omega t \tag{10.13}$$

with solution

$$\delta O = a\cos\omega t + b\sin\omega t \ , \tag{10.14}$$

where

$$\begin{aligned} a &= \tfrac{1}{M}\cdot\tfrac{\partial h}{\partial O}\cdot\tfrac{\omega^2-\omega_0^2}{(\omega^2-\omega_0^2)^2+4\omega^2\alpha^2} \simeq \\ &\simeq \tfrac{1}{2M\omega_0}\cdot\tfrac{\partial h}{\partial O}\cdot\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha^2} \ , \\ b &= -\tfrac{1}{M}\cdot\tfrac{\partial h}{\partial O}\cdot\tfrac{2\omega\alpha}{(\omega^2-\omega_0^2)^2+4\omega^2\alpha^2} \simeq \\ &\simeq -\tfrac{1}{2M\omega_0}\cdot\tfrac{\partial h}{\partial O}\cdot\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ , \end{aligned} \tag{10.15}$$

for ω near ω_0. The mean "power" dissipated (absorbed) by the oscillator is

$$\begin{aligned} \delta P_{osc} &= M\overline{\delta\dot{O}[(\partial/\partial t)\dot{O}^{cl}]_{int}} = \\ &= M\overline{(-a\omega\sin\omega t + b\omega\cos\omega t)}\times \\ &\times\overline{[-(1/M)(\partial h/\partial O)\cos\omega t)]} = \\ &= -\tfrac{1}{2}b\omega\tfrac{\partial h}{\partial O} \simeq \tfrac{(\partial h/\partial O)^2}{4M}\cdot\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \to \\ &\to \tfrac{\pi(\partial h/\partial O)^2}{4M}\delta(\omega_0-\omega) \end{aligned} \tag{10.16}$$

(for $\alpha \to 0^+$). As a function of ω, this is a typical resonance curve. As we shall see immediately, δP_{osc} is only the variation of the mean absorbed power with respect to the quantum numbers, as a consequence of the small effects produced by the classical interaction.

Indeed, it is worth comparing this result with the quantum-mechanical theory of perturbation. Let

$$\psi = \varphi_n e^{-\frac{i}{\hbar}E_n t} + \sum_k{}' c_{kn}\varphi_k e^{-\frac{i}{\hbar}E_k t} \tag{10.17}$$

be the wavefunction produced to the first order of the perturbation theory by the interaction $H_{int}(t) = h\cos\omega t$; from the Schrodinger equation $i\hbar\partial\psi/\partial t = (H + H_{int})\psi$ we get

$$i\hbar\dot{c}_{kn} = \frac{1}{2}h_{kn}\left[e^{i(\omega_{kn}+\omega)t+\alpha t} + e^{i(\omega_{kn}-\omega)t+\alpha t}\right] \ , \tag{10.18}$$

where the interaction is introduced adiabatically ($\alpha \to 0^+$); hence,

$$c_{kn} = -\frac{h_{kn}}{2\hbar}\left[\frac{e^{i(\omega_{kn}+\omega)t+\alpha t}}{\omega_{kn}+\omega-i\alpha} + \frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha}\right] \ . \tag{10.19}$$

The transition from the state n to the state k with the absorption of the quanta of energy $\hbar\omega_{kn} = E_k - E_n$ corresponds to the coefficient

$$c_{kn} \simeq -\frac{h_{kn}}{2\hbar}\cdot\frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha} \ ; \tag{10.20}$$

it produces

$$\begin{gathered} R = \frac{\partial|c_{kn}|^2}{\partial t} = \frac{|h_{kn}|^2}{2\hbar^2}\cdot\frac{\alpha}{(\omega_{kn}-\omega)^2+\alpha^2} \to \\ \to \frac{\pi|h_{kn}|^2}{2\hbar^2}\delta(\omega_{kn}-\omega) \end{gathered} \tag{10.21}$$

transitions per unit time and absorbs (dissipates) a power

$$P = \frac{|h_{kn}|^2}{2\hbar}\omega_{kn}\frac{\alpha}{(\omega_{kn}-\omega)^2+\alpha^2} \to \frac{\pi|h_{kn}|^2}{2\hbar}\omega_{kn}\delta(\omega_{kn}-\omega) \ . \tag{10.22}$$

We set $n \to m$ and $k \to m+s$ and get

$$P = \frac{|h_s|^2}{2\hbar}\omega_0\frac{\alpha}{(\omega_0-\omega)^2+\alpha^2} \to \frac{\pi\,|h_s|^2}{2\hbar}\omega_0\delta(\omega_0-\omega) \ . \tag{10.23}$$

We compare δP given by equation (10.23) with δP_{osc} given by equation (10.16); for these two quantities be equal we should have

$$\delta\left(\frac{|h_s|^2}{2\hbar}\omega_0\right)=\frac{(\partial h/\partial O)^2}{4M}\ ; \tag{10.24}$$

such an equality is not fulfilled in general; it gives the deviation of the quasi-classical approximation (based on harmonic oscillators) from the quantum-mechanical dynamics. Equation (10.24) is satisfied for a harmonic oscillator, as expected; indeed, we have

$$\begin{gathered}\delta\left(\tfrac{|h_s|^2}{2\hbar}\omega_0\right)=\tfrac{h_s\delta h_s}{\hbar}\omega_0= \\ =\tfrac{h_s(\partial h_s/\partial O)\delta O}{\hbar}\omega_0=\tfrac{(\partial h/\partial O)^2}{4M}\ ,\end{gathered} \tag{10.25}$$

or

$$h\delta O=\frac{\hbar}{4M\omega_0}(\partial h/\partial O)\ , \tag{10.26}$$

where we dropped out the suffix s and assumed a constant ω_0. Equation (10.26) can also be written as

$$h\delta O=\frac{\hbar}{4M\omega_0 s}\cdot\frac{\partial h}{\partial O}\delta n\ ; \tag{10.27}$$

for $h=f_rO^r$ we get $O=\sqrt{(\hbar r/2M\omega_0 s)n}$ from equation (10.27), which, for $r=s=1$, is the matrix element of the displacement operator for a harmonic oscillator with mass M and frequency ω_0. For $h=fO$, we get $\delta P_{osc}=(\pi f^2/4M)\delta(\omega_0-\omega)$ from equation (10.16) and $P_{osc}=(\pi f^2/4M)n\delta(\omega_0-\omega)$, which coincides with equation (10.23) for large n. This is precisely the result obtained by means of the first-order theoretical-perturbation calculation using the effective harmonic-oscillator hamiltonian given by equation (10.3) and the interaction hamiltonian $H_{int}=fO\cos\omega t$ in the limit of large n. In general, for interactions of the form $h=fO$, we get from equation (10.24) $\delta(O^2\omega_0)=\hbar/2M$, or $\delta(O\dot{O})=\hbar/2M$, $\delta(OP)=\hbar/2$, which corresponds to the uncertainty relations $\delta P\delta O\simeq\hbar/2$. As we shall see from examples below, for most simple cases the difference between P and P_{osc} is only a numerical factor of the order of the unity.

Similarly, the mean value of an operator O for the wavefunction ψ given by equation (10.17) is

$$\overline{O} = O_{nn} + \sum_k{}' \left(c_{kn} O_{kn}^* e^{-i\omega_{kn} t} + c_{kn}^* O_{kn} e^{i\omega_{kn} t} \right) \ ; \tag{10.28}$$

hence, we may see that the change brought about by the interaction in the (quasi-) classical matrix elements of an operator are included in

$$\frac{h}{2\hbar} O \left(\frac{e^{-i\omega t}}{\Delta\omega + i\alpha} + c.c. \right) = \frac{h}{\hbar} O \frac{\Delta\omega \cdot \cos\omega t - \alpha \sin\omega t}{(\Delta\omega)^2 + \alpha^2} \ \ , \tag{10.29}$$

where $\Delta\omega = \omega_0 - \omega$, the interaction has been removed adiabatically from t to $t \to \infty$ (in accordance with the relaxation term in the harmonic-oscillator equation) and irrelevant phase factors have been left aside. Now we compare the variation of this change with the classical solution given by equation (10.14),

$$2\frac{h}{\hbar}\delta O = \frac{(\partial h/\partial O)}{2M\omega_0} \ \ , \tag{10.30}$$

which is identical with equation (10.26) (the factor 2 in the *lhs* of equation (10.30) comes from the fact that the final state k is both $n + s$ and $n - s$).

10.3 Example 1. Planar rotator

Consider a dipole $\mathbf{d}$, consisting of a charge q with mass m, which can rotate freely in plane at a distance l form its axis (plane rotator); since $\mathbf{l} = l(\cos\varphi, \sin\varphi)$ and $\dot{\mathbf{l}} = l\dot{\varphi}(-\sin\varphi, \cos\varphi)$, we get the hamiltonian

$$H = \frac{1}{2} ml^2 \dot{\varphi}^2 = \frac{1}{2ml^2} L^2 \ \ , \tag{10.31}$$

where $L = ml^2\dot{\varphi}$ is the angular moment and $I = ml^2$ is the moment of inertia. Since $L = -i\hbar\frac{\partial}{\partial\varphi}$, we get the wavefunctions $\psi_l = \frac{1}{\sqrt{2\pi}} e^{il\varphi}$ and the energy levels $E_l = \hbar^2 l^2/2I$, $l = 0, 1, 2, ...$ (l denotes here both the quantum number and the dipole length); the matrix elements of the dipole moment $\mathbf{d}$ involve only states l and $l \pm 1$, with the frequency $\omega_{l\pm1,l} = (E_{l\pm1} - E_l)/\hbar{=}\frac{\hbar}{I}(\pm l + \frac{1}{2})$.

The angle φ is not a dynamical variable, so it is not suitable for a quasi-classical dynamics (though for large l there exists the classical limit, in the sense that φ can be localized by wavepackets with a high accuracy). Indeed, from the commutation relation $[L, \varphi] = -i\hbar$ we get $(l - l^{'})\varphi_{ll'} = -i\delta_{ll'}$, and $\varphi_{ll'} = 0$ for $l \neq l^{'}$, while φ_{ll} is undetermined. This result can be verified directly on the matrix elements

$$\begin{aligned} \varphi_{ll'} &= \tfrac{1}{2\pi}\int d\varphi \cdot \varphi e^{i(l^{'}-l)\varphi} = \\ &= \tfrac{\partial}{\partial[i(l^{'}-l)]}\tfrac{1}{2\pi}\int d\varphi e^{i(l^{'}-l)\varphi} = 0 \ , \ l \neq l^{'} \ ; \end{aligned} \tag{10.32}$$

similarly, $\dot{\varphi} = (i/\hbar)[H, \varphi] = L/I$, $\dot{\varphi}_{ll'} = (i/\hbar)(E_l - E_{l'})\varphi_{ll'} = (\hbar l/I)\delta_{ll'}$ and $\dot{\varphi}_{ll'} = 0$ for $l \neq l^{'}$; the classical motion proceeds with $\dot{\varphi} = L/I = const.$[6]

The projection of the dipole on an axis can play the role of a dynamical variable. Such an axis can be provided by an external electric field $\mathbf{E}(t) = \mathbf{E}\cos\omega t$. The orientation of the rotator is given by the direction of its angular momentum $\mathbf{L}$. In a local reference frame we may take $\mathbf{L}$ directed along the z axis; then, the electric field has the components $\mathbf{E} = E(\sin\theta, 0, \cos\theta)$ and the dipole can be written as $\mathbf{d} = d(\cos\varphi, \sin\varphi, 0)$. The interaction hamiltonian reads

$$H_{int}(t) = -\mathbf{dE}\cos\omega t = -dE\sin\theta\cos\varphi\cos\omega t \ ; \tag{10.33}$$

we take $x = l\cos\varphi$ as a dynamical variable and write the interaction hamiltonian as

$$H_{int}(t) = -(dE/l)x\sin\theta\cos\omega t = -qEx\sin\theta\cos\omega t \ . \tag{10.34}$$

We can see that the matrix elements $x_{ll'}$ are non-vanishing for $l^{'} = l \pm 1$; therefore we can write $\ddot{x}_s + \omega_s^2 x_s = 0$, where $s = 1$ and $\omega_s = (\hbar/I)(l +$

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[6] The direct calculation by parts of the integral in equation (10.32) requires the dismissal of the "surface" term, according to the rules of the Quantum Mechanics regarding orthogonal sets of eigenfunctions (see, for instance, E. Schrodinger, *Colected Papers on Wave Mechanics*, Am. Math. Soc., Chelsea Publishing, Providence, Rhode Island (1982)).

$1/2) \simeq (\hbar/I)l$ for $l \gg 1$ (indeed, we need $\hbar\omega_s/E_l = 2l+1 \gg 1$, in order to have energy levels densely distributed). It is worth noting that $\omega_s = (\hbar/I)l = L/I$ is the classical frequency in $x = l\cos(Lt/I)$ and, indeed, $\ddot{x} + (L/I)^2x = 0$. We drop out the label s in x_s and denote $\omega_0 = (\hbar/I)l$ with a fixed l; therefore, the corresponding quasi-classical equation of motion reads $\ddot{x} + \omega_0^2x = 0$ (also, we use x instead of δx). The force acting upon this harmonic oscillator is $(dE/l)\sin\theta\cos\omega t$, so that we have the quasi-classical equation of motion

$$\ddot{x} + \omega_0^2x = \frac{qE}{m}\sin\theta\cos\omega t \ . \tag{10.35}$$

The mean absorbed power is

$$\begin{aligned}\delta P_{osc} = \overline{qE\dot{x}\sin\theta\cos\omega t} = \tfrac{1}{2}qEb\omega\sin\theta = \\ = \tfrac{q^2E^2\sin^2\theta}{4m}\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ .\end{aligned} \tag{10.36}$$

According to equation (10.23) the power absorbed by quantum-rotation jumps is given by

$$P = \frac{\pi d^2E^2\sin^2\theta}{8\hbar}\omega_0\delta(\omega_0 - \omega) \ ; \tag{10.37}$$

since $\omega_0 = (\hbar/I)l$ we can see that $\delta P = (\pi q^2E^2\sin^2\theta/8m)\delta(\omega_0 - \omega)$, which differs from δP_{0sc} given by equation (10.36) by a factor 1/2. Such a discrepancy reflects the deviation of the quasi-classical approximation, based on harmonic oscillators, from the original dynamics.

It is worth noting that for large l we are in the classical limit, with the hamiltonian $L^2/2I - dE\sin\theta\cos\varphi\cos\omega t$; the equation of motion reads

$$\ddot{\varphi} = -\frac{dE}{I}\sin\theta\sin\varphi\cos\omega t \ ; \tag{10.38}$$

we solve this equation by perturbation theory, with a series $\varphi = \varphi_0 + \lambda\varphi_1 + ...$, where $\lambda = dE\sin\theta/I \ll 1$. With convenient initial conditions we get

$$\begin{aligned}\varphi = \omega_0t + \tfrac{\lambda}{2}\{\tfrac{\sin(\omega_0+\omega)t-(\omega_0+\omega)t}{(\omega_0+\omega)^2} + \\ + \tfrac{\sin(\omega_0-\omega)t-(\omega_0-\omega)t}{(\omega_0-\omega)^2}\} + ... \ ,\end{aligned} \tag{10.39}$$

which indicates a rotation with small oscillations. As expected, this classical solution is fundamentally different from the quantum-mechanical jumps and from the quasi-classical approximation. A friction term can be included in φ_0 (with the coefficient α such that $\alpha\lambda \ll 1$), with a similar conclusion.

10.4 Example 2. Spherical pendulum

The spherical pendulum (spatial, rigid rotator, spherical top) consists of a point of mass M which rotates freely in space at the end of a radius $\mathbf{l} = l(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, as described by the hamiltonian

$$H = \frac{1}{2}M\dot{\mathbf{l}}^2 = \frac{1}{2}Ml^2(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) \; ; \tag{10.40}$$

if the point has a charge q, it is a dipole $\mathbf{d} = q\mathbf{l}$ which can couple to an external electric field $\mathbf{E}\cos\omega t$, with an interaction hamiltonian $H_{int}(t) = -dE\cos\theta\cos\omega t$. We take the electric field directed along the z-axis.

As it is well known, the angular momentum $\mathbf{L} = M\mathbf{l}\times\dot{\mathbf{l}}$ has the components $L_x = Ml^2(-\dot{\theta}\sin\varphi - \dot{\varphi}\sin\theta\cos\theta\cos\varphi)$, $L_y = Ml^2(\dot{\theta}\cos\varphi - \dot{\varphi}\sin\theta\cos\theta\sin\varphi)$, $L_z = Ml^2\dot{\varphi}\sin^2\theta$ and the hamiltonian can be written as

$$H = \frac{1}{2I}L^2 \; , \tag{10.41}$$

where $I = Ml^2$ is the moment of inertia. The eigenfunctions are the spherical harmonics Y_{lm} with the eigenvalues $\hbar^2 l(l+1)$, $l = 0, 1, ...$. The z-component of the angular momentum is $L_z = -i\hbar\frac{\partial}{\partial\varphi}$, with the same eigenfunctions Y_{lm}, $L_zY_{lm} = \hbar mY_{lm}$, $m = -l, -l+1, ...l$. The energy levels of the spherical pendulum are $E_l = \frac{\hbar^2}{2I}l(l+1)$; they are degenerate with respect to the quantum number m, which takes $2l+1$ values. (l denotes here both the length of the dipole and the quantum number of the angular momentum).

The angles φ and θ do no admit a quasi-classsical approximation, in the sense discussed here for dynamical variables (this is a typical situation for the free motion). Indeed, the matrix elements $\varphi_{lm,lm'}$

are vanishing for $m \neq m^{'}$, while the matrix elements $\theta_{l,m;l+s,m}$ do not fall off rapidly with increasing s.

We can take $z = l\cos\theta$ as a quasi-classical variable with $s = 1$, corresponding to transitions from l to $l+1$; the generalized force is

$$(\partial/\partial t)(\dot{z}^{cl}) = \frac{qE}{M}\cos\omega t \tag{10.42}$$

and the equation of motion reads

$$\ddot{z} + \omega_0^2 z = \frac{qE}{M}\cos\omega t \ . \tag{10.43}$$

The mean absorbed power is given by

$$\delta P_{osc} = \frac{1}{2}qEb\omega_0 = \frac{q^2E^2}{4M}\frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ , \tag{10.44}$$

which should be multiplied by $2l+1 \simeq 2l$ in order to account for the degeneracy; we get $\delta P_{osc} = (\pi q^2E^2/2M)l\delta(\omega_0-\omega)$.

The transition rate of quantum jumps for $\omega_0 = (E_{l+1}-E_l)/\hbar = (\hbar/I)(l+1)$ is

$$\frac{\partial\left|c_{lm}\right|^2}{\partial t} = \frac{\pi d^2E^2}{2\hbar^2}\left|(\cos\theta)_{lm}\right|^2\delta(\omega_0-\omega) \ , \tag{10.45}$$

where

$$(\cos\theta)_{lm} = (\cos\theta)_{l+1,m;l,m} = -i\sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}} \ ; \tag{10.46}$$

the absorbed power is

$$\begin{aligned} P &= \hbar\omega_0 \textstyle\sum_{m=-l}^{l} \frac{\partial|c_{lm}|^2}{\partial t} = \\ &= \tfrac{\pi d^2E^2}{2\hbar}\omega_0 \textstyle\sum_{m=-l}^{l}\left|(\cos\theta)_{lm}\right|^2\delta(\omega_0-\omega) = \\ &= \tfrac{d^2E^2}{6\hbar}\omega_0(l+1)\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} = \\ &= \tfrac{d^2E^2}{6I}(l+1)^2\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ . \end{aligned} \tag{10.47}$$

We can see that $\delta P = (\pi d^2 E^2/3I) l \delta(\omega_0\text{-}\omega)$ (for $l \gg 1$), which differs from δP_{osc} given above by a factor 2/3.

We may consider the classical limit of the motion, corresponding to large values of $m \simeq l \gg 1$; in this case the φ-motion is in the classical limit (for large m and $\hbar \to 0$ the component L_z remains finite) and the associated Legendre polynomials P_{lm} in the spherical harmonics Y_{lm} are localized near the equator; indeed, $P_{ll} \sim \sin^l \theta$. For small variations $\delta\theta$ around $\pi/2$ we have $\delta\theta \simeq \sin\delta\theta = \cos(\pi/2 - \delta\theta) = \cos\theta$, so we have to take the matrix elements of $\cos\theta$, which are different from zero for $l^{'} = l \pm 1$. Consequently, we take $\delta\vartheta$ for O in the quasi-classical equation, $s = 1$ and $\omega_0 = (E_{l+1} - E_l)/\hbar \simeq (\hbar/I)l$, for a fixed $l \gg 1$; in addition, $\cos\theta$ in the interaction hamiltonian may be approximated by $\delta\theta$, where $\delta\theta$ is the new quasi-classical variable θ_s; the equation of quasi-classical motion is

$$\ddot{\theta}_s + \omega_0^2 \theta_s = -\frac{dE}{I}\cos\omega t \ . \tag{10.48}$$

The mean absorbed power is given by

$$\delta P = -dE\overline{\dot{\theta}_s \cos\omega t} = -\tfrac{1}{2} dEb\omega \simeq \tfrac{d^2E^2}{4I}\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ , \tag{10.49}$$

which coincides with equation (10.44) and the $m = l$-component of δP in equation (10.47), as expected (up to the degeneracy factor).

10.5 Extension to condensed matter

In condensed matter the energy levels have a limited meaning, as a consequence of the interaction between the atomic constituents. A coarse graining is meaningful in this case, which consists in taking a number N of atomic constituents, labelled by $i = 1, 2, ...N$, around each point in the sample, such that $N \gg 1$, but N is still much smaller than the total number of atomic constituents in the sample. The coarse graining implies averages of the type $O = (1/N)\sum_{i=1}^N O_i$ for any physical quantity O, so that any change δO is of the order $\delta O \sim \delta O_i/N$ (for an incoherent motion, like in "normal" condensed matter), or $\delta O/\delta O_i \sim 1/N \ll 1$; therefore, the quantum states (and the energy levels) are densely distributed and the quasi-classical approximation can be applied. Moreover, the quantum-mechanical states for each atomic constituent i are usually limited in number (like magnetic-moment states, for instance), so that the comparison between the quasi-classical approximation and the quantum-mechanical computations involves small quantum numbers; in this case δO is practically O, and P_{osc} is practically P, up to numerical factors of the order of unity. Usually, the (normal) condensed matter is at finite temperatures, which implies both direct and reverse quantum transitions (jumps). Making use of equation (10.22), the temperature-dependent power can be written as

$$\begin{gathered} P_{th}=\tfrac{\pi}{2\hbar}\omega_0\left(\sum\nolimits_n'\right)\times \\ \times\{\sum\nolimits_{m(n)}\left|h_{n+s,n}(m)\right|^2e^{-\beta E_n}- \\ -\sum\nolimits_{m(n+s)}\left|h_{n,n+s}(m)\right|^2e^{-\beta E_{n+s}}\}\times \\ \times\delta(\omega_0-\omega)/Z\ \ , \end{gathered} \tag{10.50}$$

where $(\sum_n')$ stands for the summation over those states n which are separated by the same frequency ω_0 from states $n+s$; $\sum_{m(n)}$ indicates a summation over possible degenerate states labelled by $m(n)$ for n (and $m(n+s)$ for $n+s$), which may affect the matrix elements of the interaction hamiltonian h; $\beta=1/T$ is the reciprocal of the temperature T; and

$$Z=\sum_n\sum_{m(n)}e^{-\beta E_n} \tag{10.51}$$

is the partition function. In the quasi-classical approximation equation (10.50) can be written approximately as

$$\begin{gathered} P_{th}=\left(\sum\nolimits_n'\right)\tfrac{\pi\left|h_s\right|^2}{2\hbar}\omega_0(\beta\hbar\omega_0)f(n)e^{-\beta E_n}\delta(\omega_0-\omega)/Z= \\ =\left(\sum\nolimits_n'\right)P(n)(\beta\hbar\omega_0)f(n)e^{-\beta E_n}/Z\ \ , \end{gathered} \tag{10.52}$$

where $\left|h_s\right|^2f(n)$ is the approximate result of the summation $\sum_{m(n)}\left|h_{n+s,n}(m)\right|^2$ and $\beta\hbar\omega_0$ was assumed to be much smaller than unity. In equation (10.52) P_{osc} may approximately be used for $P(n)$, according to the discussion above. For the particular case of a harmonic oscillator there is no degeneracy and summation in equation (10.52) extends over all the states ($P(n) \sim n$). The partition function is $Z = \sum_{n=o} e^{-\beta\hbar\omega_0 n} \simeq 1/\beta\hbar\omega_0$ and $\sum_{n=0} ne^{-\beta\hbar\omega_0 n} = 1/(\beta\hbar\omega_0)^2$, so that P_{th} is independent of temperature.

10.6 Example 3. Nuclear magnetic resonance

We consider the motion of a magnetic moment $\overrightarrow{\mu}$ in a constant (static) and uniform magnetic field $\mathbf{H}_0$ directed along the z-axis (the longitudinal field) and an oscillating magnetic field $\mathbf{H}(t) = \mathbf{H}\cos\omega t$, directed along the x-axis (the transverse field), where ω is the oscillation frequency. The interaction hamiltonian can be written as

$$H_{int} = -\overrightarrow{\mu}[H_0\mathbf{e}_z + H(t)\mathbf{e}_x] \ , \tag{10.53}$$

where $\mathbf{e}_{x,z}$ are the corresponding unit vectors. The Larmor equation $\dot{\overrightarrow{\mu}} = \gamma\overrightarrow{\mu} \times [H_0\mathbf{e}_z + H(t)\mathbf{e}_x]$ reads

$$\begin{gathered}\dot{\mu}_x = \gamma\mu_y H_0 \ , \\ \dot{\mu}_y = -\gamma\mu_x H_0 + \gamma\mu_z H\cos\omega t \ , \\ \dot{\mu}_z = -\gamma\mu_y H\cos\omega t \ ,\end{gathered} \tag{10.54}$$

where γ is the gyromagnetic factor.

The magnetic moment in the equations written above is a quantum-mechanical operator; it is related by the quantum-mechanical operator of the angular momentum $\mathbf{J}$ (spin) by $\overrightarrow{\mu} = g\mu_B\mathbf{J} = \gamma\hbar\mathbf{J}$, where g is a Lande factor, μ_B is a Bohr magneton (atomic or nuclear) and γ is a gyromagnetic factor (the magnetic moment of a particle, or assembly of particles, is given by $\mu = g\mu_B J = \gamma\hbar J$; it is convenient to use a suffix for this magnetic moment, and write, for instance, $\mu_p = g\mu_B J = \gamma\hbar J$, where the suffix p stands for "particle", in order to distinguish it from the magnitude $[(\overrightarrow{\mu})^2]^{1/2}$ of the operator $\overrightarrow{\mu}$). Making use of the commutation relations $[J_i, J_j] = i\varepsilon_{ijk}J_k$ of the operators of the angular momentum, the Larmor equations of motion written above are obtained from the quantum-mechanical equation of motion $\dot{\overrightarrow{\mu}} = (i/\hbar)[H_{int}, \overrightarrow{\mu}]$. The interaction $-\overrightarrow{\mu}\mathbf{H}_0 = -\mu_z H_0 = -\gamma\hbar J_z H_0$ splits the degenerate level according to $-\gamma\hbar m_z H_0$, where $m_z = -J, -J+1, ...J$ is the quantum number of the component J_z; it is convenient to introduce the frequency $\omega_0 = \gamma H_0$ and write the energy levels as $-\hbar\omega_0 m_z$. The states labelled by m_z are eigenstates of the operator J_z and μ_z; for each of these states J_z and μ_z are constant, while $\mu_{x,y}$ (and $J_{x,y}$) are undetermined; the mean value of $\mu_{x,y}$ (and $J_{x,y}$) over any state m_z is vanishing. The interaction $-\overrightarrow{\mu}\mathbf{H}(t) = -\gamma\hbar J_x H(t)$ produces transitions between the states m_z and $m_z \pm 1$, so it mixes up such states; consequently, we measure mean (average) values (expectation values) of the operators $\overrightarrow{\mu} = (\mu_x, \mu_y, \mu_z)$.

Therefore, we take the average of the magnetic moment over the quantum motion in equations (10.54) (quantum-mechanical averages); this means that we can replace the operator $\overrightarrow{\mu} = \gamma\hbar\mathbf{J}$ by its average, denoted $\overrightarrow{\mu_{av}}$ and given by

$$\overrightarrow{\mu_{av}} = \sum_{\sigma\sigma'} \int d\mathbf{r}\psi^*_{\sigma'}(\overrightarrow{\mu})_{\sigma'\sigma}\psi_\sigma \ , \tag{10.55}$$

where ψ_σ is the spinor corresponding to the angular momentum $\mathbf{J}$; $\overrightarrow{\mu_{av}}$ is now a classical variable which can be measured. It is this quantity which is often viewed as the magnetic moment, especially for assemblies of particles (a similar average $\mathbf{J}_{av}$ can be introduced for the angular momentum, so we can preserve the equation $\overrightarrow{\mu_{av}} = \gamma\hbar\mathbf{J}_{av}$); we note that equations (10.55) define also a density of magnetic moment (magnetization). For a sample of condensed matter $\overrightarrow{\mu_{av}}$ can carry a position label $\mathbf{r}_i$, denoting the position of the i-th particle with this magnetic moment; in a course-graining average, specific to the continuum models of matter, the label $\mathbf{r}_i$, may become the continuous, local position $\mathbf{r}$, so that the corresponding average magnetic moment $\overline{\overrightarrow{\mu_{av}}}$ may be a function $\overline{\overrightarrow{\mu_{av}}}(t, \mathbf{r})$ of the time t and position $\mathbf{r}$. Moreover, the measurable quantities in condensed matter are statistical averages, so that we may assume that we have a local thermodynamic equilibrium and $\overline{\overrightarrow{\mu_{av}}}(t, \mathbf{r})$ is also averaged over such a statistical distribution, which can be written as $\overline{\overline{\overrightarrow{\mu_{av}}}}$. If we are not interested in the spatial variations (which may imply diffusion of the moments), we may leave aside the

r-dependence; for simplification we may also leave aside the average bars and the suffix av, and write simply $\overrightarrow{\mu}$ for this classical quantity; in fact, it is more convenient to use the magnetization **M** (the magnetic moment of the unit volume, accordingly averaged), which obeys the equations of motion

$$\begin{aligned} \dot{M}_x &= \gamma M_y H_0 \ , \\ \dot{M}_y &= -\gamma M_x H_0 + \gamma M_z H \cos\omega t \ , \qquad (10.56) \\ \dot{M}_z &= -\gamma M_y H \cos\omega t \ , \end{aligned}$$

derived from equations (10.55) by the succession of averages described above (quantum-mechanical, coarse-graining, statistical). We consider here the particular situation of magnetic moments associated with atomic nuclei, but the procedure described above is more general and can also be applied to other magnetic moments. The average procedure described here for the magnetic moments in condensed matter is the quasi-classical approximation as presented in this paper.

At thermal equilibrium the statistical average of the magnetization is zero; applying the magnetic field $\mathbf{H}_0$ an interaction $-\overrightarrow{\mu}\mathbf{H}_0$ appears, which restores the thermal equilibrium with a non-zero average magnetic moment directed along the longitudinal field $\mathbf{H}_0$. Since the interaction energy μH_0 is much smaller than the temperature T, we may use the distribution $\sim e^{\overrightarrow{\mu}\mathbf{H}_0/T}$ of the classical statistics; we get the statistical average of the magnetic moment $\overline{\mu_z} = \mu^2 H_0/3T$ and the longitudinal magnetization $M_0 = n\overline{\mu}_z = n\mu^2 H_0/3T$, where n is the density of particles; the transverse components of the magnetization are vanishing ($M_{x,y} = 0$); here μ is the "magnetic moment of the particle" ($\mu = \mu_p = \gamma\hbar J$). As it is well known, this is the Curie-Langevin-Debye law.[7] The relaxation of the longitudinal mag-

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[7] P. Curie, "Lois experimentales du magnetisme. Proprietes magnetiques des corps a diverses temperatures", Ann. Chim. Phys. **5** 289 (1895); P. Langevin, "Sur la theorie du magnetisme", J. Physique **4** 678 (1905); P. Langevin, "Magnetism et theorie des electrons", Ann. Chim. Phys. **5** 70 (1905); P. Debye, "Einige Resultate einer kinetischen Theorie der Isolatoren", Phys. Z. **13** 97 (1912).

netization is governed by the kinetic equation

$$\frac{dM_z}{dt} = \alpha_1(M_0 - M_z) \ , \tag{10.57}$$

where α_1 is a (longitudinal) damping coefficient; the solution is $M_z = M_0(1 - e^{-\alpha_1 t})$, for zero initial magnetization. The average transverse magnetization is vanishing; if, by external means, we take the transverse magnetization out of equilibrium ($M_{x,y0} \neq 0$ initially), it will relax according to

$$\frac{dM_x}{dt} = -\alpha_2 M_x \ , \ \frac{dM_y}{dt} = -\alpha_2 M_y \ , \tag{10.58}$$

where α_2 is a transverse damping coefficient. The solution is $M_{x,y} = M_{x,y0}e^{-\alpha_2 t}$.[8] By including these damping coefficients, equations (10.56) become

$$\begin{aligned} \dot{M}_x &= \gamma M_y H_0 - \alpha_2 M_x \ , \\ \dot{M}_y &= -\gamma M_x H_0 + \gamma M_z H \cos\omega t - \alpha_2 M_y \ , \\ \dot{M}_z &= -\gamma M_y H \cos\omega t - \alpha_1(M_z - M_0) \ ; \end{aligned} \tag{10.59}$$

for small values of the field H we may approximately put $M_z \simeq M_0$ in these equations and neglect the time-dependence of the longitudinal component M_z of the magnetization; then, equations (10.59) can be approximated by

$$\begin{aligned} \dot{M}_x &\simeq \gamma M_y H_0 - \alpha_2 M_x \ , \\ \dot{M}_y &\simeq -\gamma M_x H_0 + \gamma M_0 H \cos\omega t - \alpha_2 M_y \ , \end{aligned} \tag{10.60}$$

or

$$\begin{aligned} \dot{M}_x &\simeq \omega_0 M_y - \alpha_2 M_x \ , \\ \dot{M}_y &\simeq -\omega_0 M_x + \omega_m H \cos\omega t - \alpha_2 M_y \ , \end{aligned} \tag{10.61}$$

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[8] For more details regarding the relaxation coefficients, see, for instance, Ch. Kittel, *Introduction to Solid State Physics*, Wiley, NJ (2005).

where $\omega_0 = \gamma H_0$ and $\omega_m = \gamma M_0$. These equations can be transformed into

$$\begin{aligned} \ddot{M}_x + \omega_0^2 M_x + \alpha_2 \dot{M}_x &= \omega_0 \omega_m H \cos\omega t \ , \\ \ddot{M}_y + \omega_0^2 M_y + \alpha_2 \dot{M}_y &= -\omega \omega_m H \sin\omega t \ , \end{aligned} \qquad (10.62)$$

for $\alpha_2 \ll \omega_0, \omega_m$, which are equations of motion of damped harmonic oscillators, in accordance with their quasi-classical nature. The particular solution of equations (10.61) is given by

$$\begin{aligned} M_x &= a\cos\omega t + b\sin\omega t \ , \\ M_y &= \tfrac{-a\omega + b\alpha_2}{\omega_0}\sin\omega t + \tfrac{b\omega + a\alpha_2}{\omega_0}\cos\omega t \ , \end{aligned} \qquad (10.63)$$

where

$$\begin{aligned} a &= -\omega_0 \omega_m H \tfrac{\omega^2 - \omega_0^2 - \alpha_2^2}{(\omega^2 - \omega_0^2 - \alpha_2^2)^2 + 4\omega^2\alpha_2^2} \ , \\ b &= \omega_0 \omega_m H \tfrac{2\omega\alpha_2}{(\omega^2 - \omega_0^2 - \alpha_2^2)^2 + 4\omega^2\alpha_2^2} \ . \end{aligned} \qquad (10.64)$$

We can simplify these solutions by using $\alpha_2 \ll \omega_0$, ω_m and assuming ω close to ω_0. We get

$$M_x \simeq a\cos\omega t + b\sin\omega t \ , \ M_y \simeq -a\sin\omega t + b\cos\omega t \ , \qquad (10.65)$$

where

$$a \simeq -\tfrac{1}{2}\omega_m H \tfrac{\omega - \omega_0}{(\omega - \omega_0)^2 + \alpha_2^2} \ , \ b \simeq \tfrac{1}{2}\omega_m H \tfrac{\alpha_2}{(\omega - \omega_0)^2 + \alpha_2^2} \ . \qquad (10.66)$$

These solutions are obtained also from the oscillator equations (10.62) with $\alpha_2 \to \alpha_2/2$ in equations (10.66). From equations (10.63) we can see that the magnetization performs a Larmor precession about the z-axis with frequency ω (the frequency of the external field); the transverse magnetization rotates with constant magnitude $M_x^2 + M_y^2 = a^2 + b^2 \simeq (\omega_m H / 2\alpha_2)^2$. The power absorbed from the field and dissipated by the motion of the transverse magnetization can be obtained from equations (10.62), through

$$\tfrac{d}{dt}\left(\tfrac{1}{2}\dot{M}_x^2 + \tfrac{1}{2}\omega_0^2 M_x^2\right) + \alpha_2 \dot{M}_x^2 = \omega_0 \omega_m H \dot{M}_x \cos\omega t \ , \qquad (10.67)$$

We get

$$P_{osc} = \overline{H\dot{M}_x \cos\omega t} = \frac{1}{2}Hb\omega = \frac{1}{4}\omega_m H^2 \frac{\omega\alpha_2}{(\omega-\omega_0)^2+\alpha_2^2} \ ; \qquad (10.68)$$

or

$$P_{osc} = \frac{\pi}{4}\omega_m\omega_0 H^2\delta(\omega-\omega_0) \ , \ \alpha_2 \to 0^+ \ (\alpha_2 \ll \omega_0) \ . \qquad (10.69)$$

These are typical solutions of damped harmonic oscillators exhibiting resonance for $\omega = \omega_0$. This is the typical solution of the magnetic resonance.[9] As it is well known, equations (10.59) and (10.60) are called Bloch equations.[10]

Let us calculate now the power absorbed in magnetic resonance by quantum-mechanical transitions $m_z \to m_z \pm 1$ caused by the interaction hamiltonian $H_{int}(t) = -\gamma\hbar I_x H\cos\omega t$ (we denote the nuclear spin by $\mathbf{I}$); each of these transitions proceeds with the absorption or emission of the quanta of energy $\hbar\omega_0$; these transitions release and absorb energy, and we are interested in the net energy absorption rate per unit time.

In the presence of the longitudinal field $\mathbf{H}_0$ the energy levels are given by $-\gamma\hbar H_0 m_z = -\hbar\omega_0 m_z$; the lowest energy level has $m_z = I$ and the highest energy level has $m_z = -I$. The energy absorption proceeds from m_z to $m_z - 1$, where $m_z = I,\ I-1, ... -I+1$, with the rate

$$\frac{\partial\left|c_{m_z-1}\right|^2}{\partial t} = \frac{1}{2}\gamma^2 H^2\left|(I_x)_{m_z-1,m_z}\right|^2 \frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ ; \qquad (10.70)$$

the energy emission implies transitions from m_z to m_z+1, where $m_z = I-1,\ I-2, ... -I$; the rate of these transitions is given by

$$\frac{\partial\left|c_{m_z+1}\right|^2}{\partial t} = \frac{1}{2}\gamma^2 H^2\left|(I_x)_{m_z+1,m_z}\right|^2 \frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ ; \qquad (10.71)$$

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[9] E. M. Purcell, H. C. Torrey, R. V. Pound, "Resonance absorption by nuclear magnetic moments in a solid", Phys. Rev. **69** 37 (1946); F. Bloch, W. W. Hansen and M.Packard, "Nuclear induction", Phys. Rev. **69** 127 (1946); F. Bloch, W. W. Hansen and M. Packard, "The nuclear induction experiment", Phys. Rev. **70** 474 (1946).

[10] F. Bloch, "Nuclear induction", Phys. Rev. **70** 460 (1946).

the matrix elements of the spin component I_x are

$$\begin{aligned}(I_x)_{m_z-1,m_z} &= \tfrac{1}{2}[(I+m_z)(I-m_z+1)]^{1/2} \ , \\ (I_x)_{m_z+1,m_z} &= \tfrac{1}{2}[(I-m_z)(I+m_z+1)]^{1/2} \ .\end{aligned} \tag{10.72}$$

The transition rates must be weighted by the statistical distribution $e^{\beta\hbar\omega_0 m_z}/\sum_{m_z} e^{\beta\hbar\omega_0 m_z}$, so that the net transition rate is given by

$$\begin{aligned}R = \overline{\tfrac{\partial|c_{m_z-1}|^2}{\partial t}} - \overline{\tfrac{\partial|c_{m_z+1}|^2}{\partial t}} = \\ = \tfrac{1}{2}\gamma^2 H^2 \overline{|I_x|^2} \tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ ,\end{aligned} \tag{10.73}$$

where

$$\begin{aligned}\overline{|I_x|^2} = \{\textstyle\sum_{m_z=I}^{-I+1} |(I_x)_{m_z-1,m_z}|^2 - \\ - \textstyle\sum_{m_z=I-1}^{-I} |(I_x)_{m_z+1,m_z}|^2\}\times \\ \times e^{\beta\hbar\omega_0 m_z}/\textstyle\sum_{m_z=I}^{-I} e^{\beta\hbar\omega_0 m_z} = \\ = \tfrac{1}{4}\{\textstyle\sum_{m_z=I}^{-I+1}(I^2+I+m_z-m_z^2) - \\ - \textstyle\sum_{m_z=I-1}^{-I}(I^2+I-m_z-m_z^2)\}\times \\ \times e^{\beta\hbar\omega_0 m_z}/\textstyle\sum_{m_z=I}^{-I} e^{\beta\hbar\omega_0 m_z}\end{aligned} \tag{10.74}$$

(here, the net emission rate is equal with the net absorption rate, R in equation (10.73) being, in fact, $|R|$); the rearrangement of the summations in equation (10.74) leads to

$$\overline{|I_x|^2} = \frac{1}{2}\sum_{m_z-I}^{I} m_z e^{\beta\hbar\omega_0 m_z} / \sum_{m_z=-I}^{I} e^{\beta\hbar\omega_0 m_z} = \frac{1}{2}\overline{m_z} \ , \tag{10.75}$$

where $\overline{m_z}$ is the thermal average of the quantum number m_z. For $\beta\hbar\omega_0 \ll 1$ we get $\overline{m_z} = \hbar\omega_0 I(I+1)/3T$ (and $\overline{m_z^2} = I(I+1)/3$); we note that the average magnetic moment directed along the z-axis is $\gamma\hbar\overline{m_z} = \gamma^2\hbar^2 H_0 I(I+1)/3T$ while the same average calculated with the classical statistics is $\mu^2 H_0/3T = \gamma^2\hbar^2 H_0 I^2/3T$ (as given above); in the quantum-mechanical statistics I^2 is replaced by $I(I+1)$, as expected. Inserting $\overline{|I_x|}^2$ given by equation (10.75) in equation (10.73) we get the net absorption rate

$$R = \frac{1}{4}\gamma^2 H^2 \overline{m_z}\frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \tag{10.76}$$

and the power absorbed per unit volume

$$P = n\hbar\omega_0 R = \frac{1}{4}n\hbar\omega_0\gamma^2 H^2\overline{m_z}\frac{\alpha}{(\omega-\omega_0)^2+\alpha^2}\ , \tag{10.77}$$

or

$$\begin{aligned} P &= \tfrac{1}{4}\gamma\omega_0 M_0 H^2\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} = \\ &= \tfrac{1}{4}\omega_m\omega_0 H^2\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2}\ , \end{aligned} \tag{10.78}$$

since $n\gamma\hbar\overline{m_z}$ is the magnetization M_0 along the z-axis (and $\omega_m = \gamma M_0$). This equation should be compared with the equation (10.68) which gives the absorbed power per unit volume within the classical treatment; we can see that they are the same (near the resonance, with $\alpha = \alpha_2$, up to I^2 replaced by $I(I+1)$ in magnetization and ω_m). We note that the perturbation is applied here adiabatically (for a long time), which warrants the attaining of the thermal equilibrium.

10.7 Example 4. Nuclear quadrupole resonance

It may happen that the structure of the quantum states of the magnetic moment (spin) is not governed by an external field, as H_0 in the case of the magnetic resonance described above, but it is produced by local interactions of the magnetic moments with their environment. For instance, the hyperfine interaction acts in the case of paramagnetic (spin) resonance, the quadrupole interaction determines the nuclear quadrupole resonance, etc. In such cases the direct application of the averages technique in the equations of motion of the magnetic moment described above is not convenient, since these equations depend also on external degrees of freedom, or have a non-linear structure. First, we should take into account the effect of the local interaction with the surrounding medium. The quantum nature of the condensed matter has certain particularities, which may allow a quasi-classical description.

In normal condensed matter the wavefunctions and energy levels have a limited validity, due, on one side, to the large number of states densely distributed in energy, to the natural uncertainties arising from internal, residual interactions and, on the other side, to the inevitable interaction with the external world, which makes practically impossible the preparation of a pure quantum state. In fact, mixed states described by the density matrix, or thermodynamic states described by the statistical matrix are appropriate for condensed matter, exhibiting, to a large extent, a classical behaviour. These particularities also provide the basis for a quasi-classical dynamics in some cases in condensed matter. (This is true for usual conditions, which define a "normal" condensed matter. At low temperatures, we may encounter quantum states for condensed matter, like superfluidity, superconductivity, ferromagnetism, etc).

The nuclear magnetic moments in solids are affected by the interaction with the surrounding ions, which generate high gradients of electric field. Consequently, a quadrupole interaction

$$V_2 = \frac{1}{6}\sum_{ij} Q_{ij} V_{ij} \ , \ V_{ij} = \frac{\partial^2 \Phi}{\partial x_{ai} \partial x_{aj}} \tag{10.79}$$

acts on the nuclear magnetic moments, where Q_{ij} is the tensor of the quadrupole moment, Φ is the electric potential at the location of the magnetic moment, a denotes the surrounding ions and i, j are cartesian coordinates. This interaction splits the degeneracy of the energy levels with respect to the magnetic quantum number m (and shifts the energy levels), such that transitions between such levels may be induced by an external time-dependent magnetic field (the energy levels can depend on the temperature). These transitions have a resonance character, and are known as the nuclear quadrupole resonance.[11] (The resonance frequencies are in the radiofrequency range.

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[11] W. A. Nierenberg, N. F. Ramsey and S. B. Brody, "Measurements of Nuclear

The nuclear quadrupole resonance does not appear for nuclear spins $I = 0$, $1/2$, which give a vanishing quadrupole moment. The average of the quadrupole interaction with respect to the molecular motion leads to a very weak effective interaction in liquids, so that the nuclear quadrupole resonance is not observed in liquids, or in gases, where the interaction is very weak).

Let us consider a sample of condensed matter consisting of atomic constituents (not necessarily identical), like atoms, ions, molecules, spins, magnetic moments, etc (at rest, as in solids, or in motion as in liquids, gases, etc). As independent entities, each of these atomic constituents has its own (quantum) dynamics, defined by stationary states and energy levels. Some of these states may be degenerate, as, for instance, the spin states associated with various spatial orientations of the spin (the spatial degeneray). The local interaction occurring in condensed matter, between these atomic constituents, or between them and their environment leads to changes in these quantum states, or to generation of new quantum states, as, for instance, those occurring by the removal of the degeneracies. Let us consider a collection of N such "quantum systems" labelled by $i = 1, 2...N$, each with a set of quantum states labelled by quantum numbers n_i and energy ε_{n_i}, such as the total energy of the collection is $E_n = \varepsilon_{n_1} + \varepsilon_{n_2} + ... + \varepsilon_{n_N}$; it is convenient to denote the states of the collection by $n = (n_1, n_2, ...n_N)$. Now we see that another energy $E_{n'}$ is obtained by changing at least by a unity at least one of the quantum numbers n_i, for instance $E_{n'} = \varepsilon_{n_1} + ... + \varepsilon_{n'_i} + ... + \varepsilon_{n_N}$, where $n'_i = n_i \pm 1$. Such a change implies a small difference in energy, $E_{n'} - E_n$ in comparison with the energies $E_{n,n'}$, providing $N \gg 1$. If the dynamics is such that the change in energy proceeds in time Δt, then $E_{n'} - E_n$ is of the order $\hbar/\Delta t$, where $\hbar$ is Planck's constant. This indicates a change in the mechanical action of the order $\hbar$, which is much smaller that the mechanical action associated to the whole set of N systems. Consequently, we may adopt a quasi-classical description for the dynamics of the assembly of N systems. Moreover, we may take such assemblies

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Quadrupole Moment Interactions", Phys. Rev. **70** 773 (1946); W. A. Nierenberg and N. F. Ramsey, "The radiofrequency spectra of sodium halides", Phys. Rev. **72** 1075 (1947); H.-G. Dehmelt and H. Kruger, "Kernquadrupolfrequenzen in festen dichlorathylen", Naturwiss. **37** 111 (1950); R. V. Pound, "Nuclear electric quadrupole interactions in crystals", Phys. Rev. **79** 685 (1950).

in the vicinity of any position in the sample, and take the average of the physical quantities over such coarse-graining structures; the number N of systems in each assembly is much larger than unity, but still sufficiently small at the macroscopic scale as to allow the definition of a coarse-graining averaged model (possibly continuous) for the macroscopic sample. The physical quantities defined in this manner are classical quantities which obey a (quasi-) classical dynamics.

If the perturbation hamiltonian is given by $H_{int}(t) = -\overrightarrow{\mu}\mathbf{H}\cos\omega t$, where $\overrightarrow{\mu}$ is the (quasi-) classical magnetic moment, the quasi-classical dynamics for a frequency $\omega_s = \omega_0$ is governed by the quasi-classical equations of motion

$$\dot{\overrightarrow{\mu}} = -i\omega_0\overrightarrow{\mu} + \gamma\overrightarrow{\mu^{cl}} \times \mathbf{H}\cos\omega t \ , \tag{10.80}$$

where γ is the gyromagnetic factor; in this equation $\overrightarrow{\mu}$ is the magnetic moment generated by the magnetic field $\mathbf{H}\cos\omega t$ (particular solution) and $\overrightarrow{\mu^{cl}}$ may have a non-vanishing part $\overrightarrow{\mu_0}$ generated by the statistical distribution over the states whose energies are denoted $\hbar\omega(m)$; $\hbar\omega_0$ is one of the differences $\hbar\omega(m^{'}) - \hbar\omega(m)$, according to the selection rules; it is these contributions $\overrightarrow{\mu_0}$ which are retained in $\overrightarrow{\mu^{cl}}$. Equations (10.80) for the real part of the moment $\overrightarrow{\mu}$ become

$$\ddot{\overrightarrow{\mu}} + \omega_0^2\overrightarrow{\mu} = -\gamma\omega\overrightarrow{\mu_0} \times \mathbf{H}\sin\omega t \ . \tag{10.81}$$

We may assume that the thermal average of the magnetic moment is vanishing in the absence of the interaction,

$$\overline{\overrightarrow{\mu_0}} = \sum \overrightarrow{\mu_0} e^{-\beta H} / \sum e^{-\beta H} = 0 \ , \tag{10.82}$$

where $\beta = 1/T$ is the inverse of the temperature T. In the presence of the interaction which produces the energy levels $\hbar\omega(m)$ the mean value of the magnetic moment is

$$\begin{aligned} \overline{\overrightarrow{\mu_0}} = \textstyle\sum \overrightarrow{\mu_0} e^{-\beta H - \beta\hbar\omega(m)} / \textstyle\sum e^{-\beta H - \beta\hbar\omega(m)} \simeq \\ \simeq -\beta\hbar\overline{\overrightarrow{\mu_0}\omega(m)} \ , \end{aligned} \tag{10.83}$$

for $\beta\hbar\omega(m) \ll 1$; it is differences of the type $\hbar\omega(m^{'}) - \hbar\omega(m)$ which matters in this mean value, so we may write conveniently $\overline{\overrightarrow{\mu_0}\omega(m)} =$

$\mathbf{c}\mu\omega_0$, where $\mathbf{c}$ is an undetermined numerical vectorial coefficient directed along the mean magnetization (magnetic moment $\overrightarrow{\mu_0}$) and μ is the magnetic moment. Now, equations (10.81) can be written for magnetization (including damping) as

$$\ddot{\mathbf{M}} + \omega_0^2\mathbf{M} + 2\alpha\dot{\mathbf{M}} = \omega\omega_m\mathbf{c} \times \mathbf{H}\sin\omega t \ , \tag{10.84}$$

where $\omega_m = \gamma n\mu(\hbar\omega_0/T)$, n being the density of magnetic moments; $\mathbf{M}_0 = n\beta\hbar\mu\omega_0\mathbf{c} = (\omega_m/\gamma)\mathbf{c}$ is a static magnetization. We can see now that the situation is very much similar to the nuclear magnetic resonance ; in fact, the classical equations (10.84) apply also to the nuclear magnetic resonance with $\mathbf{c} = \mathbf{e}_z$. We note the occurrence of the vector $\mathbf{c}$ in the nuclear quadrupole resonance, which indicates the anisotropy of the magnetization.

The (particular) solution of equations (10.84) is

$$\mathbf{M} = \mathbf{c} \times \mathbf{H}(a\sin\omega t + b\cos\omega t) \ , \tag{10.85}$$

where

$$a = -\frac{1}{2}\omega_m\frac{\omega - \omega_0}{(\omega - \omega_0)^2 + \alpha^2} \ , \ b = -\frac{1}{2}\omega_m\frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} \tag{10.86}$$

(for ω near the resonance frequency ω_0); the absorbed (mean) power (per unit volume) is given by

$$\begin{aligned} P = \overline{(\mathbf{c} \times \mathbf{H})\dot{\mathbf{M}}\sin\omega t} = -\tfrac{1}{2}\omega_0 b(\mathbf{c} \times \mathbf{H})^2 = \\ = \tfrac{1}{4}\omega_m\omega_0(\mathbf{c} \times \mathbf{H})^2\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ . \end{aligned} \tag{10.87}$$

The magnetization induced by the external field $\mathbf{H}\cos\omega t$ performs a rotation about $\mathbf{H}$ in the plane perpendicular to $\mathbf{H}$ and $\mathbf{c}$ with the angular frequency ω. The power computed by means of the quantum transitions of the interaction hamiltonian $H_{int}(t) = -\overrightarrow{\mu}\mathbf{H}\cos\omega t$ coincides with the absorbed power given by equation (10.87), providing the numerical vector $\mathbf{c}$ is determined from the matrix elements of the magnetic moment $\overrightarrow{\mu}$ (the thermal average of the transition rate being taken). We emphasize again that the considerations made above assume the thermal equilibrium which requires times longer than the damping (relaxation) times; for short pulses of the external field the magnetization suffers a sudden nutation and precession; the mean value can be computed by means of the perturbation theory; it is of the order $n\mu$ multiplied by a reduction factor $\left|H_{int}\right|/\hbar\Delta\omega \simeq \gamma H/\Delta\omega$, where $\Delta\omega$ is the bandwidth generated by the pulse (the inverse of the duration of the pulse); this estimation may be taken as M_0 in the damped free-oscillation solution (free induction) of the harmonic oscillator equation.

The quadrupole interaction V_2 exhibits, in general, an anisotropy; its diagonalization, which leads to eigenfreqencies denoted by ω_0 in the quasi-classical approximation, defines an ellipsoid (the principal axes of the quadratic form); the external radiofrequency field **H** may have an arbitrary orientation with respect to these axes, as expressed by the vectorial product $\mathbf{c} \times \mathbf{H}$ in equation (10.85). If the sample is an amorphous solid, or it is impurified, or it is a powder, etc, an average must be taken over the orientations of the sample, as given by $\overline{\sin^2\theta}$ in the equation for the absorbed power, where θ is the angle between **H** and **c**.

An external, uniform magnetic field H_0 can be applied in NQR experiments; it produces energy levels $\hbar\omega(m) = \gamma\hbar m H_0$, which combine now with the energy levels produced by the quadrupole interaction V_2 to give the frequencies ω_0.

10.8 Discussion and conclusions

The time dependence of the quantum-mechanical operators (Heisenberg representation) has been investigated here in the quasi-classical approximation, where the energy levels are densely distributed. It has been shown, in these circumstances, that physical quantities behave approximately as classical harmonic oscillators, with eigenfrequencies given by the difference in energy levels. Under the action of a time-dependent external field these classical oscillators absorb (dissipate) energy, which approximates the variation, with respect to the quantum numbers, of the energy absorbed in quantum-mechanical transitions. Two examples of simple quantum-mechanical systems are given in this respect (planar and spatial rigid rotators endowed with an electric dipole moment), which may serve to further enlighten the details of the approximation involved. In condensed matter the coarse graining average provides a natural means for the quasi-classical approximation. This approximation has been illustrated here for magnetic resonance and the nuclear quadrupole resonance. The quasi-classical equations of motion presented in this paper may shed further light upon the relationship between Quantum Mechanics and Classical Mechanics.

11 Epilogue

11.1 Introduction

The temporal Fourier series of a function $\psi(t)$ reads

$$\psi(t)=\frac{1}{T}\sum_{\omega}a_{\omega}e^{-i\omega t}=\sum_{n}\varphi_{n}e^{-i\frac{2\pi}{T}nt}\quad , \tag{11.1}$$

where the period of $\psi(t)$ is T and $\varphi_n=a_\omega/T$; it includes all the harmonics $\omega=\omega_n=\frac{2\pi}{T}n$ of the fundamental frequency $\omega_1=\frac{2\pi}{T}$, where n is any integer. The independent coordinates Q_i and momenta P_i of a finite mechanical motion with s degrees of freedom ($i=1,2,...s$) are periodic functions with periods T_i, so they may be represented by a temporal Fourier series of the type given by equation (11.1). The motion implies the mixture of the coordinates Q_i and momenta P_i, so that the normal coordinates q_i and the corresponding momenta p_i are, in general, functions of Q_i and P_i, and so is any physical quantity $F=F(\{q_i\},\{p_i\})=F(\{Q_i\},\{P_i\})$. Therefore, the coordinates q_i and momenta p_i, as well as any physical quantity are represented by multiply periodic Fourier series, of the form

$$q_i=\sum_{n_1n_2,...n_s}q^{(i)}_{n_1n_2...n_s}e^{-i2\pi(\frac{n_1}{T_1}+\frac{n_2}{T_2}+...\frac{n_s}{T_s})t}\quad ; \tag{11.2}$$

in general, such a series is not periodic anymore. If the motion is not multiply periodic, the labels n_i are continuous and the series become integrals. For brevity, we denote $n=(n_1,\,n_2,...n_s)$, $\omega_n=2\pi(\frac{n_1}{T_1}+\frac{n_2}{T_2}+...\frac{n_s}{T_s})$ and $q^{(i)}_n=q^{(i)}_{n_1n_2...n_s}$ and omit the upper label i; we get

$$q(t)=\sum_{n}q_{n}e^{-i\omega_n t} \tag{11.3}$$

for any coordinate q_i and conjugate momentum p_i, as well as

$$\psi(t) = \sum_n \varphi_n e^{-i\omega_n t} \tag{11.4}$$

for any function of q_i and p_i.

If, according to Planck and Einstein,[1] the energy is $E_n = \hbar\omega_n$, the series given above read

$$\psi(t) = \sum_n \varphi_n e^{-\frac{i}{\hbar}E_n t} \;,\; q(t) = \sum_n q_n e^{-\frac{i}{\hbar}E_n t} \;. \tag{11.5}$$

We measure only differences of energy $E_n - E_{n'}$, so any measurable quantity should contain only such differences; consequently, we write

$$q(t) = \sum_{nn'} q_{nn'} e^{\frac{i}{\hbar}(E_n - E_{n'})t} \;,\; F(t) = \sum_{nn'} F_{nn'} e^{\frac{i}{\hbar}(E_n - E_{n'})t} \;, \tag{11.6}$$

where q is any (measurable) coordinate and F is any measurable physical quantity; similar series expansions are valid for momenta. Equation (11.6) is Heisenberg's new, quantum-mechanical "Umdeutung kinematischer und mechanischer Beziehungen", which marked the beginning of the Quantum Mechanics.[2] F in equation (11.6) is a quantum quantity and the labels n, $n^{'}$ are called quantum numbers.

11.2 Old Quantum Mechanics

For large n, $n^{'}$ we may limit ourselevs to $n^{'}$close to n; writing $E_{n'} = E_n + s\partial E_n/\partial n$ for fixed n we have

$$F(t) = \sum_s F_{n,n+s} e^{-\frac{i}{\hbar}s(\partial E_n/\partial n)t} \;, \tag{11.7}$$

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[1] M. Planck, "Zur Theorie des Gesetzes der Energieverteilung in Normalspektrum", Verhandl. der Deutschen physikalischen Gesellschaft **2** 237 (1901); A. Einstein, "Uber einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt", Ann. Phys. **17** 132 (1905); A. Einstein, "Zur Quantentheorie der Strahlung", Phys. Z. **18** 121 (1917) (Mitteil. physikalischen Gesellschaft Zurich **18** (1916)).

[2] W. Heisenberg, "Uber Quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen", Z. Phys. **33** 879 (1925); W. Heisenberg, *The Physical Principles of the Quantum Theory*, Dover, NY (1949).

which is easily recognizable as the temporal Fourier series of a classical quantity $F(t)$; the dependence on n in equation (11.7) is weak. Therefore, in the limit of large quantum numbers, the quantum quantities become classical quantities (and the quantum numbers may be approximated by continuous numbers); *i.e.*, under such circumstances we get the classical limit of the Quantum Mechanics. This is Bohr's correspondence principle, which guided guesses in the "Old Quantum Mechanics", *i.e.* before 1925 Heisenberg's paper.[3] We note that the approximations involved in the correspondence principle imply large amounts of relevant mechanical action (the product energy by time, for instance) in comparison with Planck's constant $\hbar$.

Moreover, if $F_{n,n+s}$ in equation (11.7) depends slightly on s, denoting $\omega_0 = (1/\hbar)(\partial E_n/\partial n)$, we get from equation (11.7)

$$F(t) \simeq \overline{F}\frac{2\sin\Delta s\omega_0 t}{\omega_0 t} \ , \tag{11.8}$$

by integration over s from $-\Delta s$ to Δs, where $\overline{F}$ is an average of $F_{n,n+s}$. $F(t)$ as given by equation (11.8) has a maximum for $t = 0$, extended over $\Delta t \simeq \pi/\Delta s\omega_0 = \pi/\Delta\omega$ (since $\Delta s\omega_0 = \Delta\omega$) and decays by oscillations. The quantity $F(t)$ is a "wavepacket"; actually, in the classical limit Δs is very small, and, consequently, Δt is very large; therefore, in the classical limit the physical quantities are represented by wavepackets, extended in time and sharp in energy. First, we note that the representation of the physical quantities in Quantum Mechanics implies "waves", which, in classical limit become wavepackets,[4] more or less localized (here, in time or in energy). Second, we note that $\Delta t\Delta\omega \geq \pi$ for quantum-mechanical of physical quantities, or $\Delta t\Delta E \geq \pi\hbar = h/2$. A similar relation holds for the deviations in coordinate q and the corresponding momentum p, since a superposition of waves of the form $e^{\frac{i}{\hbar}pq}$ over an extension Δq interfere constructively

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[3] N. Bohr, "On the quantum theorie of line-spectra", Kgl. Danske Vidensk. Selsk. Skr., nat.-math. Afd. 8 Raekke IV, 1 (1918-1922); N. Bohr, "Uber die Serienspektra der Elemente", Z. Phys. **2** 423 (1920); N. Bohr, "Uber die Anwendung der Quantentheorie auf die Atombau I: Grundpostulate der Quantentheorie", Z. Phys. **13** 117 (1923).

[4] P. Debye, "Wellenmechanik und Korrespondenzprinzip", Phys. Z. **28** 170 (1927); C. G. Darwin, "Free motion in the Wave Mechanics", Proc Roy. Soc. London **A117** 258 (1927).

only for $\Delta p \geq \pi\hbar/\Delta q$, so we have $\Delta p\Delta q \geq h/2$; these relations (in the form $\Delta t\Delta E \geq \hbar/2$, $\Delta p\Delta q \geq \hbar/2$) have been recognized later in Quantum Mechanics as Heisenberg's relations of uncertainty (or the "uncertainty principle").[5] As long as the vawepackets remain localized their motion is governed by Classical Mechanics.[6] We are led to admit a "wave-particle duality" in the behaviour of the quantum objects. This duality is probably best illustrated by the δ-function: an infinite superposition of plane waves with equal amplitudes is infinite at the origin, where the waves' phases add "constructively" and is vanishing at any other point, where the phases add "destructively"; it is worth noting that waves exist at any point different from the origin, only they cancel each other other.

Another guiding principle in the "Old Quantum Mechanics" was the so-called "adiabatic hypothesis". From $\Delta E_n = s\partial E_n/\partial n = \hbar\Delta n\omega_0$ written above for the quasi-classical limit, we infer $\Delta S = \Delta E \cdot T_0 = 2\pi\hbar\Delta n$, or, in general, $S = 2\pi\hbar n$ for the variation of the mechanical action along a periodic orbit, where T_0 is the period of the motion; similarly, $S = \oint pdq = 2\pi\hbar n$, where the integration is performed along the classical periodic orbit; because $I = (1/2\pi)\oint pdq$ is the adiabatic invariant in the Classical Mechanics, *i.e.* it is practically constant for a slow change in the parameters of the motion; in Quantum Mechanics the constant is $\hbar n$; similarly,

$$I = \frac{1}{2\pi}\oint pdq = \frac{\Delta E}{2\pi}\oint \frac{\partial p}{\partial E}dq = \frac{\Delta E}{2\pi}\oint \frac{dq}{v} = \frac{\Delta E}{2\pi}T = \hbar n \quad , \qquad (11.9)$$

where v is the velocity and T is the period of the motion. Therefore, the quantum motion proceeds by constants adiabatic invariants $\hbar n$, providing the parameters do not change rapidly, as in the Classical Mechanics and in the quasi-classical limit. This is the adiabatic hypothesis, emphasized by Ehrenfest[7] (and called the "principle of

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[5] W. Heisenberg, "Uber den anschaulichen inhalt der quantentheoretischen Kinematik und Mechanik ", Z. Phys. **43** 172 (1927); see also E. H. Kennard, "Zur Quantenmechanik einfacher Bewegungstypen", Z. Phys. **44** 326 (1927) and H. Weyl, *Gruppentheorie und Quantenmechanik*, Hirzel, Leipzig (1928).

[6] P. Ehrenfest, "Bemerkung uber die Angenaherte Gultigkeit der klassischen Mechanik innerhalb der Quantenmechanik", Z. Phys. **45** 455 (1927).

[7] P. Ehrenfest, "Adiabatic Invariants and the Theory of Quanta", Phil. Mag. **33** 500 (1917).

mechanical transformability" by Bohr, and "adiabatic hypothesis" by Einstein); it points out, in fact, the existence of so-called stationary states, characterized by quantum number n, where the energy E_n is constant (there could be degenerate states, with distinct n's and same E_n; the adiabtic hypothesis holds for non-degenerate states). Moreover, the phase space has a minimum volume $\Delta p \Delta q = 2\pi\hbar$ by the adiabtic hypothesis, which allows the definition of the number of states, the definition of the entropy, and the complete formulation of the Second Law of Thermodynamics.

Moreover, equation

$$I = \frac{1}{2\pi} \oint p dq = \hbar n \tag{11.10}$$

is the Bohr-Sommerfeld quantization condition (in the quasi-classical limit).[8] Indeed, Bohr resolved the hydrogen atom by assuming that in a circular electronic orbit with $mv^2/r = Ze^2/r^2$ (the centrifugal force equals the Coulomb force) and the energy $E = mv^2/2 - Ze^2/r = -Ze^2/2r$, the orbital momentum is $L = mvr = \hbar n$ (with usual notations); therefore, $r = L^2/mZe^2$ and $E = -Ze^2/2r = -mZ^2e^4/2\hbar^2n^2$, which are the energy levels of the hydrogen-like atoms. The quantization condition $L = mvr = I = \hbar n$ can also be written as $2\pi r/(h/mv) = n$, which suggests that the motion is possible only for the circumference of the orbit equal with an integer multiple of the wavelength $\lambda = h/mv$; therefore, the electron and quantum particles behave like waves, and the condition $p = mv = h/\lambda$ is the de Broglie quantization condition[9] (similar with Einstein's quantization condition $E = \hbar\omega = h\nu$, where ν is frequency and ω is the angular frequency).

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[8] N. Bohr, "On the quantum theorie of line-spectra", Kgl. Danske Vidensk. Selsk. Skr., nat.-math. Afd. 8 Raekke IV, 1 (1918-1922); A. Sommerfeld, "Zur Quantentheorie der Spektrallinien", Ann. Phys. **51** 1 (1916); A. Sommerfeld, *Atombau und Spektrallinien*, 4th ed., Vieweg&Sohn, Braunschweig, (1924); see also, W. Wilson, "The quantum theorie of radiation and line spectra", Phil. Mag. **29** 795 (1915).

[9] L. de Broglie, *Recherches sur la Theorie des Quanta*s, Thesis, Paris, 1924 (Ann. Physique (Paris) **3** 22 (1925)).

11.3 Matricial Quantum Mechanics

Turning now to equation (11.6) we can see that any physical quantity is a matrix[10] of the type $F_{nn'}$, or $F_{nn'}(t) = F_{nn'}e^{\frac{i}{\hbar}(E_n - E_{n'})t}$; in order to preserve the dependence on $E_n - E_{n'}$, the product of two such quantities is performed according to the matrix multiplication rule, namely $(FG)_{nn'} = \sum_{n_1} F_{nn_1}G_{n_1n'}$; all the rules of the matrix algebra apply.

Any quantity F expressible by a matrix is, in general, undetermined, because it has, in general, two labels. There is a case when the matrix carries only one label, namely, when it is diagonal. Therefore, there should exist eigenvectors $\varphi_n^{n'} = \varphi_n \delta_{nn'}$ for the diagonal matrix $F_{nn'} = f_n \delta_{nn'}$, where φ_n are given by equation (11.5), such as

$$\sum_{n'} F_{nn'}\varphi_{n_1}^{n'} = f_{n_1}\varphi_{n_1}^{n} \ . \tag{11.11}$$

The quantity F has the value f_n in the "state" φ_n (or n); F is an "operator" which acts upon state vectors. Since f_n are real, F and $F_{nn'}$ should be hermitian. The diagonalization in equation (11.11) is performed by a unitary matrix S, such as[11]

$$\sum_{n'} S_{nn'}\varphi_{n_1}\delta_{n_1n'} = S_{nn_1}\varphi_{n_1} = \varphi_{n_1}^{n} \ . \tag{11.12}$$

The eigenvectors are unit orthogonal vectors (orthonormal), with respect to the scalar product

$$(\varphi_n, \varphi_{n'}) = \sum_{n_1} \varphi_n^{n_1 *}\varphi_{n'}^{n_1} = \delta_{nn'}; \tag{11.13}$$

from

$$F\varphi_n = f_n\varphi_n \tag{11.14}$$

we get

$$(\varphi_{n'}, F\varphi_n) = f_n\delta_{nn'} \ , \tag{11.15}$$

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[10] M. Born and P. Jordan, "Zur Quantenmechanik", Z. Phys. **34** 858 (1925).

[11] M. Born, W. Heisenberg and P. Jordan, "Zur Quantenmechanik II", Z. Phys. **35** 557 (1926).

i.e. $F_{nn'} = f_n \delta_{nn'}$; the matrix elements are the scalar products of the operator between two vectors. The most general form of $\psi(t)$ given by equation (11.5) is a linear superposition with coefficients c_n of eigenvectors $\varphi_n(t) = \varphi_n e^{-\frac{i}{\hbar}E_n t}$,

$$\psi(t) = \sum_n c_n \varphi_n e^{-\frac{i}{\hbar}E_n t} \ ; \tag{11.16}$$

the scalar product (or diagonal matrix element)

$$(\psi, F\psi) = \sum_{nn'} c_n^* c_n F_{nn'} e^{\frac{i}{\hbar}(E_n - E_{n'})t} = \sum_n |c_n|^2 f_n \tag{11.17}$$

leads to identify $(\psi, F\psi)$ with a mean (average) value, called expectation value, and denoted $\overline{F}$ and $|c_n|^2$ with the probability of the state φ_n;[12] we have the normalization condition

$$(\psi(t), \psi(t)) = \sum_n |c_n|^2 = 1 \tag{11.18}$$

and the amplitude of probability

$$(\varphi_n, \psi(t)) = c_n e^{-\frac{i}{\hbar}E_n t} \ ; \tag{11.19}$$

in addition,

$$\psi(t) = \sum_n (\varphi_n, \psi(t)) \varphi_n \ \ , \tag{11.20}$$

which indicates the so-called completeness of the set of eigenvectors φ_n. In equation (11.20) $c_n e^{-\frac{i}{\hbar}E_n t} = (\varphi_n, \psi(t))$, or $c_n = (\varphi_n(t), \psi(t))$ is the amplitude of probability for realizing the state φ_n in state ψ, for state φ_n to exist in state ψ, and $|c_n|^2 = |(\varphi_n, \psi(t))|^2$ is the probability. We note that the probability amplitude is a scalar product; in a simplified notation[13] we may write $< \varphi_n \mid \psi >$ for the amplitude, or even $< n \mid \psi >$, where $\mid n >$, $\mid \psi >$ are called "ket" vectors and $< n \mid$, $< \psi \mid$ are called "bra" vectors; we may also write $< n \mid \varphi >= \varphi_n$ (a "bracket"), or $\varphi(n)$, and $< n \mid \psi >= \psi_n$, or $\psi(n)$.

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[12] M. Born, "Zur Quantenmechanik der Stossvorgange", Z. Phys. **37** 863 (1926).

[13] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Oxford Univ. Press, Oxford (1930).

From equation (11.6) we get the time derivative

$$\dot{F}_{nn'} = \frac{i}{\hbar}(E_n - E_{n'})F_{nn'} \ , \tag{11.21}$$

which, by taking the scalar products, can also be written as

$$\dot{F} = \frac{i}{\hbar}(HF - FH) = \frac{i}{\hbar}[H, F] \ , \tag{11.22}$$

where H is the hamiltonian and $[H, F]$ defined by equation (11.22) is the commutator of the hamiltonian with the operator F; we have also $F(t) = e^{\frac{i}{\hbar}Ht}Fe^{-\frac{i}{\hbar}Ht}$, providing H is independent of time (Heisenberg representation). The standard hamiltonian of a particle with mass m moving in the potential $V(q)$ is $H = p^2/2m + V(q)$, where p is the momentum; in order to recover the classical equations of motion in the classical limit we need to assume the basic commutation relation[14]

$$[p, q] = -i\hbar \ ; \tag{11.23}$$

p and q are called canonical conjugate quantities (operators); for different degrees of freedom i, j we have $[p_i, q_j] = -i\hbar\delta_{ij}$. The equations of motion read $\dot{q} = (i/\hbar)[H, q] = (i/\hbar)[p^2/2m, q] = p/m$ and $\dot{p} = (i/\hbar)[H, p] = (i/\hbar)[V, p] = -\partial V/\partial q$. It is easy to see that

$$\begin{aligned} \dot{F} &= \tfrac{i}{\hbar}[H, F] = \tfrac{i}{\hbar}(HF - FH) = \\ &= \tfrac{i}{\hbar}[\tfrac{\partial H}{\partial p}(-i\hbar\tfrac{\partial F}{\partial q}) - \tfrac{\partial F}{\partial p}(-i\hbar\tfrac{\partial H}{\partial q})] = \{H, F\} \end{aligned} \tag{11.24}$$

in the classical limit, *i.e.* the commutator becomes the Poisson bracket, and, in the limit $\hbar \to 0$, we recover the equations of motion of the Classical Mechanics.[15]

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[14] M. Born and P. Jordan, "Zur quantenmechanik", Z. Phys. **34** 858 (1925); M. Born, W. Heisenberg and P. Jordan, "Zur Quantenmechanik II", Z. Phys. **35** 557 (1926).

[15] P. A. M. Dirac, "The fundamental equations of Quantum Mechanics", Proc. Roy. Soc. **A109** 642 (1926).; P. A. M. Dirac, "Quantum Mechanics and a preliminary investigation of the hydrogen atom ", Proc. Roy. Soc. **A110** 561 (1926).

11.4 Wave Mechanics

From equation (11.23), we may view the coordinate q as a (continuous) variable, and write $p = -i\hbar\frac{\partial}{\partial q}$; this is called the q-representation (or the coordinate representation; similarly, we may put $q = i\hbar\frac{\partial}{\partial p}$ for the p-, or momentum representation); then, the hamiltonian becomes

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + V(q) \ . \tag{11.25}$$

The eigenvector $\varphi_n(t) = \varphi_n e^{-\frac{i}{\hbar}E_n t}$ in equation (11.5), contains the time-independent eigenvector φ_n which depends on q; we have $\varphi_n(q) = =< q \mid \varphi_n >$ (or $< q \mid n >$); it gives the probability $|\varphi_n(q)|^2$ for the coordinate to have the value q in the state n. $\varphi_n(q)$ or $\varphi_n(q,t) = \varphi_n(q)e^{-\frac{i}{\hbar}E_n t}$ is called wavefunction; it satisfies the equation

$$i\hbar\frac{\partial\varphi_n(q,t)}{\partial t} = E_n\varphi_n(q,t) \ \ , \tag{11.26}$$

or

$$i\hbar\frac{\partial\varphi_n(q,t)}{\partial t} = H\varphi_n(q,t) \ \ , \tag{11.27}$$

or

$$H\varphi_n(q) = E_n\varphi_n(q) \ ; \tag{11.28}$$

this is Schrodinger's equation.[16] This way, the Quantum Mechanics acquires its differential-equations form, called also the Wave Mechanics, in contrast with the algebraic form described above, called also the matricial Quantum Mechanics. Schrodinger's equation (11.28) is the eigenvalue equation for the hamiltonian; a similar eigenvalue equation for the momentum,

$$p\varphi_n(q) = -i\hbar\frac{\partial\varphi_n(q)}{\partial q} = p\varphi_n(q) \tag{11.29}$$

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[16] E. Schrodinger, "Quantisiserung als Eigenwert Problem", Ann. Phys. **79** 361 (1926); "Quantisiserung als Eigenwert Problem", Ann. Phys. **79** 489 (1926); "Uber das Verhaltniss der Heisenberg-Born-Jordanschen Quantenmechanik zu der meinen", Ann. Phys. **79** 734 (1926); "Quantisiserung als Eigenwert Problem", Ann. Phys. **80** 437 (1926); "Quantisiserung als Eigenwert Problem", Ann. Phys. **81** 109 (1926); see also E. Schrodinger, *Colected Papers on Wave Mechanics*, Am. Math. Soc., Chelsea Publishing, Providence, Rhode Island (1982).

(or $p_n\varphi_n(q)$) gives the solution $\varphi_n(q) = const \cdot e^{\frac{i}{\hbar}pq}$ (or $\varphi_n(q) = const \cdot e^{\frac{i}{\hbar}p_nq}$); this is also the solution of the Schrodinger equation for a free particle, where the hamiltonian is $H = p^2/2m = -(\hbar^2/2m)\partial^2/\partial q^2$.

In an eigenstate of the hamiltonian the energy is well determined and can be measured; similarly, for an eigenstate of any other operator; two or more operators have common eigenvectors, and their eigenvalues are well determined and can be measured, if (and only if) they commute; indeed, for instance $[H, F]\varphi_n = H(F\varphi_n) - E_nF\varphi_n = 0$, which shows that $F\varphi_n$ is proportional to φ_n, *i.e.* $F\varphi_n = f_n\varphi_n$.

Apart from a few cases which admit an exact solution, a perturbation theory is developed for approximate solutions of Schrodinger's equation. Schrodinger's equation is linear, so it admits a linear superposition of solutions; for instance, $c_1\varphi_1 + c_2\varphi_2$ ($\left|c_1\right|^2 + \left|c_2\right|^2 = 1$); this leads to an interference of probabilities, for instance, $\left|c_1\right|^2 \left|\varphi_1\right|^2 + \left|c_2\right|^2 \left|\varphi_2\right|^2 + c_1^*c_2\varphi_1^*\varphi_2 + c_2^*c_1\varphi_2^*\varphi_1$. A time-dependent perturbation causes transitions between states (quantum jumps), which, like the probabilities, can be measured.[17]

11.5 Additional remarks

By 1927 (with Heisenberg's uncertainty principle) the birth of Quantum Mechanics as described above was almost done. It should be completed with Pauli's proposal of the electron's spin 1/2 (electron's "classically non-describable two-valuedness"; "eine eigentumliche, klassisch nicht beschreibbare Art von Zweideutigkeit der quantentheoretischen

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[17] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Oxford Univ. Press, Oxford (1930).

Eigenschaften des Leuchtelektrons"),[18] Pauli's exclusion principle[19] and Pauli's solution to the hydrogen atom with matricial Quantum Mechanics.[20] It is also worth noting that the quantum objects are entangled, *i.e.* their wavefunction is not analyzable, in general, in terms of individual particles. In addition, the symmetry of the wavefunction under permutations of many particles must be included[21] and the second quantization regarding the creation and destruction operators for the occupation numbers.[22] The quantum theory was further developed with the quantization of the electromagnetic field,[23] and the quantum theory of electromagnetic radiation.[24] The relativistic theory of the electron was given by Dirac.[25]

There is also an important observation regarding the Quantum Me-

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[18] W. Pauli, "Uber den Einfluss der Geschwindigkeitsabhangigkeit der Elekronenmasse auf den Zeemaneffekt", Z. Phys. **31** 373 (1925); W. Pauli, "Zur Quantenmechanik des magnetischen Elektrons", Z. Phys. **43** 601 (1927); see also G. E. Uhlenbeck and S. A. Goudsmit, "Ersetzung der Hypothese vom unmechanischen Zwang durch eine Forderung bezüglich des inneren Verhaltens jedes einzelnen Elektrons", Naturwiss. **13** 953 (1925); R. de L. Kronig, "Spinning electron and the structure of spectra", Nature **117** 550 (1926); R. de L. Kronig, "The magnetic moment of the electron", Proc. Nat. Acad. Sci. USA **12** 328 (1926) and L. H. Thomas, "The motion of the spinning electron", Nature **117** 514 (1926).

[19] W. Pauli, "Uber den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren", Z. Phys. **31** 765 (1925).

[20] W. Pauli, "Uber das Wasserstoffspektrum vom Standpunkt der neuen Quantenmechanik", Z. Phys. **36** 336 (1926).

[21] P. A. M. Dirac, "On the theory of Quantum Mechanics", Proc. Roy. Acad. London **A112** 661 (1926); W. Heisenberg, "Mehrkorperproblem und Resonanz in der Quantemechanik", Z. Phys. **38** 411 (1926).

[22] P. Jordan and O. Klein, "Zur Mehrkorperproblem der Quantentheorie", Z. Phys. **45** 751 (1927); P. Jordan and E. Wigner, "Uber das Paulische Aquivalenzverbot", **47** 631 (1928).

[23] P. Jordan and W. Pauli, "Zur Quantenelektrodynamik ladungsfreier Felder", Z. Phys. **47** 151 (1928); W. Heisenberg and W. Pauli, "Zur Quantendynamik der Wellenfelder", Z. Phys. **56** 1 (1929).

[24] P. A. M. Dirac, "The quantum theory of the emission and absorption of radiation", Proc. Roy. Soc. London **A114** 243 (1927); P. A. M. Dirac, "The quantum theory of dispersion", Proc. Roy. Soc. London **A114** 710 (1927); P. A. M. Dirac, "On the annihilation of electrons and protons", Proc. Camb. Phil. Soc. **26** 361 (1930); see also E. Fermi, "Quantum theory of radiation", Revs. Mod Phys. **4** 87 (1932).

[25] P. A. M. Dirac, "The quantum theory of the electron", Proc. Roy. Soc. London **117** 610 (1928); P. A. M. Dirac, "The quantum theory of the electron. Part II", Proc. Roy. Soc. London **118** 341 (1928).

chanics, which is related to its two aspects, Wave Mechanics and Matricial Mechanics. Making use of the Matricial Mechanics, we can see that the quantum phenomena obey the causality, as expressed in statistical equations; however, these equations do not give a description in space and time. On the other hand, if we wish a space-time description, we can use the Wave Mechanics; but, in this case, we lose the causality, in the statistical interpretation, for instance, of the coordinate distribution. This fundamental feature of the Quantum Mechanics is called "Bohr's complementarity principle" (or the "interpretation of the Copengahen School");[26] it signifies the lack of objectivity, since we are not able anymore to separate the observer and the observed.

11.6 Fundamental experiments

Radioactive rays emitted from atomic nuclei generate a track in the Wilson chamber filled with droplets of supersaturated water vapours.[27] Consequently, we may admit that they have a trajectory (straight lines for α-rays, irregular curves for β-rays). For an energy $E = 1MeV$ of the β-radiation (electrons) we have a vawelength $\lambda = h/\sqrt{2mE} \simeq 10^{-10}cm = 0.01\text{Å}$ ($m = 10^{-27}g$ is the electron mass); this is indeed a very small wavelength (atomic dimension 1Å, the dimension of the atomic nucleus $\simeq 10^{-5}\text{Å}$); a quasi-classical trajectory can be defined, the radiation may be approximated by a particle, and the "wave" can be seen as a "particle". In addition, cathode rays (electrons) passed through a thin foil of matter exibit diffraction, with wavelength $\lambda = h/p$, p being the momentum (de Broglie relation).[28] The

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[26] N. Bohr, "The quantum postulate and the recent development of atomic theory", Nature **121** 580 (1928); N. Bohr, "Das Quantenpostulat und die neuere Entwicklung der Atomistik", Naturwissenschaften **16** 245 (1928); N. Bohr, *Atomic Theory and the Description of Nature*, Cambridge Univ. Press, Cambridge (1934).

[27] C. T. R. Wilson, "On a method of making visible the paths of ionising particles through a gas ", Proc. Roy. Soc. **A85** 285 (1911).

[28] C. Davisson and L. H. Germer, "Diffraction of electrons by a crystal of nickel", Phys. Rev. **30** 705 (1927); G. P. Thomson, "Experiments on the diffraction of cathode rays", Proc. Roy. Soc. **A117** 600 (1928); G. P. Thomson, "Experiments on the diffraction of cathode rays. II", Proc. Roy. Soc. **A119** 651

same dual nature should be accepted for electromagnetic radiation, which diffracts as any wave (X-rays on crystals) and, at the same time, is absorbed in the photoelectric effect according to Einstein's condition $E = h\nu$;[29] since $E = cp$, we get also $c/\nu = h/p$, where E is the energy, ν is the frequency, p is the momentum of the radiation and c is the speed of ligh; $h \simeq 6.6 \times 10^{-27} erg \cdot s$ is Planck's constant. X-rays passing through supersaturated water vapors eject recoil electrons from water molecules, while scattered in other direction, where they produce photoelectrons; these processes occur with the conservation of energy and momentum, as if the X-rays were particles; this is the Compton effect.[30] When a uniform beam of electrons with moderate energies passes through a gas, the electric current exhibits discontinuities at certain values of the energy (velocity).[31] This is the famous Franck-Hertz experiment, which indicates directly the existence of discrete energy levels in atoms.

11.7 Concluding remarks

The present book deals with the quasi-classical approximation regarding Heisenberg's equation of motion of the quantum-mechanical operators. Chapter 1 includes a brief summary of this approximation and its context. Chapter 2 is devoted to a brief sketch of Maxwell's equations of the electromagnetism. Chapter 3 is devoted to classical theory of electric and magnetic dipole moments, electronic, atomic, molecular and nuclear electric and magnetic dipole moments, polarizability, polarization and magnetization of matter and diamagnetism, paramagnetism and ferromagnetism. Chapter 4 includes the classical limit of the electromagnetic field and matter, the treatment of the ef-

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(1928).

[29] A. Einstein, "Uber einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt", Ann. Phys. **17** 132 (1905).

[30] A. H. Compton, "A Quantum Theory of the scattering of X-rays by light elements", Phys. Rev. **21** 483 (1923); A. H. Compton and A. W. Simon, "Measurement of β-rays associated with scattered X-rays", Phys. Rev. **25** 306 (1925).

[31] Franck and Hertz, "Uber Zusammenstosse zwischen Elektronen und den Molekulen des Quecksilberdampfes und die Ionisierungsspannung desselben", Verhandl. der Deutschen Physikalische Gesellschaft **16** 457 (1914).

fects of external time-dependent interactions within the quasi-classical approximation, and an illustrative discussion of the orientational polarizability and the equations of motion of the magnetization (Larmor equations). The quasi-classical motion of magnetization in matter, magnetic resonance and nuclear quadrupole resonance are presented in Chapter 5. Chapter 6 is devoted to a more extensive presentation of the quasi-classical approximation for the equation of motion of the quantum-mechanical operators and its applications to electric dipolar vibrations, rotations, the later both free and in the presence of a (high) static electric field; the notion of dipolar parametric resonance is introduced here in the molecular rotation spectra. The electric dipolar parametric resonance is discussed in more details in the next Chapter 7, while Chapter 8 is devoted to a more detailed presentation of the magnetic resonance phenomena, all in the quasi-classical approximation. Chapter 9 deals with "exact" solutions to the motion of the operators of the angular momenta; the concept of stimulated emission in magnetic resonance is introduced here. The concluding Chapter 10 presents in a more systematic way the quasi-classical approximation for the equation of motion, its application to a few simple quantum-mechanical motions and its application to condensed matter for the electric dipolar resonance, magnetic resonance and nuclear magnetic resonance as examples. The final Chapter 11 includes a brief sketch of the fundamental ideas and techniques of the Quantum Mechanics

Samples of condensed matter, like gases, liquids, solids, are made of atomic constituents like atoms, molecules, electrons, assembled to a greater or lesser extent by cohesion forces, usually at equilibrium under the action of various external agents, like pressure or temperature. They are characterized by a certain degree of homogeneity and by a density (concentration) of the constituents.

The motion of the atomic constituents in condensed matter involves a great variety of degrees of freedom, coupled to each other to a greater or lesser extent. For instance, the atoms may move or vibrate about equilibrium positions, the molecules may move, vibrate or rotate, the electrons may move, electric and magnetic moments (dipoles) may precess and align, and so on. The condensed matter has a great variety of excited states, analyzed, conveniently, in terms of elementary excitations, both single- (quasi)-particle or collective, both localized or delocalized and propagating (waves). Due to the large number of degrees of freedom, the energy levels and wavefunctions are extremely dense in usual condensed matter in normal conditions; due to the permanent residual interactions, both internal and external, the quantum states in condensed matter are not, in fact, well resolved; they are affected by intrinsic uncertainties, which make only superpositions of quantum states to be meaningful. These superpositions, which can be performed either locally or globally, are wavepackets (quasi-particles or quasi-waves). The individual, quantum movements, which may imply rapidly varying quantities both in space and time, are smoothed out by the interference in such superpositions, which amount to a "coarse-graining" average. This amounts to a (quasi-) classical description of matter. The quantum motion, which involves small amounts of mechanical action, may be neglected in comparison with the amount of mechanical action stored in "coarse-graining" averages. In addition, the lack, in fact, of well defined wavefunctions in condensed matter makes the relevant physical quantities to be described by averages with density matrices or the statistical matrix. Viewed in itself, the condensed matter looks like a (quasi-) classical condensed matter.

Matter couples to external fields, and a great deal of information is obtained about condensed matter by its coupling to time-dependent external electric and magnetic fields. Quantum transitions are generated by optical fields acting between electronic levels, by infrared fields acting between vibration levels, by radio-frequency fields acting between rotational or angular-momentum (spin) levels, all these transitions involving the motion of electric and magnetic moments (dipoles). The main element of all such spectroscopies is the transition rate determined by the time-dependent interaction hamiltonian of the external field and the associated absorbed power, which is measured experimentally. Usually, the external fields acting upon the condensed matter are extremely weak (in comparison with the internal fields), such that the amount of mechanical action carried by them is much smaller than the amount (quanta) of action associated with the transition between two energy levels. The condition of the external field to be weak is equivalent with the condition of validity of the perturbation theory. Under these circumstances, the action of the external fields upon condensed matter may be treated approximately as a (quasi-)

classical action. In addition, the external electromagnetic fields, either coherent or incoherent, are usually classical fields, since they consist of a large number of photons; the absorption or emission of a photon in this case is to be compared with the large number of photons in the field, which makes the dynamics of the field to be a classical one. The condition of weakness of the external field for the validity of a quasi-classical dynamics is not sufficient. The classical dynamics goes by the force, according to Newton's law, while the quantum dynamics goes by the quantum jumps caused by the interaction hamiltonian. Since the force is the derivative of the hamiltonian with respect to the relevant coordinate (dynamical variable), we can see that the classical dynamics holds both for small variations of the coordinate and small variations of the interaction hamiltonian, *i.e.* for small variations of the energy levels.

Let $H_{int} = h\cos\omega t$ be the interaction hamiltonian with an external field. The transition rate from state n to state $n+s$ is

$$\frac{\partial\left|c_{n+s,n}\right|^2}{\partial t} = \frac{2\pi}{\hbar^2}\left|\frac{1}{2}h_{n+s,n}\right|^2\delta(\omega_{n;s}-\omega) \tag{11.30}$$

and the absorbed power is

$$\begin{aligned} P = \tfrac{\partial\left|c_{n+s,n}\right|^2}{\partial t}\hbar\omega_s = \tfrac{2\pi}{\hbar}\left|\tfrac{1}{2}h_{n+s,n}\right|^2\omega_s\delta(\omega_{n;s}-\omega) = \\ = \tfrac{2}{\hbar}\left|\tfrac{1}{2}h_{n+s,n}\right|^2\tfrac{\omega_{n;s}\alpha}{(\omega-\omega_{n;s})^2+\alpha^2}\ ,\ \alpha\rightarrow 0\ , \end{aligned} \tag{11.31}$$

where $\omega_{n;s} = (E_{n+s}-E_n)/\hbar$, E_n being the energy levels, and α is a damping coefficient. The transition rate $n \rightarrow n+s$ is equal to the reverse transition rate $n+s \rightarrow n$ (principle of detailing balance) and, in general, these transition rates must be mutiplied by the weigths corresponding to degeneracies, or density matrices, or thermal weigths (in order to get the mean power). The perturbation theory is valid as long as the jump frequency given by equation (11.30) is much smaller than the relevant frequency ω_s, *i.e.* $\left|h_{s+n,n}\right|^2/\hbar^2\omega_s \ll \omega_s$, or $h \ll \hbar\omega_s$, where h stands for the absolute value of the matrix element of the interaction. We can see that this condition is the condition of quasi-classical behaviour too.

Since the quantum states in condensed matter are dense, we may approximate $\omega_{n;s}$ by ω_s $\omega_{n;s} \simeq \omega_s$; on the other hand, the matrix elements $O_{n,n+s}$ of an operator O depend slightly on n (in the sense that there are many states $n^{'}$ in the close neighbourhood of any n). We may neglect the suffix n in $O_{n,n+s}$ and write $O_{n,n+s} \simeq O_s$. The equation of motion $\dot{O} = \frac{i}{\hbar}[H, O]$ leads, in the energy representation, to

$$\dot{O}_s = -i\omega_s O_s \ . \tag{11.32}$$

This equation shows that O_s is the s-th Fourier component $O_s(t) = O_s e^{-i\omega_s t}$ of a classical quantity O (the two matrix indices n, $n+s$ are replaced by one, s); in condensed matter, the dynamics is quasi-classical. If we add the external interaction H_{int}, which behaves quasi-classically according to the discussion above, its contribution to the rate of change in time of the operator O is $\dot{O} = \frac{i}{\hbar}e^{\frac{i}{\hbar}Ht}[H_{int}, O]e^{-\frac{i}{\hbar}Ht} \simeq \{H_{int}, O\} = (\dot{O}^{cl})_{int}$, where H is the hamiltonian with energy levels E_n, $\{,\}$ is the Poisson bracket and all the quantities are classical quantities; moreover, H_{int} commutes with H. We get the quasi-classical equation of motion

$$\dot{O}_s \simeq -i\omega_s O_s + (\dot{O}^{cl})_{int} \ \ , \tag{11.33}$$

or, with $O_s^{(1)} = Re(O_s)$ and $O_s^{(2)} = Im(O_s)$,

$$\dot{O}_s^{(1)} = \omega_s O_s^{(2)} + (\dot{O}^{cl})_{int} \ , \ \dot{O}_s^{(2)} = -\omega_s O_s^{(1)} \ \ , \tag{11.34}$$

or

$$\ddot{O}_s^{(1)} + \omega_s^2 O_s^{(1)} = (\frac{\partial}{\partial t}\dot{O}^{cl})_{int} \ ; \tag{11.35}$$

we can see that $(\frac{\partial}{\partial t}\dot{O}^{cl})_{int}$ is the (generalized) classical force produced by interaction, which drives a harmonic oscillator with (quantum) eigenfrequency ω_s. With standard notations, the hamiltonian of the harmonic oscillator is $\frac{1}{2}P_s^2 + \frac{1}{2}\omega_s^2 O_s^2$.

Let $(\frac{\partial}{\partial t}\dot{O}^{cl})_{int} = f\cos\omega t$, where f is the generalized force generated by H_{int} with respet to O_s. The quasi-classical equation of motion

$$\ddot{O}_s + \omega_s^2 O_s + \gamma\dot{O}_s = -\frac{f}{m}\cos\omega t \ \ , \tag{11.36}$$

where a damping γ-term is introduced and m denotes the mass parameter ($O_s^{(1,2)}$ are classical quantities); equation (11.36) has solution

$$O_s = a_s\omega t + b_s\sin\omega t \ \ , \tag{11.37}$$

with

$$\begin{aligned} a_s &= \tfrac{f}{m}\tfrac{\omega^2-\omega_s^2}{(\omega^2-\omega_s)^2+\omega^2\gamma^2} \simeq \tfrac{f}{2m\omega_s}\tfrac{\omega-\omega_s}{(\omega-\omega_s)^2+\gamma^2/4} \ , \\ b_s &= -\tfrac{f}{m}\tfrac{\omega\gamma}{(\omega^2-\omega_s)^2+\omega^2\gamma^2} \simeq -\tfrac{f}{2m\omega_s}\tfrac{\gamma/2}{(\omega-\omega_s)^2+\gamma^2/4} \end{aligned} \tag{11.38}$$

for ω close to ω_s. These are typical equations of resonance. From equation (11.36) we have

$$\frac{d}{dt}(\frac{1}{2}\dot{O}_s^2+\frac{1}{2}O_s^2)+\gamma\dot{O}_s^2=-\frac{f}{m}\dot{O}_s\cos\omega t \ , \tag{11.39}$$

and we get the average absorbed power

$$\begin{gathered} P=\overline{\gamma m\dot{O}_s^2}=-\overline{f\dot{O}_s\cos\omega t}= \\ =-\tfrac{1}{2}f\omega b_s=\tfrac{f^2}{4m}\tfrac{\gamma/2}{(\omega-\omega_s)^2+\gamma^2/4}\rightarrow \\ \rightarrow\tfrac{\pi f^2}{4m}\delta(\omega_s-\omega) \ , \ \gamma\rightarrow 0 \ , \end{gathered} \tag{11.40}$$

which should be compared with equation (11.31). It is worth noting that in classical dynamics we have an absorbed power only when dissipation (γ coefficient) is present, in contrast with the quantum dynamics (quantum jumps) where the net absorption should include the reverse, relaxation quantum transitions.

In a typical magnetic resonance an external, constant and uniform magnetic field H_0 is applied, which align the spins $\mathbf{I}$ (nuclear, electron spins) to give a constant magnetization $M_z=\gamma\hbar I_z$, where γ is the gyromagnetic factor. The interaction (Zeeman) energy $-\mathbf{MH}_0=-\gamma\hbar H_0 I_z$ splits equally the degenerate energy levels with respect to the quantum number m of the component I_z, giving a characteristic energy $\hbar\gamma H_0=\hbar\omega_0$ and a characteristic frequency $\omega_0=\gamma H_0$ (typically, in the $1-10MeV$ range), corresponding to the difference $\omega_0=[\gamma\hbar H_0(m+1)-\gamma\hbar H_0 m]/\hbar$ between two adjacent energy levels $E_m=\gamma\hbar H_0 m$. A radio-frequency magnetic field $H_x(t)=H\cos\omega t$ is applied at right angle, with the interaction hamiltonian $H_{int}=-M_x H\cos\omega t$ (where $M_x=\gamma\hbar I_x$). M_x has non-vanishing matrix elements only between states m and $m+1$, such that only the characteristic frequency ω_0 is involved. The interaction energy $M_x H$ is extremely small, we have only a few states (since $\mathbf{I}$ has a small finite dimension), such that the quasi-classical approximation can be applied. In addition, the classical equation of motion $\dot{\mathbf{M}} = \gamma \mathbf{M} \times \mathbf{H}$ coincides formally with the quantum-mechanical equation of motion $\dot{\mathbf{M}} = \frac{i}{\hbar}[-\mathbf{MH}, \mathbf{M}]$, based on the commutation relations $[I_i, I_j] = i\varepsilon_{ijk} I_k$ of the angular momentum. We get

$$\dot{M}_x = \omega_0 M_y - \alpha \dot{M}_x \ , \ \dot{M}_y = -\omega_0 M_x - \alpha M_y + \omega_s H \cos \omega t \ , \quad (11.41)$$

or

$$\ddot{M}_x + \omega_0^2 M_x + \alpha M_x = \omega_0 \omega_s H \cos \omega t \quad (11.42)$$

and a similar equation for M_y, where $\omega_0 = \gamma H_0$, $\omega_s = \gamma M_z$ and α is a small damping factor. This is the equation (11.36) of quasi-classical motion. M_x in H_{int} should be replaced by a c-number denoted (M_x), such that ω_s may have an additional factor (M_x); this factor can be determined from the comparison of the absorbed power computed by means of the harmonic-oscillator equation of motion with the absorbed power computed from the transition rate of the quantum jumps.

In nuclear quadrupole resonance the role of the external field H_0 is played by the nuclear quadrupole interaction $V_2 = \sum_{ij} V_{ij} I_i I_j$, where V_{ij} is the quadrupole interaction tensor. The diagonalization of this interaction gives energy levels, and transitions between such energy levels are caused by an external radio-frequeny magnetic field $H_x(t) = H \cos \omega t$. The interaction hamiltonian reads $H_{int} = -\gamma \hbar H I_x \cos \omega t$. The interaction energy $\gamma \hbar H I$ is very small in comparison with the transition energy $\hbar \omega_s$, such that we may apply the quasi-classical approximation for transitions which imply the lowest energy levels (the selection rules depend now on the diagonalization of the interaction, such that we may have many transitions). The equation of quasi-classical motion is $\dot{I}_y = -i\omega_s I_y + (\dot{I}_y^{cl})_{int}$, where $(\dot{I}_y^{cl})_{int} = \gamma H (I_z) \cos \omega t$, whence

$$\ddot{I}_y^{(1)} + \omega_s^2 I_y = (\ddot{I}_y^{cl})_{int} = -\omega \gamma H (I_z) \cos \omega t \ ; \quad (11.43)$$

we can see that we limit ourselves to the first-order approximation in H. A similar equation holds for I_z,

$$\ddot{I}_z^{(1)} + \omega_s^2 I_z = (\ddot{I}_z^{cl})_{int} = \omega \gamma H (I_y) \cos \omega t \ ; \quad (11.44)$$

the c-numbers (I_z) and (I_y) can be conveniently replaced by $(I)\cos\alpha$ and $(I)\sin\alpha\sin\beta$, respectively, in order to account for various orientations of the spin. We solve the above harmonic-oscillator equations (with damping) and compute the absorbed power. It depends on $(I)^2(\cos^2\alpha+\sin^2\alpha\sin^2\beta)$; the angular part is either known from the orientation of the crystal, or, for example, if the spins are randomly distributed we average this angular part (and get $\overline{\cos^2\alpha}=\frac{1}{3}$). The c-number $(I)^2$ is obtained by comparing the result with the absorbed power computed by means of the transition rates.

The vibrations of the molecular dipoles, with frequency in the range $10^{13}-10^{14}s^{-1}$ (infrared region), can be driven by an external electric field $E\cos\omega t$, with the interaction hamiltonian $H_{int}=-dE\cos\omega t$, where d is the electric dipole; the free vibrations are those of a harmonic oscillator with eigenfrequency ω_0(for one degree of freedom); the only non-vanishing matrix elements of d (and H_{int}) are those between states n and $n+1$, $n=0,1,2,...$, given by $d_{n+1,n}=ql_{n+1,n}=q\sqrt{\frac{\hbar}{2m\omega_0}}\sqrt{n+1}$, where q is a generic charge, l is the coordinate (around the equilibrium position) and m is the oscillator mass. The interaction energy dE is extremely small, such that the quasi-classical approximation is applicable for the lowest energy levels; it reads

$$\ddot{d}+\omega_0^2d+\gamma\dot{d}=\frac{q^2}{m}E(\alpha)\cos\omega t \ , \tag{11.45}$$

where (α) is a c-number reminiscent of the classical variable l in the classical interaction hamiltonian. The comparison with the absorbed power computed by using the transition rates of the quantum jumps gives $(\alpha)=n+1$. For the lowest-energy states $n\simeq 0$, this c-number is $\simeq 1$. For large quantum numbers the quasi-classical approximation gives the variation of the power with respect to the quantum numbers.

The molecular rotations have the hamiltonian $L^2/2I$, or, with standard angular notations, $\frac{1}{2I}(\dot{\theta}^2+\dot{\varphi}^2\sin^2\theta)$, with energy levels $\hbar^2l(l+1)/2I$, $l=0,1,2,...$, where L is the angular momentum and I is the moment of inertia; the eigenfunctions are the spherical harmonics $Y_{lm}(\theta,\varphi)$, where $m=-l,-l+1,...l$. This is the spherical pendulum (spatial rotator, spherical top); for $\theta=\pi/2$, we get the planar rotator, with the hamiltonian $L_z^2/2I$ and energy levels $\hbar^2m^2/2I$, $m=0,1,2,...$, where L_z $(=-i\hbar\partial/\partial\varphi)$ the z-component of the angu-

lar momentum; the eigenfunctions are $e^{im\varphi}$. The interaction hamiltonian is $H_{int}=-dE\cos\theta\cos\omega t$, with non-vanishing matrix elements between states l and $l+1$ (the matrix elements of $\cos\theta$), for the same m; $E\cos\omega t$ is the radio-frequency electric field and d is the dipole moment. The transition frequencies are $\omega_l=\frac{\hbar}{I}(l+1)$, typically in the range $10^{11}-10^{13}s^{-1}$ (far infrraed region); they depend on l. The equation of the quasi-classical motion may imply the angle θ; it reads $\ddot{\theta}_l+\omega_l^2\theta_l=(\ddot{\theta}^{cl})_{int}$ (though θ is not a suitable dynamic variable). It is necessary, first, to study the classical motion. The classical equation of motion $\frac{d}{dt}(\dot{\varphi}\sin^2\theta)=0$ indicates the conservation of the L_z-component of the angular momentum; it leads to an effective potential energy $U_{eff}=L_z^2/2I\sin^2\theta$, which has a minimum value for $\theta_0=\pi/2$ (the classical spherical pendulum moves, practically, as a planar rotator). For the lowest energies we limit ourselves to an expansion in powers of $\theta-\pi/2$, which indicates a classical (generalized) force $(\ddot{\theta}^{cl})_{int}=-\frac{dE}{I}(\cos\theta)_l\cos\omega t$; the variable θ_l corresponds $\theta-\pi/2$; the c-number $(\cos\theta)_l$ is determined from the absorbed power computed by means of the transition rates of the quantum jumps (the result has an m-degeneracy given by $2l+1$) . Similar results are obtained for free rotations with an additional constant, uniform electric field (of weak strength). The planar rotator with the interaction hamiltonian $H_{int}=-dE\cos\varphi\cos\omega t$ moves with the frequencies $\omega_m=\frac{\hbar}{I}(m+1/2)$, between states m and $m+1$, according to the equation of quasi-classical motion $\ddot{\varphi}_m+\omega_m^2\varphi_m=-\frac{dE}{I}(\sin\varphi)_m\cos\omega t$. The above results for rotational transitions are valid for free rotations, like in dilute gases, or without an additional constant, uniform electric field. In condensed matter strong local electric fields may appear, which align the electric dipoles (quenched dipoles). Consider a constant, uniform electric field $\mathbf{E}_0=E_0(0,0,1)$ oriented along the z-axis; the potential energy of an electric dipole
$\mathbf{d}=d(\sin\theta\cos\varphi,\sin\theta\sin\varphi,\cos\theta)$ of arbitrary orientation is $U=-dE_0\cos\theta$. The hamiltonian of rotation in this field is given by

$$H=\frac{1}{2}I(\dot{\theta}^2+\dot{\varphi}^2\sin^2\theta)-dE_0\cos\theta\ , \qquad (11.46)$$

where I is the moment of inertia of the dipole, considered as a sherical pendulum (spherical top). The equation of motion

$$I\frac{d}{dt}(\dot{\varphi}\sin^2\theta)=0 \tag{11.47}$$

indicates that the component L_z of the angular momentum is conserved, $\dot{\varphi}\sin^2\theta=L_z/I$; consequently, an effective potential function

$$U_{eff}=\frac{L_z^2}{2I\sin^2\theta}-dE_0\cos\theta \tag{11.48}$$

occurs in the hamiltonian. Consider that the dipole energy dE_0 is much greater than the rotation energy L_z^2/I, which is of the order of the temperature T. For typical value $d=10^{-18}esu$ and temperature $T=300K\simeq 4\times 10^{-14}erg$ this condition requires an electric field $E_0\gg T/d=4\times 10^4 statvolt/cm\simeq 1.6\times 10^9 V/m$. This is a strong electric field, wich may appear as an internal field in polar condensed matter. For instance, the electric field created by an electron charge at distance $1\text{Å}=10^{-8}cm$ is $4.8\times 10^{-10}/10^{-16}=4.8\times 10^6 stavolt/cm$. In this case, the effective potential given by equation (11.48) has a minimum value for $\theta_0\simeq(L_z^2/IdE_0)^{1/4}\simeq(T/dE_0)^{1/4}\ll 1$ and it can be expanded in powers of $\widetilde{\theta}=\theta-\theta_0$ around this minimum value as

$$U_{eff}\simeq -dE_0+2dE_0\widetilde{\theta}^2\ ; \tag{11.49}$$

the hamiltonian given by equation (11.46) becomes

$$H\simeq\frac{1}{2}I\dot{\widetilde{\theta}}^2+\frac{1}{2}I\omega_0^2\widetilde{\theta}^2-dE_0\ \ , \tag{11.50}$$

where $\omega_0=2\sqrt{dE_0/I}$ is known as Rabi's frequency; according to our condition of strong field, we have $\omega_0\gg 10^{12}s^{-1}$. Therefore, the dipoles are quenched in the internal electric field, where they execute small oscillations. The angle φ rotates freely with the frequency $\dot{\varphi}\simeq L_z/I\sin^2\theta_0=\frac{1}{2}\omega_0$ ($\varphi=\frac{1}{2}\omega_0 t$).

Consider an external radio-frequency field $\mathbf{E}(t)=E(t)(\sin\alpha,0,\cos\alpha)$, $E(t)=E\cos\omega t$, which makes an angle α with the z-axis; its interaction with the dipole is

$$H_{int}=-dE(t)(\sin\alpha\sin\theta\cos\varphi+\cos\alpha\cos\theta)\ \ , \tag{11.51}$$

which provides two relevant interaction hamiltonians:

$$\begin{gathered} H_{1int} = -\tfrac{1}{2} dE \sin\alpha \left[\cos(\omega + \tfrac{1}{2}\omega_0)t + \cos(\omega - \tfrac{1}{2}\omega_0)t\right] \delta\theta \ , \\ H_{2int} = \tfrac{1}{2} dE \cos\alpha \cos\omega t \cdot \delta\theta^2 \ . \end{gathered} \tag{11.52}$$

The interaction hamiltonian H_{1int} produces transitions between the harmonic-oscillator states n and $n+1$ with the resonance frequency $\Omega = \frac{1}{2}\omega_0$, $\frac{3}{2}\omega_0$. The absorbed power is

$$\begin{gathered} P = \tfrac{\pi}{16 I \omega_0} d^2 E^2 \Omega (n+1) \sin^2\alpha \delta(\omega - \Omega) = \\ = \tfrac{1}{16 I\omega_0} d^2 E^2 \Omega(n+1) \sin^2\alpha \tfrac{\alpha}{(\omega-\Omega)^2 + \alpha^2} \ , \ \alpha \to 0^+ \ , \end{gathered} \tag{11.53}$$

which is a typical resonance curve. In order to compute the mean power the thermal weigths $e^{-\beta\hbar\omega_0 n} / \sum e^{-\beta\hbar\omega_0 n}$ should be introduced, where $\beta = 1/T$ is the inverse of the temperature T; for $\beta\hbar\omega_0 \gg 1$, only the lowest states n are excited by interaction, and, consequently, the absorbed power depends slightly on the temperature.

The harmonic-oscillator hamiltonian given by equation (11.50) and the interaction hamiltonian H_{2int} given by equation (11.52),

$$H^{'} = H + H_{2int} = \frac{1}{2} I \dot{\widetilde{\theta}}^2 + \frac{1}{2} I \omega_0^2 (1 + h\cos\omega t) \widetilde{\theta}^2 \ , \tag{11.54}$$

where $h = \frac{E}{2E_0}\cos\alpha$, leads to the classical equation of motion

$$\ddot{\widetilde{\theta}} + \omega_0^2 (1 + h\cos\omega t) \widetilde{\theta} = 0 \ , \tag{11.55}$$

which is the well-known equation of parametric resonance (Mathieu's equation). As it is well known, besides periodic solutions, the classical equation (11.55) has also aperiodic solutions, which may grow indefinitely with increasing time; these are (parametrically) resonant solutions, which occur for ω in the neighbourhood of $2\omega_0/n$, $n = 1, 2, 3...$. As we can see immediately, the solutions of equation (11.55) are determined by the initial conditions $\widetilde{\theta}(t=0)$ and $\dot{\widetilde{\theta}}(t=0)$ (as for any homogeneous equation). Since fluctuations generate vanishing initial conditions, the classical solutions of equation (11.55) are vanishing.

The quantum-mechanical dynamics is different. The interaction hamiltonian H_{2int} produces transitions between the harmonic-oscillator states n and $n+2$ (due to the matrix elements of $\widetilde{\theta^2}$). These transitions have frequency $2\omega_0$, in accordance with the classical dynamics. The transition rate is

$$\frac{\partial\left|c_{n+2,n}\right|^2}{\partial t}=\frac{\pi h^2}{128}\omega_0^2(n+1)(n+2)\delta(2\omega_0-\omega) \tag{11.56}$$

and the absorbed power

$$\begin{aligned}P=2\hbar\omega_0\tfrac{\partial\left|c_{n+2,n}\right|^2}{\partial t}=\tfrac{\pi h^2}{64}\hbar\omega_0^3(n+1)(n+2)\delta(2\omega_0-\omega)\simeq\\ \simeq\tfrac{h^2}{64}\hbar\omega_0^3(n+1)(n+2)\tfrac{\alpha}{(2\omega_0-\omega)^2+\alpha^2}\ ,\ \alpha\rightarrow 0^+\ ,\end{aligned} \tag{11.57}$$

where we may put $n=0$. The intensity given by equation (11.57) is small, because, especially, of the factor $(E/E_0)^2$.

The parametric resonance disappears for $\alpha=\frac{\pi}{2}$, *i.e.* for the applied radio-frequency field $\mathbf{E}$ at right angle with the quenching field $\mathbf{E}_0$. The quenching field may ocurr, very likely, in (polar) solids; the effect of the parametric resonance depends on the orientation of the crystal; in amorphous samples the absorption is averaged over angles α ($\overline{\cos^2\alpha}=\frac{1}{3}$). The parameter α in equation (11.57), which gives the width of the absorption line, is a damping parameter; in solids it originates, very likely, in the dipolar interaction. Since the dipolar interaction is taken mainly in the quenching effect, we may expect a small damping, and, consequently, a rather sharp resonance line. In liquids, besides the random distribution of the dipoles (and the average over angle α), we may expect the usual motional narrowing of the line. In gases the quenching field is weak, and the parametric resonance is not expected to occur.

The equation of the quasi-classical motion reads

$$\ddot{\theta}+(2\omega_0)^2\theta=-\omega_0^2h(\theta)\cos\omega t\ , \tag{11.58}$$

where the c-number (θ) is determined by comparing the absorbed power with the absorbed power computed by means of the transition rate of the quantum jumps.

All the examples presented above of quasi-classical description involve additional approximations, more or less motivated, indicating the limits of the quasi-classical treatment.

12 References

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Index