A Philosophical Essay on Molecular Structure

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To everyone who loves chemistry

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PREFACE

We can take an X-ray photograph of molecules. But we cannot take any photograph whatsoever of molecular structure. Why? What is molecular structure in the first place? The idea of writing this book arose from my own curiosity about molecular structure. I wanted to know whether or not what we assume to be molecular structure is relevant to the real structure of the molecule, if molecular structure exists at all.

It was not “skepticism” but “curiosity” that drove me to writing the book. As someone once kindly pointed out to me in personal communication, skepticism is of a social nature, if it means the doctrine that knowledge in a particular area is subject to being doubted. Skepticism can be personal as well, if it involves an attitude toward a particular object. This kind of skepticism can be shared, however, with people who regard an object in the same way. On the other hand, curiosity is quite personal by nature, for it is supported by emotions like comfort or discomfort, which originate from and belong to a particular individual. (Dogs are very curious but not skeptical—probably!) Accordingly, while skepticism can be either agreed or disagreed with, curiosity is seen with empathy. I hope this book receives your warm empathy.

As a practitioner of organic chemistry, I know that the concept of molecular structure is sufficient for many purposes. A moment's reflection is enough to realize this. Let us say we want to synthesize chemical compounds which have a certain physiological effect. Without knowledge of molecular structure, we have no way to proceed other than to rely upon trial and error. We would be back in the nineteenth century. In fact, present-day drug research is performed with great precision and in an amazingly efficient manner because it is based on structure-activity relationships. Our knowledge of molecular structure also enables logic-guided chemical synthesis.

Thus, there is no problem with assuming the existence of molecular structure for practical purposes. There is no skepticism of either type, at least among chemists. But, to me, the case I described above seems only to show that it is empirically adequate. Since the molecule is too small to see, visual evidence is not available. Everything we know about molecular structure is circumstantial. Reality may be different from what we assume it to be. Moreover, since submicroscopic entities are subject to the laws of quantum mechanics, the details of these entities may be hard to represent by analogy with things around us. For instance, we can find nothing parallel to the particle-wave duality of electrons in the world of possible experience.

My questions can be specified as follows: In what sense is our concept of molecular structure relevant to reality? Can we (or how can we) defend it from criticism of the kind that it cannot be derived from quantum mechanical calculations of the molecule? (It is customary to think that an ab initio method provides exact accounts of molecules because it is grounded on fundamental physical principles. It is more reliable than what is conceived of based on empirical data. In fact, "ab initio" does not mean starting from scratch.) Is it that "molecular structure" is an ingenious device to describe the chemical properties of molecules but that the true nature of molecules is otherwise? Structure is a concept that has a proper use within the bounds of the senses. Then, is it legitimate to talk about the structure of what exists beyond those bounds? I believe that these questions are fascinating, both for practical chemists and for philosophers of chemistry.

The arguments in this book lead us to consider the meaning of reality. In everyday life we take things we perceive as real. But the way of perceiving objects depends on the conditions under which perception occurs. (It depends on cognitive abilities as well: kestrels, which perceive UV rays, might be seeing a world quite different from ours.) Since we, unlike the Omnipotent, cannot enjoy a view from anywhere but a first-person perspective, what we perceive has to be conditional and provisional. We need to reconsider the idea of objective reality.

The majority of chemists may be too busy with their work to care about the questions described above. But not to take anything for granted, or at least to reconsider what is taken for granted, is needed for practitioners to deepen their understanding of what they are doing. Some people do not hesitate to equate what we assume to be molecular structure with reality, for example those who take orbitals to have physical significance. As Scerri pointed out, orbitals are none other than mathematical wave functions. (Scerri 2008, pp.200-213) Critical faculties are essential for scientists as well as for philosophers.

Most of the arguments in this book are based on Kant's *Critique of Pure Reason*. Kant is the figure in philosophy most comparable to Kekulé in chemistry. Just as Kekulé synthesized two seemingly conflicting claims about molecular constitution into the theory of molecular structure, Kant settled disputes between empiricists and rationalists and provided science with firm philosophical grounds. His theory of knowledge serves as a guiding principle for our arguments. Its significance is twofold: first, it shows us how our cognition of objects is possible and how concepts are legitimately or illegitimately applied to those objects; second, it warns us not to mistake a subjective conception for an objective one.

As you see from the description above, this book does not aim to be a textbook or a review article of a particular field of philosophy or chemistry. Rather, it will find its value in stimulating your mind by shaking your beliefs about chemistry. (Hence it is desirable for readers to have an undergraduate-level knowledge of chemistry. But, of course, those who are merely interested in chemistry or philosophy are welcome.) You may find several arguments in this book hard to agree with. If so, try to explain to yourself why. Understand clearly with what point or in what sense you cannot agree. In so doing, confirm your philosophical standpoint and make alternative—or your original—arguments. That is how we learn philosophy. I hope this book gives you a chance to learn about the philosophy of chemistry. Actually, I am not sure whether my intention will be successful. In the end, it is you who will decide. I would appreciate your honest opinions and advice.

I have another word about the composition of the book: The arguments in Chapter 2 and Chapters 5 through 8 are based on my original works. Some of them have been published in *Foundations of Chemistry* and *Hyle—International Journal for Philosophy of Chemistry*. The minimum knowledge necessary for reading these chapters is provided in Chapters 1, 3 and 4. Since there are potentially as many ways of choosing the necessary minimum as viewpoints, what I show you in these chapters is the contents of my tool-box, as it were. When I think, I always refer back to pieces of information collected in these chapters. So, I hope they are helpful for you, too. It is said that, if you have a look at a person's tool-box, you can see what he is thinking about. The arguments in Chapters 1 and 3 are based on secondary sources. Chapter 4 is an abstract of Kant's *Critique of Pure Reason*, which provides the basis for the chapters that follow.

You may find confusion or contradictions in the arguments. Such may be a sign that the writer is going astray. He is groping his way, which is neither straight nor easy to find. With a big heart, go along with him for a while, and you can enjoy this book as a memoir of a philosophical journey.

I thank the journals mentioned above for allowing me to reproduce the principal arguments of my articles. I also express my thanks to the reviewers of my articles published in these journals, who gave me valuable comments and advice to make my arguments coherent and convincing. I express my special thanks to Jeffrey I. Seeman. In our personal communication at the beginning of 2020 he reminded me of how important it is to be exact with words in philosophical arguments. Finally I express my cordial gratitude to Eric Scerri, who kindly opened the door for me to “The International Society for the Philosophy of Chemistry” where I have become acquainted with many fellow philosophers of chemistry. Without their support and intellectual stimulation this small book was not written.

CHAPTER 1

A HISTORICAL OVERVIEW OF THE THEORY OF MOLECULAR STRUCTURE

Significant developments in chemistry in the 19th century

1800	Volta invents the Voltaic pile, the first electric battery.
1803	Dalton presents his atomic theory in *A New System of Chemical Philosophy*.
	Berzelius develops the “theory of electrochemical dualism”.
1807	Davy isolates Na and K by electrolysis of molten alkaline salts.
1808	Gay-Lussac discovers the law of combining volumes.
1811	Avogadro presents the “equal volumes equal numbers hypothesis”.
1828	Wöhler succeeds in creating urea from inorganic materials.
1830-7	Liebig develops the elemental analysis of organic compounds.
1837	Laurent develops the non-electrochemical “nucleus theory”.
	Berzelius develops the “radical theory”.

1838	Dumas prepares trichloroacetic acid and develops the “type theory”.
1839	Gerhardt puts forward the “theory of residues”.
1839-41	Berzelius develops the “copula theory”.
1845-49	Hofmann prepares secondary and tertiary amines.
1848	Pasteur succeeds in the optical resolution of tartaric acid.
1848-49	Kolbe and Frankland try to isolate alkyl radicals.
1849	Wurtz prepares primary amines. Frankland stumbles on the first organometallic compounds.
1850	Williamson prepares various ethers.
1852	Gerhardt prepares various mixed acid anhydrides. Frankland puts forward the concept of saturation capacity.
1853	Gerhardt develops the “new type theory”.
1857	Kekulé presents the concept of the C-C bond.
1858	Canizzaro calculates atomic weights from vapor densities. Couper’s suggestion of the C-C bond is publicized.
1860	Cannizzaro’s system of atomic weights is accepted at the Karlsruhe Congress.
1864	Crum-Brown begins using a prototype of structural formulas.
1865	Hofmann first uses the croquet-ball model. Kekulé proposes the structure of the benzene ring.

1866	Frankland proposes the concept of the chemical bond.
1869	Mendeleev presents the table of elements.
1874	van ’t Hoff proposes the concept of the tetrahedron carbon atom.
	Le Bel introduces the idea of the tetrahedron with regard to molecular types.
	Körner uses the word “molecular structure”.

1. The dawn of structural chemistry

Nineteenth-century chemistry developed around the following two poles: the invention of the Voltaic pile, Dalton’s chemical atomism. The impact of these historic events cannot be fully appreciated without understanding the philosophical and scientific contexts in which they took place. To put it simply, the dominant philosophical atmosphere in that era was characterized by a belief in dualism, and the dualistic philosophical framework fostered scientific ideas in which electricity played a central role. (Articles collected in Knight 1968 illustrate the philosophical atmosphere in the nineteenth century.)

The Voltaic pile was not only the first electrical battery but also a symbolic apparatus that revealed the dynamic nature of matter. Making use of the Voltaic pile Davy achieved the electrolysis of various molten salts, which resulted in the discovery of alkaline and alkaline earth elements such as sodium, potassium and calcium. These discoveries suggested that the essence of chemical affinity is electric attraction, and that when the attractive and repulsive forces exerted by electrodes were stronger than chemical affinity, electropositive and electronegative elements would be pulled apart and attracted to electrodes with an opposite charge. It is reasonable that Berzelius, who advocated electrochemical dualism, appreciated Davy's Bakerian Lecture in 1806 and wrote "that it must be placed among the finest memoirs with which chemical theory has been enriched." (Knight 1998, p.62) It was awarded the prize for the best work on electricity given by the Institute in Paris. This prize was offered on the instructions of Napoleon and was open to citizens of any nation.

If it is Davy who should be remembered for linking chemical action with electrolysis, it is Berzelius who gained historical fame by linking chemical atomism with dualism. He thought that chemical compounds consist of electropositive and electronegative elements or groups of elements, as is suggested by the composition of sodium chloride and sodium sulfate, for instance. His theory of the binary constitution of inorganic compounds was widely accepted in the 1810s and 20s. Then, he went one step further and claimed that organic compounds also consist of electropositive and electronegative components. Methyl sulfate may be a simple example which illustrates his idea. Such an electropositive organic component as the methyl in methyl sulfate he later named "radical."

The concept of the radical originated in 1787 with Guyton de Morveau who spoke of it as “the simple substance of an acid which modifies oxygen,” consistent with Lavoisier’s notion of the radical. (Russell 1971, p.23) Lavoisier considered organic acids to be oxides of radicals which contained carbon and hydrogen. During the 1830s “the concept of the radical developed in the arguments of electrochemical dualism and took on a number of epistemologically interesting characteristics.” (Ramberg 2003, p.17) The idea was simple: if radicals play the same role in organic molecules as chemical elements do in inorganic compounds, they could be isolated just as chemical elements can be isolated from inorganic compounds. Given electrochemical dualism, “determining the true nature of radicals would be the endpoint of chemical investigation.” (ibid. idem, p.18) It is not surprising that many chemists were absorbed in isolating radicals. Among others the studies on the benzoyl radical by Liebig and Wöhler, the cacodyl radical by Bunsen, etc., are famous examples. Actually, in spite of great efforts, all attempts to isolate organic radicals failed, though some of them bore unexpected fruit. For instance, Kolbe and Frankland pioneered electrochemistry and organometallic chemistry, respectively, in their joint research aimed at isolating alkyl radicals. The regularity found in the number of organic ligands would lead Frankland to the concept of saturation capacity, another name for valence of our day.

In addition to the failures to isolate radicals, another problem that was unfavorable to the radical theory arose. From the late twenties to the thirties it was discovered that the electropositive hydrogen of hydrocarbon radicals could be replaced by electronegative chlorine. In 1827 Dumas found that chlorine-based bleaching agents could chlorinate wax. This was incomprehensible to chemists who took the tenets of electrochemical dualism for granted. The sodium of sodium sulfate could not be replaced by chlorine, but the hydrogen of wax could! What difference was there between them? In the 1830s Laurent discovered that the hydrogen of naphthalene could be replaced by chlorine and Dumas chlorinated acetic acid to make trichloroacetic acid. Also, Dumas' assistant Louis Melsens found a method of reducing chlorinated compounds back to their starting materials. With this accumulation of facts, the radical theory—and the copula theory, which was the modified version of the former—became highly controversial.

Why and how could electronegative chlorine replace electropositive hydrogen? In order to understand the meaning of this question we need to consider the notion of atoms in the whole picture of nineteenth-century chemistry. We also need to understand the relation between the notions of elements, atoms and radicals. The questions we have to address are as follows: What was chemical atomism? What role did Dalton's theory play in the development of chemistry in the nineteenth century and thereafter?

Simply put, Dalton made atoms objects to be measured on a chemical balance. That is to say, the historical as well as the scientific significance of Dalton's theory consists in that it converted atoms from the metaphysical objects of antiquity into the material constituents of chemical compounds. The essence of the chemical atomic theory becomes clear when it is stated in relation to certain regularities observed in the weight proportions of elements that combine to form chemical compounds. The chemical atomic theory states the following: "*there exists for each element a unique atomic weight, a chemically indivisible unit that enters into combination with similar units of other elements in small integral multiples*." (Rocke 1984, p.12) In this sense chemical atoms served as a sound basis for the concept of elements defined by Lavoisier. He describes in *Elements of Chemistry* (1789) that "those things that have not been broken down into simpler substances should be considered elemental." (Ede 2006, p. 61)

The easiest way of understanding the chemical atomic theory might be to take a look at the situation which existed before its appearance. Before Dalton, it was the corpuscular theory that was most widely accepted among those who were interested in natural philosophy. "The atoms of the seventeenth- and eighteenth-century corpuscular philosophy were all composed of the same stuff and differed only in shape and size. Various arrangements of these particles formed larger units which, in their turn, composed the various substances we encounter." (Knight 1968, p.xv) Boyle and Newton maintained that things were made up of different arrangements of a few kinds of prime matter. Such being the case, the corpuscular philosophy led to no detailed predictions or explanations of phenomena and it was regarded by most chemists to be of little value in chemistry. By ascribing an atomic weight to each element Dalton's theory made it possible to say something meaningful about things happening beyond the bounds of the senses in relation to things observed within those bounds. In other words, it enabled "transdiction" in chemical reasoning, which we shall discuss in Chapter 5.

The radical theory was the first structure theory in the history of chemistry. Chemists of the Berzelian school sought a true and absolute picture of the microscopic world based on empirical knowledge of chemical reactions. In other words, they made a kind of inference (a projective inference in the vertical direction to the empirical horizon) and tried to make a link between what was within and what was outside the bounds of the senses. This is the key to understanding the reason why the isolation of radicals did not succeed. The concept of the radical derived from the dualistic view of chemical compounds. "The concept of the radical was not related to the study of the microscopic world but only to the manipulation of chemical formulas." (Ramberg 2003, p.17) In the four-volume formulation of the day acetic acid was believed to consist of an electropositive C_2H_6 radical and an electronegative $C_2O_3 \cdot H_2O$

part—oxalic acid in their formulation—because the chemical property of acetic acid was explicable by their combination. “Radicals were discovered simply by manipulating formulas on paper.” (idem)

2. The composition and the type of chemical compounds

Is acetic acid a copulated compound represented as $C_2H_6 \cdot C_2O_3 \cdot H_2O$? The term “copula” was originally used by Gerhardt to indicate the organic part of a molecule. (Russell 1971, p.28) Berzelius used this concept to defend his dualistic view of the molecule. He claimed that the hydrogen of an organic copula could be replaced by chlorine because this reaction “occurred only in the passive, chemically unimportant copula.” If so, it would “not be a surprise that the fundamental chemical property of the compound did not change” due to the introduction of chlorine. (Rocke 1993, p.56) But does acetic acid really consist of a hydrocarbon copula and oxalic acid? Does it have a water molecule in it? No. Neither radicals nor copulas can be isolated after all. Another point to be considered is the system of chemical stoichiometry: Does acetic acid consist of four carbons, eight hydrogens and four oxygens? In other words, is the four-volume formulation correct? All these questions were to be solved together because they derived from one and the same historical fact.

Berzelius combined Dalton’s theory and Davy’s idea to postulate electrochemical dualism and, during that process, by his determination of atomic weights, transformed chemistry into a science based on exact data. He assumed that all atoms are spherical and of equal size—and so, he thought, the volumes of gases were proportional to the number of atoms—and determined chemical formulas for non-metallic compounds systematically, based on data of vapor densities. The most important thing from a historical point of view is that he determined the formulas of organic acids based on silver acetate and took silver and lead acetates as $[Ag]O \cdot C_4H_6O_3$ and $[Pb]O \cdot C_4H_6O_3$, respectively. Because of this mistake the molecular weights of organic acids became double the present values. (Summarized and quoted from Rocke 1984, pp.75-78; 2001, p.91) On the other hand, since the molecular weights of simple inorganic molecules such as water and carbon dioxide were determined by a different method and had correct values, the dehydration condensation reactions of acids produced H_4O_2 instead of H_2O. It was Gerhardt who addressed head-on the inconsistency in molecular weight between the organic and inorganic domains. He proposed either to halve the molecular weights of organic compounds or double those of inorganic compounds. In view of the Avogadro-Ampere hypothesis he pointed out that the former was the proper option to take. It is easy to imagine that his proposal annoyed many chemists of the day. Liebig and Wöhler rightly feared his adjustment would destroy all the relationships between compounds that had been painstakingly built up since the early work of Berzelius.

Gerhardt was “accused of doing algebra and not chemistry.” (Buckingham 2004, p.167) In fact, by virtue of his adjustment, the molecular formula of acetic acid became $C_2H_4O_2$ and, consequently, there was no room for radicals or copulas appearing in molecules. Thus, the unitary view of acetic acid, and of other organic compounds as well, was established.

Gerhardt was a former student of Liebig and spent many years in Paris, where he collaborated with Laurent, an assistant of Dumas. Paris in the mid-nineteenth century was under the influence of Auguste Comte (1798-1857), the founder of positivism. He taught that science progresses from a theological interpretation of nature to a metaphysical one and from there to a “positive” view where final causes are no longer sought and outward phenomena are all that matter. “It is more than a coincidence that its chief expositor was the friend and teacher of some of the leading chemists of Paris.” (Russell 1971, p.48)

Another feature common in nineteenth-century science was the use of analogy. This trend reached its highest around the mid-nineteenth century. Darwin thought that, just as massive crustal movements and deformations over a geological time had made the present landscape, every living creature had evolved over many generations. The idea of biological evolution must have been natural for him, since he had happened to witness crust uplifting from the Beagle. Chemistry was no exception. Comparison of all organic compounds with a limited number of types of simple inorganic compounds was quite in keeping with the general scientific outlook.

When Gerhardt came to Paris in 1838, Dumas was just fashioning his theory of types. Dumas prepared trichloroacetic acid from acetic acid and discovered that both compounds had almost the same chemical properties. He thought that something like chemical type was retained in substitution reactions. In fact, “Dumas based his theory not only on his experimental work on substitution reactions but also on the ideas of Laurent.” (Rocke 1984, p.201) As early as 1831 Laurent had studied the chlorination of naphthalene and put forward the nucleus theory. He regarded naphthalene as the fundamental radical that could be altered to form various derived radicals. Although he called it a radical, it was actually what we refer to as a hydrocarbon group. Laurent thought that the chemical properties of compounds were not directly connected to the properties of chemical elements, but rather to the positions of atoms in molecules. Both hydrogen and chlorine in a “nucleus”—a molecular skeleton consisting of hydrogen and carbon—could be electrically neutral. Laurent’s theory pioneered the structure theory not only through its unitary view of the molecule but also through the classificatory principle based on the types of compounds. In view of the later development made by Kekulé—the point of his claim was that each atom in the molecule was ontologically equivalent—"Laurent’s classificatory principle was far more fruitful than that of Dumas.” Dumas defined types as “bodies which are shown to be formed from the same number of chemical equivalents united in the same manner.” (ibd. idem, p.198) Those types were conserved in substitution reactions, and so fundamental chemical properties were retained in all compounds of a given type. But since there existed many groups of compounds, as was the case with dimethyl ether and ethanol, that satisfied this definition and had different properties, Dumas asserted that “such compounds were not to be thought of as belonging to the same chemical type though they did belong to the same mechanical type.” It is easy to see the influence of “nucleus” on “mechanical type.” (ibid. idem, p.199)

Gerhardt put forward his theory of residues in 1839, in which he assumed that “double decomposition reactions involve the rearrangement of residues which were atomic complexes left over through those reactions.” (Russell 1971, p.47) To apply his idea to esterification, the hydrogen of alcohol combines with the hydroxide of acid, and the residues—alkoxide and acyl—unite to give the ester. Although his residues retained a similarity to radicals, residues had no independent existence. Gerhardt claimed that they were merely the expressions of the mode of reactions. Gerhardt’s theory served as a link between Dumas’ and Laurent’s unitary view and the radical theory.

In 1853, Gerhardt proposed to classify every organic compound based on four types of simple inorganic compounds, that is, ammonia, water, hydrochloric acid and hydrogen. Later, the last one was replaced by the methane type; hydrochloric acid, water, ammonia and methane were regarded by Odling, Frankland and Williamson as the typical compounds representing valences I through IV. This is the reason why H, O, N and C are now called typical elements. Anyway, it was Gerhardt who systematized the existing speculation on types.

It was as early as 1840 that Liebig suggested that "ammonia could be considered as the prototype of all organic bases and predicted the possibility of ethyl-substituted ammonia." (Rocke 1984, p.223) This prediction was achieved by his former student Adolphe Wurtz in 1849. Another of Liebig's former students, A.W. Hofmann, prepared a variety of secondary and tertiary amines and regarded them as the results of the substitution of hydrocarbon radicals for hydrogen in ammonia. He established the ammonia type.

As Hofmann is associated with the ammonia type, A.W. Williamson is strongly associated with the water type. When Williamson became interested in the theory of etherification, there existed two different views: Dumas, who held the unitary view of the molecule, claimed that ethyl alcohol $C_2H_4 \cdot 2H_2O$ was dehydrated to give ethyl ether $C_2H_4 \cdot H_2O$; on the other hand Liebig claimed, from a radical theoretical point of view, that alcohol $C_4H_{10} \cdot H_2O$ was dehydrated to ether $C_4H_{10}O$. Williamson began his research with the intention of producing homologous alcohols through the action of potassium ethoxide on ethyl iodide. If Dumas' and Liebig's formulas were correct, the product would contain two oxygen atoms. The new substance he obtained, however, contained only a single oxygen atom. He also obtained a certain mixed ether by the action of potassium ethoxide on methyl iodide. These results suggested that ethyl alcohol was C_2H_5OH, and that potassium salt and ether were C_2H_5OK and $C_2H_5OC_2H_5$, respectively. In 1851 he read his third and the final paper of a series on ether synthesis at the annual meeting of the British Association. “I believe that throughout inorganic chemistry, and for the best-known organic compounds, one single type will be found sufficient; it is that of water, represented as containing 2 atoms of hydrogen to 1 of oxygen,” thus publicizing his water type. (This paragraph is partially modified and quoted from Rocke 1984, p.220)

In contrast to Hofmann, who was careful to limit his idea of types to a small number of volatile organic bases, Williamson viewed the vast majority of chemical reactions as analogous to the formation of salts by means of double decomposition reactions between acids and bases. It led him to predict that acid anhydrides could be prepared by the dehydration of monobasic organic acids just as ethers were prepared from alcohols. Williamson thought that acid anhydrides were nothing but the ethers of organic acids. This was proved correct in 1852 by Gerhardt who prepared benzoic acid anhydride through the reaction of sodium benzoate with benzoyl chloride. Gerhardt also prepared a variety of acid anhydrides through the reactions of benzoic, cinnamic, salicylic and acetic acids. He stated that “water could serve as the type of all organic acids as ammonia does for the organic bases.” In addition, Williamson developed concepts such as “monobasic” and “bibasic” moieties, from which the theory of valence is derived. These are the reasons why it is Williamson, and not Hofmann, who deserves most of the credit for the development of the mature theory of types. (Summarized and quoted from Rocke 1984, p.221)

3. From valence to structure

Why does the element of nitrogen combine with three equivalents of hydrogen, whereas oxygen combines with only two equivalents of hydrogen? Is it not because elements themselves have saturation capacities? In the 1850s it became apparent that an atom of a given element could combine with only a limited number of atoms of other elements. But ever since the days of Dalton, “the existence of indivisible atomic particles had been in dispute among chemists.” Many chemists used the term “atom” purely as a convention without commitment to its etymological meaning. The term “atom” was what Nye calls “a perfect instance of polysemy in metaphor,” because “it combined the property of concrete objects with the opposite property of infinitesimal points.” (Nye 1993, p.80)

Wurtz, whose name is remembered for the so-called Wurtz coupling, was engaged in an attempt to isolate alkyl radicals through the action of metallic sodium on alkyl halides. With the same intention he investigated the reactions of glycerin and glycol. It was these investigations that led him to the idea of polybasic radicals. He wrote in 1855 that "one can consider glycerin as a species of tribasic alcohol, that is, an alcohol containing 3 equivalents of hydrogen capable of being replaced by 3 groups [...] thus forming a link between 3 molecules of conjugated water." (Rocke 1984, p.256) Wurtz, influenced by Williamson's water type, further developed his idea and speculated about why an atom of an element could combine with a fixed number of atoms of other elements. He wrote, "Just as glycerin was a tribasic radical consisting of three groups of atoms bound together, each group capable of carrying one alcoholic or ester function, so also might the nitrogen atom and the phosphorus atom each consist of three smaller particles bound together, with each particle capable of forming a bond to an equivalent of hydrogen, say, or chlorine." (Rocke 2001, p.206)

A little earlier than Wurtz's publication of his subatomic speculation, Frankland, who was attempting to isolate radicals using a similar approach to Wurtz's, had stumbled on organozinc compounds. He carried out extensive experiments to prepare a variety of novel organometallic compounds and, during these investigations, he noticed that there exists a maximum combining value or a capacity of saturation in metallic elements. He wrote in 1849, "it was evident that the atoms of zinc, tin, arsenic, antimony etc., had only room, so to speak, for the attachment of a fixed and definite number of the atoms of other elements." (Rocke 1984, p.239)

Frankland's "combining power" or "saturation capacity" was the same as the "atomicity" of Wurtz, who defined it as "the force or power of combination which resides in atoms, and which is exercised in different manner according to the nature of the atoms." Hofmann objected that "atomicity was a barbarous expression because it suggested atomic structure." He preferred an observational word such as "quantivalence" which was later shortened, by Kekulé and Hermann Wichelhaus, to "valence." (Nye1993, p.80)

The concept of valence was essential not only to putting an end to Berzelian electrochemical dualism but also to the reconsideration of the type theory, because valence led chemists to the notion that each atom in the molecule was ontologically equivalent and none should dominate within the molecule. Every atom was in principle as important as every other and could combine with the atoms of other elements in such a way that the valence of each atom was satisfied. This was in marked contrast to Kolbe's model, which was based on "a strict hierarchy of constituent radicals," where only one radical was taken as "fundamental" and distinguished from other radicals. (Rocke 1993, p.311)

Although there is no doubt that the concept of valence played an important role in the future development of structural chemistry, it must have been an elusive one for many chemists of the day. It was concerned only with the number of atoms united with one atom of an element. It possessed no physical significance at all. In addition, nobody knew how it could be actualized. Wurtz's subatomic speculation was only speculation after all. They could find no explanation about it. This became an obstacle to gaining acceptance of the concept of directed valence, on which van 't Hoff's tetrahedral carbon hypothesis was based. How could an atom's chemical affinity be split into different parts? The physics of that period asserted that "the direction of an attractive force was determined by the positions of the attracted bodies." "Neither electrical nor gravitational forces could explain combining power." (Ramberg 2003, p.39)

Thus, valence was a mysterious concept whose elucidation had to be left for the next century. But chemists could go ahead with their projects, with unknown things left as such. Such was the case with Kekulé, who could postulate the idea of a sequential connection of carbon atoms. In view of the fact that there existed molecules consisting of like atoms, he accepted the idea that atoms of one element could combine with one another. It was such empirical flexibility that enabled Kekulé to discover the architecture of molecules.

Friedrich August Kekulé is regarded, together with Archibald Scott Couper, as one of the most important architects of structural chemistry in the nineteenth century. The essence of his theoretical achievement may be summarized in the following points: he assumed a constant combining power for the atoms of the typical elements and suggested for the first time that carbon was tetravalent; he suggested that a carbon atom could satisfy the affinity of other carbon atoms, or in other words, that the self-linking of carbon atoms was possible; finally, thinking that each atom in the molecule was ontologically equivalent, he proposed to construct chemical formulas that truly depicted the positions of atoms in molecules and conveyed all of the chemical properties. (Summarized and quoted from Ramberg 2003, pp.21-23)

Kekulé thought that both the radical theory and the type theory "implicitly assigned a privileged status to certain parts of molecules." "Radicals and types were relative terms that depended entirely on the reaction under consideration." "A radical was simply the unreactive part of a molecule" in a particular reaction, while a type was a conventional grouping of molecules based on the connecting atom, such as oxygen in the water type or nitrogen in the ammonia type. (ibid. idem, pp.21-22) The same molecule reacts with different reagents in different ways and reveals different aspects of its constitution. It is clear that a substance belongs to more than one type and contains different constituent radicals. A single reaction reveals a single type-radical relationship and all such relationships should be summarized in a rational formula.

To rephrase the point, Kekulé considered that chemical formulas were nothing but reaction formulas, because the chemical properties of substances could emerge only through their transformations. But a chemical formula should depict the entire chemical nature of a substance and not simply a reaction at a particular moment. A reaction formula that expresses simultaneously the largest number of transformations is the most rational. In this sense a formula exhibiting atomic groupings as revealed by chemical reactions is worth the name "rational formula." The most important thing for Kekulé was that a rational formula derived from the empirical knowledge of chemical reactions should express chemists' ideas in a clear fashion.

A rational formula represents the chemical properties, but not the constitution, of the molecule. This point was clearly expressed by the Russian chemist Aleksandr Butlerov in his unique conception of chemical structure: it is the chemical arrangement or the manner of the mutual binding of atoms which can be realized through the rules of valence. It is, therefore, concerned with chemical, not physical, structure. Butlerov thought that "chemistry was concerned only with bodies in a state of transformation." "Chemistry was powerless to judge physical structure" because the relation between the relative chemical positions of the atoms in molecules and their relative physical positions was not known. Butlerov wrote, "We do not even know whether, in such a molecule, two atoms which directly affect each other chemically are in fact situated next to one another." (Ramberg 2003, p.24) In view of the later acceptance of the concept of physical structure among chemists we should not underestimate the implication of this statement. We have to consider the historical circumstances in which this was written. One thing we need to take into consideration is that Butlerov was, like Kekulé, under the influence of Gerhardt's structural agnosticism.

4. The synthesis of chemical and physical structure

Before the 1870s it was not taken for granted that there exists a relation between chemical and physical structure, namely, a relation between what is inferred from the chemical properties of substances and the spatial arrangement of atoms in molecules. For instance, Kekulé's cyclohexatriene model of benzene implied neither that the ring itself was hexagonal nor that the six hydrogen atoms were placed on the corners of the hexagon. What was meant was merely that six hydrogen atoms were chemically equivalent: any of them could be lost in substitution reactions. There were several other models such as Albert Ladenburg's prism model, Lothar Meyer's octahedron, and Josef Loschmidt's, and so on. None of them had the hexagonal distribution of carbons and hydrogens. They seem strange to us, our being familiar with cyclohexatriene arrangement. Actually, all of them satisfied the requirement of the chemical equivalence of six hydrogen atoms. They were taken to be alternatives to Kekulé's model.

One important clue to resolving this situation had already been given in 1848 by Louis Pasteur. It was his optical resolution of paratartrate. (Ramberg 2003, pp.34-35) Pasteur noticed that sodium ammonium salt of racemic acid, when recrystallized below 27°C, contained two sets of crystals, that is, those having faces oriented toward the right and those with faces oriented toward the left. He painstakingly separated the two types of crystals by hand and tested each for its effect on polarized light. He found that the solution of the right-handed crystals rotated light to the right with a magnitude equal to that of the well-known dextrorotatory tartrate, while the solution of the left-handed crystals rotated light to the left with a magnitude equal to that of tartrate—this was the hitherto unknown levorotatory acid. A solution containing equal amounts of the two types of crystals had no effect on polarized light. He concluded that the right-handed and the left-handed crystals were composed of right-handed and left-handed asymmetric molecules of tartrate; the optical inactivity of paratartrate was attributed to equal amounts of the right-handed and the left-handed isomers, each of which canceled the effect of the other. An optical activity was now the primary indicator of asymmetry at the molecular level.

It seems a little strange that it was not until the late 1860s that the conclusion was reached, by Johannes Wislicenus, that some sort of physical cause was necessary to explain the difference in optical rotation between the two isomers of lactic acid. (Details are illustrated in Ramberg 2003, pp.40-52) Wislicenus was struggling to represent the dual behavior of lactic acid by somehow combining the theories of radicals and types. The attempt resulted in merely juggling radicals in the formula because lactic acid behaved like carboxylic acid in some reactions and like alcohol in other reactions. He regarded lactic acid—namely, 2-hydroxypropionic acid or ethylidene lactic acid in his terminology—as an analogue of propionic acid and tried to synthesize it in the way in which propionic acid was prepared. What he obtained was, however, 3-hydroxypropionic acid or ethylene lactic acid. Wislicenus carried on working with these related compounds and found that ethyliden lactic acid was identical with paralactic acid from meat extract, except that the latter was optically active.

This discovery led him to recognize the difference between the chemical and physical properties of molecules, the former being determined by the nature of atoms and the sequence of their combination. On the other hand, physical properties such as optical rotation are due to differences in the geometrical arrangement of chemically identical molecules. Wislicenus says: "Thus is given the first certainly proved case in which the number of isomers exceeds the number of possible structures. Facts like these compel us to explain different isomeric molecules with the same structural formula by different positions of their atoms in space, and to seek for definite representations of these." (Partington 1961-70, 4, p.761) Wislicenus was convinced that the spatial arrangement of atoms in molecules had something to do with the observed phenomena, though he could not prove it.

As this episode eloquently shows, chemical formulas before van ’t Hoff were not three-dimensional. They were not two-dimensional either. Actually, they were dimensionless or rather, not meant to be a picture of the microscopic world at all. Chemical formulas represented the abstract concepts of chemical combination implied by valence. They were, as it were, “symbolic forms of representation” (in Ramberg’s words) and not windows into the physical reality of the molecule.

Pivotal discoveries in science sometimes happen to be achieved independently and simultaneously by more than one scientist. Such was the case with the discovery of the notion of the C-C bond by Kekulé and Couper. The discovery of so-called asymmetric carbon may be counted among such examples as well. Actually, the viewpoints from which van ’t Hoff and Le Bel saw their problems were distinct from one another and accordingly, what they achieved is worth separate evaluation. In brief, van ’t Hoff discovered the tetrahedral asymmetric carbon atom, whereas Le Bel, who drew on the tradition of French crystallography, discovered the tetrahedral asymmetric molecule. The significance of the former was that it showed the directed valence of a carbon atom and that of the latter was that it showed a relation between molecular forms and crystal forms. Their common claim to fame is their synthesis of chemical and physical reality or the addition of a spatial meaning to chemical formulas.

In his 14-page Dutch pamphlet in 1874 van 't Hoff made the following three assumptions: first, the tetrahedral arrangement of the valence of the carbon atom; second, that "asymmetric carbon" is a cause of optical activity; third, that all carbon atoms are tetrahedral, whether or not they are asymmetric and whether unsaturated or not. By virtue of these hypotheses van 't Hoff was able to predict the existence of spatial isomers in saturated asymmetric molecules as well as unsaturated ones. This predictive characteristic gave his theory a deductive character that was absent in Le Bel's theory. (summarized and quoted from Ramberg 2003, p.85)

Although it seems true that van 't Hoff was inspired by Wislicenus' extensive research on lactic acid, it is also the case that van 't Hoff attended Kekulé's lecture, where he saw a tetrahedral-carbon model. The point of van 't Hoff's idea is that "directed valence is so rigid that the substituents on a central carbon atom are not capable of changing their places." It is not only easy but also seems rational to think that van' t Hoff was under the influence of Kekulé's lecture. (ibid. idem, pp.56-57)

On the other hand, Le Bel introduced the idea of the tetrahedron from symmetry or asymmetry in molecular types, and not from a concern with accounting for observed isomerism. The starting point of his study was Pasteur's conclusion that "optical activity was the primary indicator of asymmetry at the molecular level." (ibid. idem, p.64) Le Bel stated, "in a molecule containing a formula of type MA_4, if three of the substituents were replaced by three different groups, the molecule would be asymmetric and optically active." (ibid. idem, p.65) Le Bel considered the molecule as a whole and so, required the accumulation of structural data in order to develop his theory. In view of the relatively low number of known compounds that displayed optical activity, it is natural that his inductive approach had lower predictive power.

5. Bond, structure and models

Valence was initially called "combining power" or "saturation capacity" by Frankland. Wurz called it "atomicity" and developed subatomic speculation. Unfortunately, since his arguments resolved nothing about how atomicity became realized, valence was taken by most chemists to be a rule of chemical stoichiometry.

It was in 1864 that Crum-Brown first used his graphic notation. (See Fig. 2-3 in Chapter 2) It is Crum-Brown who gave chemical structure a physical meaning. Most chemists, including Crum-Brown himself, however, initially took it as purely chemical and not physical structure. "They were used to express constitutional formulas, and by which, it is scarcely necessary to remark, I do not mean to indicate the physical, but merely the chemical position of atoms [...] and while it is no doubt liable, when not explained, to be mistaken for a representation of the physical position of the atoms, this misunderstanding can easily be prevented." (Crum-Brown, A.

1864; Trans. Roy. Soc. ed., 23, 708. Quoted in Ramberg 2003, p.28)

It was around the same time that Hofmann began using his croquet-ball model. In view of the philosophical as well as the chemical implication of the chemical bond, it is interesting that Frankland's first formal statement on "bond" appeared immediately after these events. In 1866 Frankland wrote: "By the term bond, I intend merely to give a more concrete expression to what has received various names from different chemists, such as an atomicity, an atomic power, and an equivalence. A monad is represented as an element having one bond, a dyad as an element possessing two bonds, etc. It is scarcely necessary to remark that by this term I do not intend to convey the idea of any material connection between the elements of a compound, the bonds actually holding the atoms of a chemical compound being, as regards their nature, much more like those which connect the members of our solar system." (Frankland, E. 1866; *J. Chem. Soc., 19,* 377-8. Quoted in Russell 1971, p.90)

Kant says we cannot cognize objects as they might exist in themselves. The objects of cognition must be given in sensibility via intuition and must be thought by the understanding through concepts. The combination of graphic notation and the term "bond" created a new reality of chemical bond. Accordingly, "the line between the chemical and the physical conceptions of structure became blurred." (Ramberg 2003, pp.26-27)

CHAPTER 2

STRUCTURE IN CHEMISTRY

Someone asks: What does “molecular structure” mean to chemists? What is it taken to be?

A possible answer: Well, it is a sequential connection and a spatial arrangement of atoms in a molecule. It is responsible for the chemical reactions possible for a given kind of molecule.

The following question: I see, but are you talking about molecular structure or rational formulas?

Actually, what chemists imagine from the term “molecular structure” is almost the same as Kekulé’s “rational formulas” or present-day structural formulas. Structural formulas are to molecular structure what maps are to the geography represented by maps.

1. What is molecular structure?

What do you imagine from the term “molecular structure”? Though there is a basic common understanding, we can imagine various things about it depending on our viewpoints and the issues to be addressed. Details aside, we think that the molecule has some structure: it consists of a sequential connection and a spatial arrangement of atoms. The way the atoms are connected is determined by the rule of valence. We can analyze molecular structure further and divide it into various subunits which are classified into different categories: a molecular skeleton, side chains, functional groups, reaction centers, etc. We represent what we take to be molecular structure with models. Worth noting is that we cannot verify in a direct manner whether they are relevant to reality.

First of all, we have to make it clear whether we are talking about what we take to be molecular structure, or the object we conceive of, or the relationship between them. We want to know whether or not our conception is relevant to the object. More specifically, we want to know in what sense and to what extent it is relevant to reality.

One reason why we are interested in this problem is that different approaches to one and the same object sometimes result in different descriptions: for instance, organic chemists think that molecules consist of atoms and bonds. Electrons in the molecule are paired and localized in bonds. But such a picture has not been derived a priori from quantum mechanical calculations. Quantum mechanics gives us no definite structure, but only molecular orbitals. It tells us that electrons are delocalized over the entire space. Which description is true? The answer is not simple: though both descriptions are relevant to some extent, neither of them is perfect. For instance, the conception of localized bonds is relevant to collective properties such as the heat of formation, whereas it is not relevant to one-electron properties such as light absorption. The latter requires us to know molecular orbitals. But this does not mean that our conception of molecular structure is irrelevant or groundless. Otherwise, to what can we credit our achievements in organic synthesis? The concept of molecular structure is the basis of the retrosynthetic analysis to be described below. On the other hand, if it is real, why can it not be derived from quantum mechanical calculations? The reason is that the molecule is not accessible to immediate observation, and so molecular structure is different in nature from structures around us.

One way to decide whether something does or does not exist is to look to causal relations. Pouring water on a fire extinguishes it; radiating an object with electrons decreases electric charges, etc. In each case there is no room for doubt about the relation between cause and effect. Then, what about the relation between designing molecules and the successful production of desired compounds? Why not take this as evidence that what we take to be molecular structure is real? The latter example is, however, not as simple as the previous ones. In order to verify the latter we have to follow a long series of causal chains. We shall discuss this problem in detail in Chapter 6.

Molecular structure offers fertile ground for philosophical imagination and is likely to give us a chance to see chemistry afresh and reconsider what we take for granted.

2. Things, stuff and molecules

We are surrounded by a variety of things such as smart phones, computers, the keyboard with which I am typing this manuscript, etc. Individual things have their own shapes and sizes. They are tangible and space-occupying: they exclude other things from the space they occupy. There is no room for doubt about their existence.

On the other hand, there are substances about whose shape and size we cannot be sure. They are the stuff things are composed of. Most chemical substances fall into this category. Let us say that we divide a pellet made of plastic. We divide it into arbitrary parts and continue dividing until we get to the level of atoms. All the parts are, regardless of their shapes and sizes, the stuff of the original pellet. It is the molecule that is regarded as the smallest unit of chemical substances. We ascribe chemical properties to constituent molecules. In reality, we do not know what is responsible for properties we observe: it might be the molecular structure of an individual molecule, interactions between molecules or something else. In drug research there are cases in which we cannot identify what is responsible for the observed pharmacological effects. Whether it is things, stuff or molecules that is responsible for what is observed, there must be something that acts on other things and makes things happen.

Things have a power to cause changes in other things by virtue of impact, contact, pressure, traction, etc., which is hence called causal power. Everything has causal power if it really exists. Therefore, we can look to it in order to decide whether or not theoretical entities really exist: we can do experiments and examine in what sense and to what extent theoretical entities are essential to the causal relations in which they are assumed to be involved.

Let us take the blue sky on a sunny day, for example. Is the blue sky real? The question is whether or not it has an effect that cannot be realized otherwise. Let us say someone is happy to see the blue sky. The blue sky seems to have the causal power to make her happy. The appearance of the sky is, however, transient and incorporeal. We are not sure whether or not the blue sky is a proper object to which to ascribe causal power.

The same is true of molecular structure because it is a creation of our mind. Chemists deal with tangible things on one hand and intervene in a world outside our experience on the other. Chemists are busy with struggling with gummy resins or product mixtures that resist every attempt at separation. On the other hand, they focus their mind's eye on what is going on in the world of molecules. Chemists go back and forth across the bounds of the senses.

The relations between things, stuff and molecules raise lots of fascinating philosophical questions, which have not been fully investigated to date.

3. Retrosynthesis and its philosophical implications

As we saw in Chapter 1, the need to classify the types of chemical reactions and the desire to understand the constitution of the molecule were both crystallized into the concept of molecular structure. The concept of molecular structure provides the basis of chemical synthesis.

One of the outstanding events in the history of organic chemistry was the total synthesis of vitamin B12. It was accomplished concurrently by Woodward at Harvard and Eschenmoser at ETH in 1972. The molecule is so big—it consists of 63 carbon atoms, including nine chiral centers at the central choline ring—that many chemists doubted if it was possible to achieve its total synthesis. Hence their work is regarded as a classic of organic chemistry and as proof that any chemical substance, no matter how complicated its constitution is, can be prepared chemically. In fact, as complexity increases, the process needed for its synthesis tends to be longer, and accordingly the number of possible choices of chemical reactions increases explosively. The total synthesis of vitamin B12 requires more than 90 steps and, reportedly, took more than 10 years and the participation of 90 or more post-doctoral students.

Despite all the ingenious ideas and hard work of both research groups, the total synthesis of such a complex molecule might not have been achieved if it had been attempted before the method of retrosynthetic analysis was established. Before the 1970s, chemical synthesis was investigated through the case studies of a series of illustrative actual syntheses. Each synthetic problem was approached as a special case in an ad hoc way. The search for a feasible synthetic route was not guided logically but attempted by trial and error. It was not until the middle of the 1960s that a systematic approach began developing. This approach rests on the recognition that the derivation of synthetic routes should be considered based not on starting materials but on the structure of reaction products. We should treat target molecules in the reverse-synthetic sense. This approach makes it easy for chemists to think logically and provides a general problem-solving procedure.

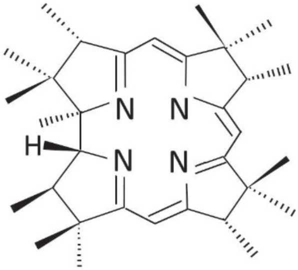

Fig. 2-1 Choline ring at the core of Vitamin B12

Retrosynthetic analysis is defined as “a problem-solving technique for transforming the structure of a target molecule to a sequence of progressively simpler structures along a pathway which ultimately leads to simple or commercially available starting materials for a chemical synthesis.” (Corey and Cheng

1989, p.6) Since chemical reactions take place at a limited number of reactive centers, we can easily find where to link possible building blocks. Through retrosynthesis the blueprints of molecules become available.

An interesting question, and one worth asking, is on what grounds retrosynthetic analysis is justified. If the molecule were an indivisible entity and a small change in composition broke it up into pieces or led to a chaotic situation, retrosynthetic analysis would not work. In fact, it works so well as to make the total synthesis of vitamin B12 possible. The molecule seems to be capable of being taken apart into its subunits like a mechanical object. But we have to be careful not to take this for granted. Submicroscopic entities are subject to the laws of quantum mechanics. It is not certain that concepts that hold good for things that exist within the bounds of the senses can be applied to objects that exist beyond those bounds. If they cannot, molecular structure is a transcendental idea, which we shall discuss in Chapter 4.

4. The logic of organic chemistry

The molecules every student encounters in chemistry textbooks have distinct physical shapes, sizes and structures. While the notion of structure is applicable to any kind of molecules, the following arguments are concerned with carbon-containing molecules. It is customary to call chemical compounds that consist of carbon-containing molecules organic compounds.

Organic chemistry is concerned with a wide variety of organic compounds, some of which are naturally occurring, while others are chemically synthesized. Organic compounds engage in a variety of chemical reactions. Structural chemistry developed as a branch of organic chemistry.

Historically speaking, the mechanistic view of molecules originated in Dalton's chemical atomism and gradually took shape through the 1850s, the period sometimes called "the quiet revolution." (Rocke 1993) Dalton thought atoms combine to form molecules according to the law of definite proportions. Hence there must be atoms in molecules. The notion of atoms in molecules is the basis of the classical concept of the molecule. However, since the atom, the indivisible unit of matter, has no quality (i.e., the secondary quality) in itself, it cannot be a component of chemical substances. It must be elements that provide substances with chemical properties. (For the detailed discussion on this topic, see, for example, Bensaude-Vincent and Simon 2012, pp.119-124) We conceive of molecular structure as consisting of atoms and bonds. It seems that the combination of atoms and bonds takes on the role of elements. As we shall discuss shortly, this is also the reason why the binding power operating between atoms is seldom taken into consideration when we discuss molecular properties.

It was Dalton who made atomic theory the object of chemistry, and it was Berzelius who developed it further and made the conceptual basis of structural chemistry. As we saw in Chapter

1, he thought that organic compounds consist of radicals—totally different from present-day radicals, which are reactive species with unpaired electrons—combined with inorganic parts through an electric force (electrochemical dualism). If molecules consist of subunits, to determine the pieces that constitute molecules would be the endpoint of chemical investigation. Therefore, many chemists, among them Kolbe and Frankland, passionately tried to isolate radicals. The logical structure of organic chemistry was already evincible in their conception of the molecule.

Today, the molecule is regarded as an entity composed of atoms and bonds, and which has a distinct shape and structure. Each part of a molecule is subject to chemical transformation independently of other parts of the molecule—the reason why retrosynthetic analysis holds. Therefore, a simple stick-and-ball model serves to explain molecular constitution. What a simple idea it is! It might be so, but a moment's reflection makes us realize that the assumptions underlying organic chemistry may not be as simple as they seem. Chemical reactions entail energy changes. For instance, atoms come closer to form a molecule when the total energy of the resultant molecule is lower than the sum of the energy of individual atoms. Therefore, it seems irrelevant to discuss a chemical matter without taking energy into consideration. Such is the case with chemical reactions that go through excited states. Actually, it was fortunate for 19th-century chemists that most of the chemical reactions investigated were ionic and associated with only the total energy of the molecule. For those reactions the localized-bond principle holds: we can see each bond as if it were independent of other parts of the molecule.

The logic of organic chemistry is also evincible in various terms and notations with which we represent molecules and reactions: the solid lines representing chemical bonds, the curved arrows showing the transfer of paired electrons, etc. (See Fig. 2-2) On the other hand, "no attempt has been made to specify forces connecting atoms. This attitude may be ascribed to an implicit assumption that the binding power operating between atoms is intrinsic to chemical elements. The chemical properties of molecules are explained by means of electronegativity, valence, electric charges, or something intrinsic to each element. State functions such as chemical potential are seldom taken into consideration. This way of thinking may be traced back beyond Dalton's chemical atomism. Lavoisier, for instance, took a substance that is not subject to further resolution to be a simple substance made of a single element." (Ochiai 2013, p.143)

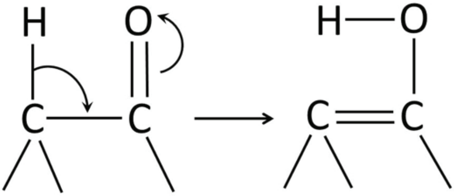

Fig. 2-2 Curved arrows denoting the transfer of paired electrons

5. Structural formulas as a kind of map

We consult a map when we look for the way to our destination. What we do with maps is not only to find a way or a place but also to imagine what we may see on the way there. We imagine crossing rivers and hills, dropping into lovely cafes, talking with people, etc. (Google Maps are a kind of gadget for replacing this mental process. It enables us to see things as if we were really there.) Thus, we both get information from maps and perform a kind of simulation. This is also true of what we do with structural formulas.

We relate the empirical contents of various chemical practices to what we take to be molecular structure and represent them with structural formulas. Structural formulas represent a sequential connection and a spatial arrangement of atoms in molecules. Actually, they also do much more than that. They serve “as a kind of map to show every possible site and every possible type of reaction allowed for a given kind of molecule.” (Ochiai 2013, p.148)

Maps provide not only geographical information but also a clue to imagining natural, social and cultural environments: why did democracy originate in ancient Greek towns, isolated from one another by natural barriers? Why did the Reformation begin in Northern Europe while the Renaissance took place in Southern Europe? What geographic factors operated on those historic events? Why were old capitals in China open to the south and closed by mountains to the north? Maps are a stimulus to the imagination. So are structural formulas. We conceive that double bonds will serve as a scaffold to elongate a molecular skeleton; formyl groups have to be protected during reduction; a bulky tertiary-butyl group is likely to exert steric hindrance, etc.

The presence of a variety of chemical elements in molecules makes them rich in chemical reactivity. Each element has its own valence, which determines the way elements are linked. Without elements we cannot tell what kind of molecule we are dealing with. Without bonds we have no structure. Without structure we cannot decipher the information obtained therough spectroscopic analysis. What we see in a structural formula is neither a mere topology of atomic linkage nor a solid geometry but the chemistry of a given kind of molecule.

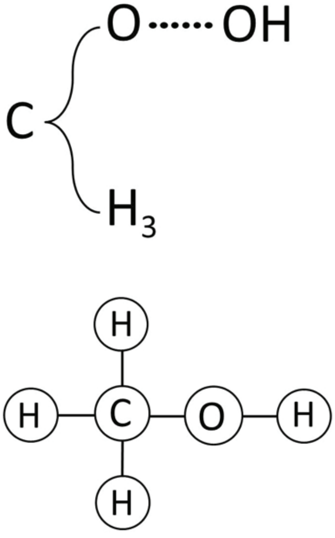

Fig. 2-3 Structural formulas of methanol.

As is noted in Chapter 1, we owe the expression of our structural formulas to the pioneering chemists of the nineteenth century. Fig. 2-3 shows Couper's (upper) and Crum-Brown's (lower) structural formulas. We can see that their formulas—especially Crum-Brown's formula— are essentially the same as those used today.

6. Intervening and molecular structure

We postulate that bulky substituents in close proximity to reaction centers are hampering the access of other molecules. We are convinced that something very close to our expectation must be happening. We can verify this by removing those substituents to see what changes are brought about. Hacking says, "we are convinced about the structures (of the cell) we seem to see (with microscopes) because we can interfere with them in quite physical ways, say by microinjecting. […] We are convinced about micro-structures because not only the development of technologies removed aberrations and artifacts but it enables us to intervene, that is, to control and create phenomena." (Hacking 2008, p.209)

Hacking describes an episode that made him a convinced scientific realist: when he asked his friend, who was hunting for quarks by using a tiny niobium ball with an electric charge, how to alter the charge, the man said, "Well, at this stage, we spray it with positrons to increase the charge or with electrons to decrease the charge." Then, he realized that there was no room for doubt about quarks. Hacking says, “So far as I’m concerned, if you can spray them, then they are real.” (ibid. idem, pp.22-23)

As far as the existence of quarks is concerned, to be able to create phenomena may be enough to be convinced of it. But it is one thing to say something does or does not exist; it is another to describe what it is in detail. The latter is much more demanding than the former. My contention is this: the relationship between chemical behavior and molecular structure has been so fully set forth that it has become possible to design and control molecular events with great precision. To an extent far beyond Hacking’s belief in quarks we are convinced that the molecule has structure. But we cannot exclude other possibilities. Things might have met our expectations just by chance. In fact, submicroscopic entities cannot be described without referring to the precise experimental conditions under which measurement is performed. The so-called pyramidal shape of ammonia, for instance, should not be taken literally and unconditionally.

7. Newton’s Method of Analysis and Synthesis

The scientific method that originates in Newton’s *Optics* is known as the Method of Analysis and Synthesis. It consists of two stages: inductive generalization from empirical data to explanatory principles (the Method of Analysis), and experimental confirmation of the consequences deduced from the generalizations (the Method of Synthesis). Although this procedure draws on the Aristotelian inductive-deductive method, Newton's method is a great improvement on the old one in the latter stage, namely, the deductive one. In Newton's method "the value of deducing consequences that go beyond the inductive evidence is emphasized." (Losee 2001, p.73)

"Using the generalizations reached by inductive inferences as premises, Aristotle deduced the original observations." (ibid. idem, p.7) This was performed in logical form: if all M are P, and all S are M, then all S are P, where P, S and M are called the major, minor and middle terms of syllogisms. "The interposition of the middle term between the subject and the predicate was construed as the deductive stage" in scientific demonstration.

The points worth noting here are: first, no more information can be conveyed than what is implied by its premises, and second, valid syllogisms with false premises, or true premises that fail to state the cause of the attribution made in the conclusion, can be constructed. Statements that are consistent in form and nonsensical in connotation can be accepted without experimental confirmation. Examples are shown below.

Example 1.
All carboxyl groups release protons. All acids have carboxyl groups. Then, all acids release protons.

Example 2.
Iodine generates anions. Anions serve as a leaving group in nucleophilic substitution reactions. Then, iodine serves as a possible leaving group in nucleophilic substitution reactions.

In the first example, though acids release protons, mineral acids do not have carboxyl groups. In the second example, what is stated in the premises is irrelevant. It is not to generate anions but to be polarizable that makes iodine a good leaving group in nucleophilic substitution reactions.

Through these arguments we can see that the focal point of Newton's method is in its hypothetico-deductive step. It opens the inductive-deductive cycle of the Aristotelian method through deducing not only original data but also testable hypotheses (i.e., theoretical predictions), which can be proved or disproved through experiments.

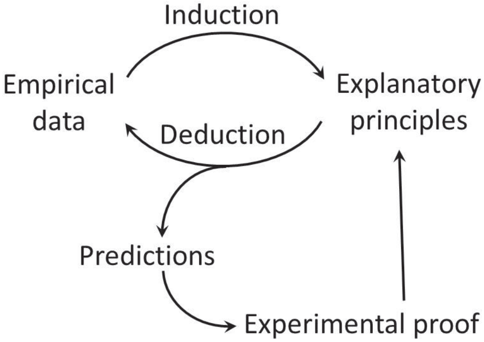

Fig. 2-4 Newton's Method of Analysis and Synthesis

According to Hacking, since “explanations are relative to human interests” and explaining is “largely a feature of the historical or psychological circumstances of a moment”, the ground for believing a theory should be “its predictive success but not its explanatory power.” (Hacking 2008, p.53) Newton’s method shows how this can be realized. The Method of Synthesis provides us with a way of excluding theoretical entities that are not real but merely empirically adequate.

From the viewpoint of Newton’s method, chemical synthesis performed with such great precision as was shown in the total synthesis of vitamin B12 seems to suggest that molecular structure is real and our structural formulas are true descriptions of reality. In fact, this is only one side of the coin. Pericyclic reactions, for instance, are inexplicable without taking molecular orbitals into consideration. Besides pericyclic reactions, one-electron properties such as ionization potentials are inexplicable without quantum mechanical theories. On the other hand, quantum mechanics does not derive molecular structure. Neither the structure theory of organic chemistry nor quantum mechanics is sufficient to provide a full description of the molecule. Each approach gives an account of what the molecule is like but fails to represent all the aspects of the molecule. While predictive success may be an indicator of a theory’s validity, this success depends on what aspect of a matter is studied. A theoretical entity that is real in one aspect can be fictitious in another.

8. A window through which to see the world

Unlike the Omnipotent, human beings are material entities placed in the phenomenal world, so that we cannot escape the influence of individual circumstances. As Kant says “we cannot cognize objects as they might exist in themselves, but only insofar as they appear to us spatiotemporally.” (Hall et al. 2010. p.3) That is, knowing is seeing. This is true of scientific experience. In science we can see objects not only with the naked eye but also with various instruments. Therefore, seeing is measuring, in which “theories serve as a kind of scale. We measure the natural world through scientific theories.” (Ochiai 2013, p.140) Scientific activities resemble perspectival drawings.

Perspective makes things nearby seem bigger and those faraway seem smaller. Any drawing includes a kind of deformation and represents a certain aspect of reality. Interestingly, as is often said, the more fictitious a drawing is, the more real it looks. A tall statue has a bigger head so as to look natural when seen from below. Take Hiroshige’s Ukiyo-e “Bridge Ohashi and Atake in Sudden Shower” as an example (you can find the digital images of the picture on the Internet). He ignored perspective. The rain falling from thick and black clouds is drawn with numerous dark lines. He has amazing success in giving the viewer a realistic feeling of pouring rain. The uniqueness of his style is evident by comparison, for instance, with Caillebotte’s “Paris Street: Rainy Day,” in which rain is expressed by darkness in the sky, wet pavements, umbrellas, and so on. We feel as if we are walking in the rain. The Ukiyo-e is more emotional and direct in expression. The solid lines around figures do not preclude a feeling of realism. On the contrary, just as the theatrical expressions in Kabuki make us involved in a play, those thick lines suggest the movement of the human figure.

As a painter's imagination is realized through her way of expression, abstract ideas of theories become materialized in theoretical models. It is through models that theories mesh with the empirical world. To put it another way, paintings are a kind of model, through which a painter's imagination takes concrete shape. Therefore, to see paintings is to see the world through the painter's eyes. As for chemistry, we have various windows through which to see a world existing outside our experience. We can enjoy a wonderful world of molecules through windows provided by various theories and viewpoints.

As far as the submicroscopic world is concerned, there is no choice but to infer in order to get knowledge about it. The more information we get, the more precise our inferences may become. But they are only inferences after all. Therefore, van Fraassen says, theories do not represent but create the contents of knowledge. (van Fraassen 2010, pp.93-101) The very practice of science—doing experiments and making observations from certain points of view—suggests that science is a kind of creation. The analogy drawn from painting is helpful again. A painter is representing her worldview through the compositional arrangement and colors she creates. Otherwise, a painting is, at best, inferior to a photograph. Pictures of molecules taken with an X-ray, for instance, are like a shadow of reality. We cannot delineate the chemical features of molecules without recourse to elements, bonds and the rule of valence.

Whether the world is just given or not, we do not see it as it is but as it is structured by ourselves. What we see depends on how we look. If we take molecules to be mechanical objects, notions like shape and structure will follow. If, on the other hand, we take them to be covered by electron clouds, the contours of molecules become blurred. Therefore, it is not scientific to arbitrarily reject one or the other approach without taking all of the available information into consideration.

9. Implications of designing molecules

What does it mean that we can design molecules? To put it simply, it is that molecules are design-able. (Ochiai 2013, pp.139-160) Though this may seem obvious, it is not at all trivial. The truth is that we have never seen the molecule. In the usual sense of the term, to “design” presupposes that the objects to be designed will be visible. What is it to design invisible objects?

In order to get a clear insight into this problem, recall the Method of Synthesis in Newton’s Method noted in the previous section: it consists of generating a testable hypothesis and proving or disproving the hypothesis. In drug research, for instance, a hypothesis is made about structure-activity relationships: it is assumed that the potency of compounds is a function of molecular structure. Through a series of experiments—making chemical modifications of lead compounds followed by performing bioassays which make the potency of compounds apparent—promising candidates are singled out. This routine practice in drug research exemplifies what it is that molecules are design-able. The pharmacological activity of compounds (therefore, promising structure) is relative to the assays we employ. That is to say, the evidence supporting what we believe is circumstantial and indirect. Therefore, we should be careful not to take things as independent of their surroundings. (Handedness provides us with an interesting example. The right hand and the left one are objective reality. But if there is only a single hand in the universe, we cannot tell whether it is right or left. It is in relation to counter-chirality that we can identify the chirality of a molecule.) (See, for example, Ochiai 2015)

When we decide the meaning of a fact, we place it in a whole body of knowledge. This kind of a whole-part relationship is also seen in linguistic systems: no single word makes sense independently of other words, for there is no such thing as an objective framework of reference.

One may suppose that we can find a bare fact, the definition of which is self-evident and hence serves as the basis of reference. That might be expected of the natural kind, whereas nobody knows what counts as such. For instance, the dog is an animal species distinct from other animal species. There would be no difference, however, if the dog were called “cat” and the cat were called “dog.” A dog is a dog because we define it in relation to other animal species. It is not likely that we can take an animal species as a natural kind.

Molecular structure makes sense in a semantic system that holds that this concept is necessary. On the other hand there might be a system which does not need it at all. This might be compared to the relation between English and Japanese. Concepts such as “wabi” and “sabi” are unique to Japanese and by no means easy to explain in English, if not impossible. This does not mean, however, that these words are nonsensical or meaningless. (“Wabi” and “sabi” are concerned with a particular taste that finds beauty in the ephemeral.)

CHAPTER 3

QUANTUM MECHANICS AND MOLECULAR STRUCTURE

> "The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be solved." (Dirac 1929, pp.714-733)

> "Is there any point in talking about the atom in a molecule? A computational chemist might say no: the computer program for molecules will give molecular properties; why bother with the artificial construct of "atom" in such a case? But this utterly ignores what chemistry is all about, for practicing chemists never for an instant forget which atoms or functional groups are in molecules with which they are dealing." (Parr and Yang 1989, p. 221)

1. Shape, size and energy

The arguments in this chapter are aimed at providing the basis for discussions that take place in the chapters that follow. They are mostly qualitative and emphasis is placed on philosophical meanings rather than technical details. Only an introductory knowledge of wave mechanics is enough to understand the following.

Why does a water molecule have a bent shape, whereas a carbon dioxide molecule is straight? It is because the energy of a H_2O molecule is least when H—O—H angle is 104.5 degrees, whereas that of a CO_2 molecule is least when O=C=O is straight. The size of a molecule is dependent on bond lengths and the angles between the bonds. The length of both bonds in a H_2O molecule is 0.096 nm. This bond length and the bond angle noted above make the total energy of a H_2O molecule least. The question of molecular shapes is, therefore, a question of molecular energy.

The total energy of a molecule is determined by calculating the energy of the electrons contained. Why electronic energy only? Because the mass of nuclei is thousands of times greater than that of electrons. Therefore, nuclei are taken to stand still compared with electronic motions—the principle known as the Born-Oppenheimer approximation. This enables us to calculate the total energy of a molecule with a Hamiltonian that contains no nuclear kinetic energy term. Holding nuclei at empirically known equilibrium geometry, we calculate the kinetic energy of electrons and the potential energy due to electron-nuclear attractions and electron-electron repulsions.

The Schrödinger wave equation is written as $H\psi=E\psi$, in which H represents the Hamiltonian, namely, the wave mechanical expression of the kinetic and potential energy of electrons involved in a given system. Kinetic energy terms are represented by differential operators. A wave function ψ specifies the quantum state of an isolated quantum system and E represents the value of energy to be observed for this quantum state. By solving a wave equation, we get ψ and E as an eigenfunction and an eigenvalue of this wave equation. Since the solution of a given equation consists of indefinitely many eigenfunctions, we have to choose a proper one based on a judgement of what is relevant to the system at issue.

In the Born-Oppenheimer approximation nuclei are fixed at predetermined geometry. This means that a molecule is in a stationary state, namely, a state with no extension in time. This is a still picture of the molecule, as it were. Actually, a real system in the physical world is exchanging things and energy between the surroundings in finite time. A molecule in a stationary state is, therefore, isolated from its surroundings and placed under an adiabatic condition. Such a fictitious state is described by a time-independent Schrödinger equation.

The Born-Oppenheimer approximation presupposes the classical concept of the molecule. Without such an approximation we cannot solve wave equations in a practical sense. Such is also the case with ab initio calculations. (Ab initio calculations use nothing other than wave equations and the values of the fundamental physical constants. Worth noting is that "ab initio" is not the same as "first principles." In the latter every particle contributes to the kinetic and potential energy terms in a wave equation on an equal footing.)

Imagine an isolated chiral molecule in a stationary state. There is no way to tell what chirality it has because any symmetry operation—the flip of coordinates, for instance—does not cause detectable changes with regard to chirality. This is known as the parity conservation. This is easy to understand by invoking a single hand in the universe: we cannot tell its handedness without referring to other chiral objects. That is to say, for a molecule to have chirality it must have interactions with its surroundings. This suggests that, whether chiral or achiral, "molecular structure is not intrinsic to the molecule but created through interactions between many-body systems." "The belief in molecular structure as a universal attribute might be a prejudice that is not founded in quantum theory." (Woolley 1978, pp.1073-1078)

2. Hybridization and the localized-bond principle

In the formation of polyatomic molecules, it is not justified to treat the pure s-, p- or d-orbitals of each atom as such because their energies get closer to each other under the influence of other atoms and they mix with each other. At any rate they are the eigenfunctions of a wave equation for a hydrogen atom. The role of atomic orbitals in calculating polyatomic systems lies in their serving as basis sets, or in other words, serving as coordinate systems with which the wave functions of molecules are expanded.

Suppose we have a set of equivalent eigenfunctions ϕ_i for a Hamiltonian H. Schrödinger's equation in which ε is its eigenvalue is written as follows:

$$H\phi_i = \varepsilon\phi_i$$

Then, we obtain a new wavefunction Ψ by making a linear combination of ϕ_i.

$$\Psi = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n = \Sigma c_i\phi_i$$

We can write a wave equation with ψ as follows:

$$\begin{aligned} H\psi &= H\,(c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n) \\ &= c_1H\phi_1 + c_2H\phi_2 + \cdots + c_nH\phi_n \\ &= c_1\,\varepsilon\phi_1 + c_2\,\varepsilon\phi_2 + \cdots + c_n\,\varepsilon\phi_n \\ &= \varepsilon\,(c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n) \\ &= \varepsilon\psi \end{aligned}$$

We find that a linear combination ψ is also the eigenfunction of a Hamiltonian H. This means that we can replace equivalent wavefunctions by a set of linear combinations constructed from them.

We can apply this theorem to the calculation of the electronic structure of methane. Methane CH_4 has a symmetric structure, with four hydrogen atoms occupying the corners of a regular tetrahedron centered on the carbon atom. "Linear combinations sh, xh, yh and zh are symmetry orbitals constructed from the four hydrogen atomic orbitals in such a way that they conform to the molecular symmetry of methane. We can replace hydrogen atomic orbitals with these symmetry orbitals. Then, we make linear combinations S, X, Y and Z from one carbon atomic orbital and one symmetry orbital. These are the true molecular orbitals of methane (since there are bonding and antibonding orbitals for each, there are in total eight orbitals). Then, once more, we make linear combinations from bonding S^+, X^+, Y^+ and Z^+ to obtain four equivalent orbitals t_1, t_2, t_3 and t_4." (Partially modified and quoted from Dewar 1969, pp.135-139)

The energies and shapes of the four t orbitals are identical. Each of these orbitals t can be converted into any of the others by rotating it about the coordinate axes. Since each orbital is represented as a combination of the 1s atomic orbital of hydrogen and a carbon atomic orbital, the four orbitals t_1, t_2, t_3 and t_4 correspond to the chemical picture of the four localized bonds in methane. "The total energy and total electron distribution of CH_4 are reproduced satisfactorily if we suppose electrons to occupy these four localized orbitals (i.e., sp^3 hybrid orbitals) in place of true molecular orbitals S^+, X^+, Y^+ and Z^+." (ibid. idem, p.139)

"If we can find a set of linear combinations such that each orbital overlaps well with an orbital of one other atom but not at all with any other orbital in the molecule, or in other words, if each orbital has a much stronger directional character than either a pure s or a pure p alone, a corresponding set of two-center localized orbitals should provide a good description." This is true as far as "collective properties" are concerned. (Collective properties are defined as the properties that depend solely on the total energy of the molecule.) This is the quantum-theoretical basis of the “localized-bond principle.” (ibid. idem. p.143)

To repeat the point, we can replace true molecular orbitals with a set of linear combinations to obtain exactly the same result as that obtained with the true orbitals. (ibid, idem. p138) But “the use of hybrid orbitals t_1 through t_4 is justifiable only for calculations of the total energy and total electron distribution” of a molecule. (ibid. idem, p.139) We can use hybrid orbitals in order to predict collective properties such as the heat of formation or dipole moments. By contrast, one-electron properties such as light absorption or ionization potentials have to be calculated based on true molecular orbitals.

What is described above is easy to understand by invoking a pie we are dividing. No matter how we divide it, the total amount of pie is the same. Likewise, no matter what structure we assume, collective properties are always consistent with assumed structure because they depend solely on the total energy of a molecule. Talking about hybrid orbitals instead of true molecular orbitals can be compared to cutting one and the same pie in different ways.

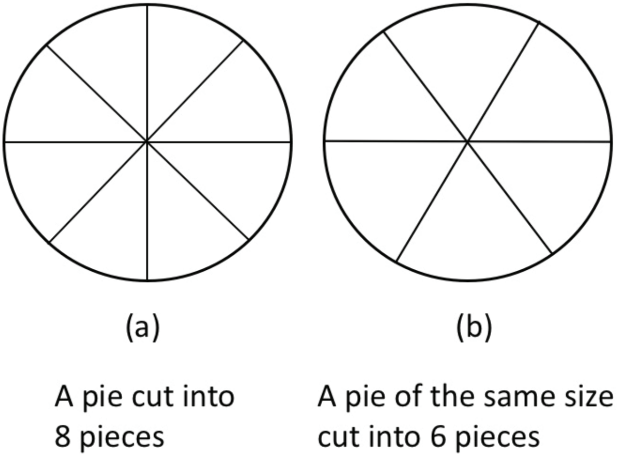

Fig. 3-1 Our problem is how to cut a pie.

3. Ab initio

Ab initio means "from scratch" in Latin. Actually, neither the Hartree-Fock method nor the Density Functional Theory (DFT) performs calculations from first principles. To know what assumptions are made is of critical importance for understanding the scope and limitation of a quantum mechanical approach to molecular structure. There are many literatures on this subject: Coulson (1953), Dewar (1969), Parr and Yang (1989) are worth reading among others. Most of the arguments in this section are based on them.

(1) The Hartree-Fock method

Suppose we have two unconnected systems separately described by wave functions ϕ_1 and ϕ_2. If the corresponding Hamiltonians are H_1 and H_2, and their energies are E_1 and E_2, then wave equations are written as follows:

$$H_1 \phi_1 = E_1 \phi_1$$

$$H_2 \phi_2 = E_2 \phi_2$$

If there is no interaction between them, a complete Hamiltonian is written as follows:

$$H = H_1 + H_2$$

Then, we suppose a joint wave equation $H\Psi = E\Psi$. This equation is satisfied by

$$\Psi = \phi_1 \phi_2$$

$$E = E_1 + E_2.$$

The fact is that there are interactions between electrons, and hence wave equations are not given in the form of separable equations. Neither numerical solutions nor analytic ones are easily obtained in such cases. One practical way of solving such many-electron systems is to apply the orbital approximation: we assume that each electron moves in an effective electric field (or a uniform electron-gas) which is obtained by averaging over all possible positions of all the other electrons. In this case each electron is described by means of a wave equation with its own coordinates. In other words, a many-electron system is reduced to a one-electron system like atomic hydrogen. “The motion of an electron is specified by a one-electron function.” (Dewar 1969, p.36) This function is called orbital.

Worth noting is that, though orbital means orbit-like, it has no physical significance as orbits do. "Orbital" is a mathematical wave function, of which we can take no photograph.

Another problem is that we must know the wave functions of all the other electrons in advance to calculate the effective electric field in which our chosen electron moves. This problem can be overcome by introducing a trial function ψ. Let us say F satisfies $H\Psi = F\Psi$. E_0 is the true ground state energy of a system. According to the variation principle it is shown that $F(\psi) > E_0$ always holds. "By testing various ψs and selecting the one which gives the lowest value of $F(\psi)$ we get the best approximation of the true energy and true wave function of a system." (Coulson 1978, p.11) This is known as the Hartree self-consistent field method.

The Pauli exclusion principle states that, with respect to the exchange of two identical particles, a total wave function is antisymmetric for fermions such as electrons. For a two-electron system consisting of ϕ_a and ϕ_b this is exemplified by Ψ_-, not Ψ_+.

$$\Psi_- = \phi_a(1)\,\phi_b(2) - \phi_a(2)\,\phi_b(1)$$

$$\Psi_+ = \phi_a(1)\,\phi_b(2) + \phi_a(2)\,\phi_b(1)$$

That is, ψ_- is antisymmetric with respect to the exchange of electrons 1 and 2. Actually, we have to take account of spins, which appear in wave functions for a single electron as α or β. Total wave functions are, therefore,

$$\Psi_+\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

$$\Psi_-\alpha(1)\alpha(2)$$

$$\Psi_-\beta(1)\beta(2)$$

$$\Psi_-\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$$

We say Ψ_+ is singlet and Ψ_- is triplet.

Imagine a closed shell structure in which each orbital is occupied by a pair of electrons with opposite spins. If we describe spin-orbitals $\phi\alpha$ and $\phi\beta$ as A and B, respectively, a total wave function is written as follows:

$$\Psi = |A_1\ B_1\ A_2\ B_2 \cdots\cdots A_n\ B_n|$$

This is known as the Slater determinant.

In the Hartree-Fock method a trial function is given as a single Slater determinant in order to satisfy the Pauli exclusion principle. Because the orbital approximation ignores the correlations between electrons, this method does not give the exact energy of a molecule. “One way to avoid this difficulty is to write a total wave function Ψ as a linear combination of two or more Slater determinants Φ_i:

$$\Psi = \Sigma A_i \Phi_i$$

By using a sufficient number of Φ_i we can take electron correlations into consideration. This way of incorporating electron correlation is known as the configuration interaction (CI).” (Partially modified and quoted from Dewar 1969, p.102)

(2) The Density Functional Theory

The density functional theory is based on the Hohenberg-Kohn theorems which “legitimize the use of electron densities as basic variables.” (Parr and Yang 1989, p.51) The Hohenberg-Kohn theorems consist of the following two theorems:

[Theorem 1]

In a nondegenerate ground state N-electron system, electron densities determine the number of electrons N and the external potential, and hence all electronic properties of a ground state.

[Theorem 2]

The theorem also provides the energy variational principle. For a trial density ρ, the energy functional $E[\rho]$ is always greater than E_0, the true energy of a nondegenerate ground state.

$$E[\rho] > E_0$$

The energy functional $E[\rho]$ consists of a kinetic energy term $T[\rho]$, potential energy terms $V_{ne}[\rho]$ and $V_{ee}[\rho]$ due to nuclear-electron attractions and electron-electron repulsions, respectively:

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

The last term $V_{ee}[\rho]$ includes the nonclassical exchange-correlation potential as well as the classical one due to electron-electron Coulomb repulsions.

The claim of the first theorem is surprising, because it makes wave functions inessential to quantum mechanical calculations using “a one-to-one mapping between ground state wave functions and electron densities.” (Parr and Yang, 1989, p.53) It goes without saying that the theorem is true only of an electron density which satisfies Schrödinger's equation. While this seems to be trivial, there can be electron densities that do not satisfy this condition. Such electron densities are among those associated with the ground state wave function of a Hamiltonian with some external potentials.

An actual problem is how to calculate T[ρ] and the nonclassical part of $V_{ee}[\rho]$. In the Thomas-Fermi-Dirac approach the exchange-correlation is ignored and $V_{ee}[\rho]$ is replaced by the Coulomb potential J[ρ]. In addition T[ρ] is calculated based on the noninteracting uniform electron gas assumption as is done in the Hartree-Fock approximation. It is redefined as the local density approximation (LDA). "The LDA is applicable to systems with slowly varying densities but cannot be formally justified for highly inhomogeneous systems." (ibid. idem, p.154) Actually, an atomic or a molecular electron cloud is not a uniform gas. The Thomas-Fermi-Dirac approach is oversimplified and characterized by poor accuracy. It is not practically useful.

It is the Kohn-Sham method that has turned the density functional theory into a practical tool for rigorous calculations. Trading simplicity for accuracy, Kohn and Sham introduced orbitals in order to calculate the kinetic energy and the nonclassical part of $V_{ee}[\rho]$. The Kohn-Sham method is based on the relationship $\rho = \Sigma|\varphi_i|^2$ which is true only of wave functions represented by a single Slater determinant. As was discussed in the preceding section, the method assumes no interaction between electrons.

Let us say the kinetic energy calculated by using this wave function is $T_s[\rho]$ and the true kinetic energy is $T[\rho]$. The difference between $T[\rho]$ and $T_s[\rho]$ is put in $E_{xc}[\rho]$ in the following equation.

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[r]$$

$E_{xc}[\rho]$ is called the exchange-correlation energy. In the case of an electron density to which LDA is applicable, the local exchange-correlation energy is available. The sum of the latter over the whole space provides $E_{xc}[\rho]$. The problem is that we do not know the exact form of $E_{xc}[\rho]$. In other words, we do not know the mechanism of electron correlation. Such being the case, justification for using this method comes from successful numerical applications. In fact, the exchange-correlation energy is given as a combination of several Gaussian-type functions. The contribution of each function is adjusted in such a way that deviations between calculated values and experimental values become as small as possible. This process is realized by making use of many small molecules as authentic samples.

In view of the fact that both the electron density and total energy of a system are obtained experimentally, we can in principle determine the form of the density functional by examining the relationship between them. This may be a reason why this method appeals to theoretical chemists.

4. Physical implications of orbitals

The orbital approximation tells us that the sequence of orbital energies in a typical atom is

$$1s < 2s < 2p < 3s < 3p < 4s \sim 3d < 4p \ldots$$

We apply this sequence to many-electron systems and say, for instance, that a nitrogen atom in the ground state has such an electron configuration as $(1s)^2(2s)^2(2p)^3$. That is to say, the “aufbau” or the building-up principle tells us that the above orbitals are filled up by electrons, two for each orbital, till all the electrons in a system have been allocated.

This type of representation is, however, a total violation of the Pauli exclusion principle which states that all electrons are indistinguishable. In addition, individual electronic momenta do not remain intact because of vector couplings between them. The truth is that this representation is a compromise between the old idea of “orbit” and the modern quantum mechanical view. The physical significance orbits had in Bohr’s model is lost in orbitals which are mathematical functions. Orbitals have no more significance than serving as a basis set with which wave functions are mathematically expanded. (Scerri 2008, pp.200-213) It is meaningless to argue about the physical meaning of unoccupied orbitals in themselves though they can participate in chemical as well as physical processes. The latter point is suggested by the existence of excitation energy, namely, a discrete amount of energy necessary for the transition of an electron from the ground state to excited ones.

The frontier orbital theory focuses attention on the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of compounds undergoing chemical reactions. The theory maintains that the sites of reactions on molecules are determined by the symmetry of the HOMOs and LUMOs of the reacting molecules. If both orbitals match in symmetry and overlap one another, reactions proceed. The effectiveness of the frontier orbital theory is shown by comparing it with the electronic theory of organic chemistry, for instance. Although the electronic theory says that nucleophiles have higher electron densities and electrophiles have lower electron densities at their reaction centers, this idea does not hold for aromatic hydrocarbons such as benzene derivatives. Electron densities on atoms are derived from all the occupied molecular orbitals and there is not much difference between the atoms in hydrocarbon molecules. By contrast it is easy for the frontier orbital theory to tell which atoms are susceptible to electrophilic substitution reactions by showing orbital symmetry.

To summarize the point, since atomic orbitals like s-, p- and d-orbitals obtained by solving Schrödinger's equation for a hydrogen atom do not remain intact in the molecule, it is not acceptable to refer to these orbitals in the explanation of the reaction mechanism. The electron configuration based on the aufbau principle has, therefore, no more value than counting the outermost electrons which may possibly participate in chemical reactions. The frontier orbital theory suggests that it is not only $|\phi|^2$ but also ϕ itself that has a physical significance. This is a controversial point of this theory.

5. Atoms in molecules

"Is there any point in talking about atoms in molecules?" The answer is of course yes, "for chemistry is all about it." (Parr and Yang 1989, p.221) Chemistry studies why particular atoms or functional groups behave in particular ways. Standard chemistry textbooks tell us that, when two atoms come closer to one another to form a diatomic molecule, the individual atoms lose their identity to some extent, but not entirely. The concept of atoms in molecules has been and continues to be useful in interpreting, predicting and classifying chemical phenomena as well as communicating chemical knowledge. Chemistry is impossible without it. Although such is the belief of most experimental chemists, computational chemists might have a different opinion. They do not need such an artificial concept to develop computer programs for molecules. For their purposes it may be more convenient to regard molecules as being composed of nuclei and electrons. This may be a problem of the kind that what you see depends on how you look. The concept of atoms in molecules is at least empirically adequate. If so, it must have some physical basis.

Bader defines atoms by his ingenious method of space-partitioning the total electron density. A surface between individual atomic regions is defined in such a way that "the normal component of a density gradient is zero on the surface." (Bader 1990, p.29) Suppose a diatomic molecule AB with a ground-state electron density ρ^0_{AB}. Bader's space-partitioning is represented as follows:

$$\rho^0_{AB} = \rho_A + \rho_B$$

with ρ_A and ρ_B being disjoint densities for atoms A and B. These A and B are not atoms in ground states but in perturbed valence states. In this partitioning, "since the overlapping between atoms is forbidden, transferability is limited and chemical bonds disappear into thin air." (Parr and Yang 1989, p.222)

The point worth noting is that we can assume a partitioning in which ρ_A and ρ_B are not disjoint but joint densities. These different ways of partitioning are schematically shown in Fig. 3-2. Since electron densities are produced from wave functions which overlap one another between atomic regions, a partitioning with joint densities (b) seems more natural and easier to understand. Actually, there are both advantages and disadvantages to each way of partitioning.

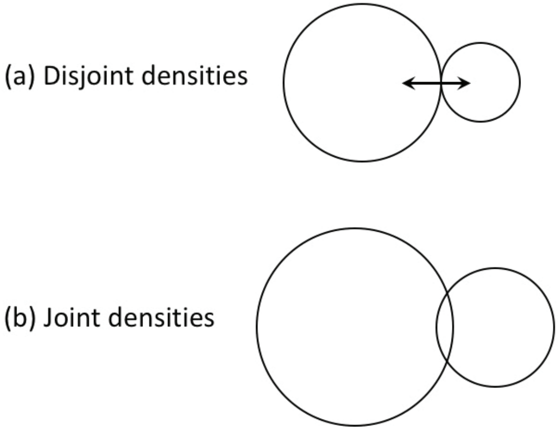

Fig. 3-2 Disjoint (a) and joint densities (b)

As is pointed out by Parr and Yang, “the concept of atoms in molecules tells us nothing particularly new or essentially different from what we learn from molecular orbital theories.” (Parr and Yang 1989, p.218) Whichever type of partitioning we may choose, they are equivalent from the point of view of quantum mechanics. In this sense the concept of atoms in molecules is akin to the concept of the hybrid orbital. We are at liberty to rely on the concept of atoms in molecules to talk about molecular structure just as we can refer to hybrid orbitals to provide explanations of collective properties.

CHAPTER 4

KANT AND INVISIBLE STRUCTURE

In everyday life we talk about various structures visible to the naked eye. There is nothing wrong with this. Then, what about discussing molecular structure?

While molecular structure is one of the essential concepts that underlie chemistry, we are not sure whether or not it is legitimate to talk about invisible structure. In this chapter we examine the philosophical grounds for molecular structure using Kant's theory of knowledge.

Why Kant?

Because it was Kant who provided the philosophical grounds for scientific knowledge by showing that synthetic *a priori* judgement is possible.

1. Kant's theory of knowledge

Since the arguments we shall develop in this chapter are based on Kant's *Critique of Pure Reason* (abbreviated as CPR), some information about the composition of CPR will be of some help: it consists of three major parts, i.e., the Transcendental Aesthetic, the Transcendental Analytic and the Transcendental Dialectic. The word "transcendental" means "antecedent to experience." Kant says, "I call all knowledge transcendental which deals not so much with objects as with our manner of knowing objects insofar as this manner is to be possible a priori.” (Kant 2007, A12/B25: unless otherwise mentioned, quotations from CPR are based on Kant 2007; the letters A and B placed before page numbers mean the first and the second editions of CPR, respectively.) The Transcendental Aesthetic and the Transcendental Analytic are concerned with sensibility and the understanding, respectively. (A63/B87) The Transcendental Dialectic, or the logic of illusion, isolates reason. It is a critique of reason in terms of the misapplication or dialectical use of the understanding’s pure concepts by reason beyond the bounds of the senses. “All our knowledge begins with the senses, proceeds thence to the understanding and ends with reason,” says Kant. (A299/B355)

What is it to be acquainted with things existing outside our mind? Is it that our ideas about external objects conform to those objects themselves? Or do they have some similarity relationship to one another? Which is the case? These questions have been asked over and over again for centuries. Even in the AI era, we are not sure whether we have an exact understanding of the relationship between our ideas and their objects. On what grounds can we say that an object exists as we believe it to be? To creatures other than human beings, the world might seem different from the one we see because of their unique sense organs. Imagine what a landscape looks like to a kestrel, which perceives UV rays.

Rationalists like Descartes believe that, “since God is not a deceiver, God ensures not only that external objects are the cause of our sensible ideas but also that what we clearly and distinctly perceive in the ideas must be true of the objects they represent.” (Hall et al. 2010, p.2) On the other hand empiricists like Locke believe that “our ideas of primary qualities resemble their causes, namely, primary qualities themselves.” (Primary qualities like shape and size are thought to be independent of any observer, and hence certain. By contrast secondary qualities like color and taste are thought to be dependent on the observer, and hence uncertain.) By contrast, Hume argues in this way: since we cannot be sure whether or not our ideas conform to external objects, all we can tell is the relationship between our ideas. This thoroughgoing skepticism is the logical consequence of the epistemological view that cognition must conform to its object, which is “the underlying assumption shared by both rationalists and empiricists.” (ibid. idem, p.2)

Kant thought that instead of thinking that our cognition must conform to its object, we should think that “the object must conform to our cognition of it.” (ibid. idem, p.3; Kant 2007, Bxvi, xxii) Kant’s contention is that things are the objects of experience only insofar as they conform to our epistemic faculties. Otherwise, how can we cognize reality existing independently of the human mind? We are not passive observers but active participants in the world of possible experience. This Copernican turn in a point of view had unfathomable implications not only for contemporary epistemology but also for philosophical trends afterword.

The point of Kant's critical philosophy, namely, transcendental idealism, can be summarized as follows: "since space and time as well as categories (the *a priori* concepts of the understanding or the rules that the understanding uses to organize the representational content of sensibility) are the contributions of the subject to her experience, the objects of experience are nothing once we leave behind the sensible and conceptual conditions of the subject." (Hall et al. 2010, p.139) Kant says "that space and time are only forms of sensible intuition, and hence are only conditions of the existence of things as phenomena: moreover, we have no conception of the understanding and consequently, no element for the cognition of things except in so far as a corresponding intuition can be given to these conceptions: accordingly, we can have no cognition of an object as a thing in itself but only as an object of sensible intuition, that is, as phenomena." (Bxxvi) The objects of cognition must be given in sensibility via intuition and must be thought by the understanding through concepts. Intuitions and concepts are both necessary for cognition to arise, for "we cannot cognize objects as they might exist in themselves but only insofar as they appear to us spatiotemporally and in accordance with our concepts of them." (Hall et al. 2010, p.3) The relationship between sensibility and the understanding might be compared to that of ingestion and digestion: what is ingested orally (given in sensibility) is to be digested in the stomach (thought by the understanding).

To repeat the point in Kant's words, "we apply the term sensibility to the receptivity of the mind for impressions, in so far as it is in some way affected; and on the other hand, we call the faculty of spontaneously producing representations, or the spontaneity of cognition, understanding. Our nature is so constituted that intuition with us never can be other than sensuous, that is, it contains only the mode in which we are affected by objects. On the other hand, the faculty of thinking the object of sensuous intuition is the understanding. Neither of these faculties has a preference over the other. Without the sensuous faculty no object would be given to us, and without the understanding no object would be thought. Thoughts without content are void; intuitions without conceptions, blind." (A50-51/B74-75)

A hominid in the Stone Age who happened to appear on a tennis court would not cognize spherical objects going back and forth. A little more realistic case is this: kids often ask their parents whether we can enjoy skating on dry ice as well as on regular ice because the former seems much colder than the latter. In reality, as we know, things tend to stick to the surface of dry ice. Anyway, it is very difficult to answer this question without having recourse to the concept of phase transition. Without proper concepts we cannot understand what we perceive, even if we have normal sensory perception. “Only through the unification of intuitions and concepts can cognition arise.” (Hall et al. 2010, p.58; see also A52/B76)

Kant’s critical philosophy has the following advantages over both rationalism and empiricism: “first, we will not misrepresent the world if we limit our cognition to the world consisting of our own minds; second, we can escape from Hume’s devastating skepticism because we do not aim to experience what is outside our experience; third, since the objects of experience must conform to our *a priori* concepts of them, we can get acquainted with objects by examining our own faculties of cognition and without appeal to experience.” (Summarized and quoted from Hall et al. 2010, pp.4-5) That is to say, synthetic *a priori* knowledge is possible.

2. Synthetic *a priori* knowledge

“Rationalists, who claim that concepts are cognitively fundamental and they intellectualize sensible intuitions, cannot show how innate ideas apply to the world of experience. In contrast, empiricists, who claim that sensible intuitions are cognitively fundamental and they sensitize concepts, cannot account for the unity of experience.” (ibid. idem, p.38) Hume went as far as to say that causal relationships are not necessary but something like custom or mental habit. Whereas “they possess a certain kind of psychological necessity, there is no reason to believe that the world of objective reality actually exhibits these kinds of causal relationships.” (Hall et al. 2010, p.6) “Hume will deny that there *is* any inference; or at least, a *rational move*, proceeding by virtue of a principle of sanction. [...] Instead of inference in the normal sense of the term, we have a customary transition, from inductive antecedent to consequent (e.g. from cause to effect).” (Buchdahl 1969, p.340) Kant, a proponent of Newton’s mechanics, took Hume’s skepticism about causation as “an existential threat to natural science” and aimed to show that there is a third way to safeguard the necessity of causal claims in natural science. (Hall et al. 2010, p.6)

Actually, Hume did not deny that there is more to reality than his own mind and its states. He said only that there is no way to ascertain what is happening in an external world, for we cannot have an acquaintance with what exists outside our minds. Let us say I am feeling warm. I am acquainted with that feeling of mine. By contrast my perception of something outside myself, say, my dog, does not have an acquaintance with it as an ingredient. I cannot be acquainted with the act of perceiving my dog. We are, as it were, “gazing at a reflection that a mountain produces of itself in a lake.” (Wolterstorff 2001, p.26)

Anyway, scientific knowledge is impossible if causal claims, or in other words, synthetic *a priori* judgements cannot be proven to be valid. For both rationalists and empiricists before Kant, propositions were either synthetic *a posteriori* (e.g., it is raining) or analytic *a priori* (e.g., squares have four sides). They could not find proper logic that makes synthetic *a priori* knowledge possible. As Kant says, "David Hume, who among all philosophers came closest to this problem, though he was far from conceiving it with sufficient definiteness and universality, confining his attention only to the synthetic proposition about the connection of an effect with its causes, believed he had discovered that such an a priori proposition is entirely impossible. According to his conclusions, everything which we call metaphysics would turn out to be a mere delusion of rational insight into what in reality is only borrowed from experience and has, by mere habit, assumed the appearance of necessity. [...] No pure mathematical science was possible either, on account of its certainly containing synthetic *a priori* propositions." (B20)

To summarize the points, first, *a priori* propositions are self-evident and necessarily true since they are known without appeal to experience (e.g., 1 is smaller than 2). By contrast, "*a posteriori* propositions cannot be known without appeal to experience. All *a posteriori* propositions are contingent since they depend on the way things which could be otherwise in fact are." (Hall et al. 2010, pp.217-218) Second, an analytic proposition is "one whose predicate concept is contained within its subject concept" (e.g., bachelors are unmarried adult males). By contrast a synthetic proposition is that "whose predicate concept is not contained within the subject concept" (e.g., Dalton is an Englishman). Then, it follows that "all analytic propositions are *a priori*" (and hence necessary), and "all *a posteriori* propositions are synthetic" (and hence contingent).

A break-through made by Kant was that he noticed that not all synthetic propositions are *a posteriori*. He pointed out that there are things which are external to our mind and known to be true without appeal to experience. For example, a straight line connecting two points provides the shortest path between them; 7 plus 5 is 12; in all alterations of the material world the quantity of matter remains unaltered, etc. (B15-24) To judge the truth or falsity of these propositions does not require an empirical intuition but a pure intuition (a pure form of sensibility). This is suggested by the fact that it is impossible to exhaust all possibilities whatever they are. We cannot demonstrate that the shortest path between two points is a straight line by investigating all the possible paths between them. Kant says "since these sciences (i.e., pure mathematics and pure natural science) really exist, it is quite proper to ask how they are possible; for that they must be possible is proved by their actuality." (B20)

A moment's reflection on the way we engage in scientific activities is enough to be convinced that it is this type of proposition that underlies scientific claims. Although science in the descriptive stage is concerned with providing synthetic *a posteriori* knowledge, science requires synthetic *a priori* judgement as to make progress. This may be due to the very nature of intellectual beings like us: we think of causal relationships between events and make an inference about "what lies far away behind our back". (A644) We cannot help asking why something is the case. For reason, "the questions never cease" in Kant's words. (Aviii)

3. Transcendental illusions

Our cognition arises only insofar as objects are given in sensibility via intuitions and are thought by the understanding through concepts. (A50-52/B74-76) In other words, the proper application of concepts is confined to objects that exist within the bounds of the senses. However, because of the very nature of human reason we cannot help transgressing those bounds.

Kant says, "human reason has a natural inclination to overstep these limits" and so "transcendental ideas are as natural to reason as categories to the understanding." (A643/B671) Categories are the pure concepts of the understanding and transcendental ideas are the concepts of pure reason. (A312/B368) Then, what is reason? Kant says "all our knowledge begins with the senses, proceeds thence to the understanding and ends with reason" as we saw at the beginning of this chapter. (A299/B355) "There is nothing higher in us than reason for working on the material of intuition and bringing it under the highest unity of thought." And "there is of reason, as there is of the understanding, a purely formal, that is, logical use, in which reason abstracts from all contents of knowledge. But there is also a real use, insofar as reason itself contains the origin of certain concepts and principles which it has not borrowed either from the senses or from the understanding.” (A300/B356) The transcendental use of concepts by reason results in transcendental ideas. The latter include, for example, the omnipotence of God and the immortality of the soul. There is no way to examine the validity of these concepts within the bounds of the senses.

The point Kant emphasizes over and over again is that the use of transcendental ideas without empirical premises inevitably leads us to empty sophisms and transcendental illusions. (A293-7/B350-4) The reason why Kant calls them illusions is that such ideas make us misunderstand subjective representations for objective ones. It is by no means easy to get the point immediately. However, this is a real issue for us, for science abounds in such examples as ether (the medium in which electromagnetic waves propagate), caloric (the unit of thermal energy, the transfer of which was assumed to make work and causes the change of temperature), and so on.

Why does human reason overstep the boundaries of possible experience? The reason is that it demands complete explanations for given facts. Reason, unlike the understanding and sensibility, does not generate experience. Instead, it asks about any given empirical judgement: why that is the case? Moreover, once it finds an answer, it asks the same question about it. Questions and answers go on and on. “Reason’s restless search for explanation is driven by its assumption that a complete explanation for each and every given fact is out there to be found." (Rohlf 2010, p.196) Such being the case, reason may be compared to a child who is always asking why something is the case. "For any answer given by his parents, he will ask why that is the case. The series of questions usually leads to a point where one is sick of answering them or one does not know how to answer." (Hall et al. 2010, p.147) That is the unconditioned. Kant says, "for that which necessarily impels us to go beyond the limits of experience and of all appearances is the unconditioned". (Bxx) "The unconditioned" is, after all, the unconditioned condition, that is, a complete explanation that needs no more explanation. "Our reason has the peculiar fate that, with reference to one class of its knowledge, it is always troubled by questions which it cannot ignore because they are prescribed by the very nature of reason itself, and which it cannot answer because they transcend the powers of human reason." (Aviii)

Because of reason's natural inclination to overstep the boundaries of possible experience, transcendental illusions inevitably arise. This reason's inclination should be distinguished from the transcendental use or abuse of the categories "which is a mere error of the power of the judgement when it is not sufficiently subdued by criticism, and so is not sufficiently attentive to the limits of the sphere within which alone our pure understanding is allowed full play". (A297/B353) In contrast to this, transcendental illusions arise through the action of transcendent principles, “which calls upon us to break down all those barriers, and to claim a perfectly new territory which does not recognize any demarcation at all.” Thus, transcendental and transcendent should be distinguished.

Kant says there are two types of illusions, of which a logical illusion is a mere imitation of the form of reason and arises entirely from want of attention to logical rules. Therefore, “it disappears at once when our attention is roused with respect to the case before us.” In contrast, a transcendental illusion “does not cease even after it has been uncovered and its worthlessness clearly revealed by transcendental criticism.” Why can we not avoid transcendental illusions despite our full awareness of their worthlessness? Kant says “the cause of this is that there exist in our reason (considered subjectively as a faculty of human knowledge) fundamental rules and maxims of its use, which have the appearance of objective principles. And this leads us to regard the subjective necessity of a certain connection of our concepts for the benefit of the understanding as an objective necessity in the determination of things in themselves.” Therefore, this type of illusion is as impossible to avoid as it is impossible “to prevent the sea from appearing to us higher at horizon than at the shore” or impossible “to prevent the moon from appearing, even to an astronomer, larger at its rising.” (A298/B355)

We tend to take molecules as the same kind of thing as those which are familiar to us in daily life. We think that they must have definite shapes and structures and behave like physical objects around us. While we know that molecules are subject to laws of nature quite different from those that govern the world of experience, we cannot help assuming, for instance, “atoms in molecules”, the idea that molecules consist of atoms linked together by chemical bonds. We also assume that chemical bonds have distinct lengths and directions. The reason why we cannot help thinking that way is that it meets “the subjective necessity of a certain connection of our concepts for the benefit of the understanding.” (A297) Otherwise, it is hard for us to imagine what molecules are.

4. Things-in-themselves or noumena

It is only insofar as the objects of cognition are given to us in sensibility via intuitions and are thought by the understanding through concepts that the cognition of objects contributes to expanding our knowledge. But Kant says there are “beings of the understanding to which our sensible faculty of intuition has no reference at all.” (B309) A noumenon (“noumena” in the plural; Ding an sich in German) is “a thing which can never be thought as an object of the senses, but only a thing in itself (thought solely through pure understanding).” (B310) A noumenon has a causal power and makes things happen, namely, it brings about phenomena. It is assumed to exist independently of the human mind, and hence it cannot be the object of our cognition. How can it be that something is not an object of cognition but responsible for phenomena we observe?

Kant says that there are two types of noumena: one is "a thing insofar as it is not an object of our sensible intuition" (negative noumenon) and the other is "an object of a non-sensible intuition" (positive noumenon). (B307) What is a non-sensible intuition? Kant says, "we cannot maintain that sensibility is the only possible kind of intuition." Intellectual intuition is also possible. But those who do not have such intuition cannot know what a positive noumenon is. Molecules are negative noumena, for they are merely too small to see. With various instruments we can detect them and understand what they are like. In contrast, the particle-wave duality of electrons seems to be noumenal in a positive sense, for it is not merely beyond the bounds of the senses but also beyond our faculty of sensibility. We can cognize particles and waves. But we cannot know by intuition what it is to be a particle as well as a wave.

How about ideal gas (or perfect gas)? Is it a noumenon or a transcendental idea? The point is that a noumenon is supposed to be real, whereas a transcendental idea is merely conceived of. As we noted in the preceding section, transcendental ideas arise from "the subjective necessity of a certain connection of our concepts" independently of the objective necessity of things in themselves. Ideal gas is, therefore, a kind of transcendental idea and not a noumenon. It is composed of randomly moving mass points, the collisions of which are assumed to be perfectly elastic. There is no such gas in a real system. It is a creation of reason and serves as a reference for thinking about real gas. In Kant's words it serves as "a regulative principle." It is a principle of reason "for the enlargement and extension of experience as far as is possible for human faculties." "It forbids us to consider any empirical limits as absolute." (A509/B537)

With orbitals (atomic as well as molecular orbitals), the argument becomes subtle, for orbitals occupied by electrons are taken as real, whereas vacant ones are nothing but mathematical functions. From this it may follow that occupied orbitals are noumenal, whereas vacant ones are transcendental. This raises a real problem to be seriously considered: we are apt to take vacant orbitals as real and make arguments about them. In fact, vacant orbitals have no physical significance. (Scerri 2008, pp.200-213) To take them as real is none other than a transcendental illusion.

Why do we have to think about noumena? The reason has already been suggested in the previous argument. The concept of noumenon is necessary "to prevent sensible intuition from extending to things in themselves; that is, in order to limit the objective validity of sensible knowledge." (A255/B310) Since we cannot understand noumena and the world beyond the sphere of appearance is to us empty, the concept of noumenon is what is "to keep the claims of sensibility within proper bounds, and therefore only of negative use." But it is not a mere arbitrary fiction. On the contrary, "it is closely connected with the limitation of sensibility, though incapable of positing anything positive outside the sphere of sensibility.” (A256/B311) From all this it follows that the understanding can only think noumena “under the name of an unknown something.”

Kant raises a question about applying the understanding to an object which is not an appearance but a noumenon. He says “the question is whether, besides the empirical use of the understanding, a transcendental use of it is possible that has to do with the noumenon as an object; and this question we have answered negatively.” (A257/B313) It is interesting to imagine what Kant would say if he witnessed what we are doing under the name “molecular science.”

5. Transcendental idealism

As can be expected from the fact that the young Kant was devoted to Hume, we can see Hume’s influence on Kant’s theory of knowledge. Kant says that only what is within ourselves can be perceived immediately and real objects outside the human mind can never be given directly in perception because perception is “a modification of inner sense.” (A368) We can only infer from our inner perception, by taking the perception as the effect of something external. But, of course, such inference is always uncertain, “because the effect may be due to more than one cause.” This way of thinking is called idealism, whereas Kant himself makes some further qualifications. That is to say, it must not be supposed that “an idealist is he who denies the existence of external objects of the senses." (A369) Instead, all he does is "to deny that this existence is known through immediate perception," and "to infer that we can never, by way of any possible experience, become perfectly certain of their reality."

Kant requires us to distinguish two kinds of idealism, transcendental idealism and empirical idealism. Transcendental idealism is the doctrine that "all appearances are regarded as mere representations, not as things in themselves, and that space and time, therefore, are only sensible forms of our intuition, not determinations given independently by themselves, or conditions of objects taken as things in themselves." Hence the objects of experience are nothing if separated from our sensibility. In contrast, transcendental realism is the doctrine that considers that "space and time is something given in itself independently of our sensibility" and "all outer appearances (their reality being admitted) are things in themselves, existing outside us." In contrast to the transcendental idealist who can affirm the reality of external objects within the bounds of the senses, the transcendental realist "considers all our representations of the senses as insufficient to render the reality of these objects certain." (A370/B416) This is a logical consequence of thinking that external objects of the senses must have an existence in themselves. The transcendental idealist is the empirical realist, for reality does not need to be inferred but immediately perceived. In contrast, transcendental realism is “obliged to give way to empirical idealism,” for it is far from certain if the objects of the outer senses do or do not exist. (A371-2)

These arguments may seem old-fashioned and outdated. Indeed, Kant lived in the eighteenth century (1724-1804), too early to see the dawn of cognitive science. There was no way to know the precise mechanism of our central nervous system. Kant’s theory of knowledge may well be without scientific basis. But the arguments we have noted above suggest that this is not the case. To see objects is to shed light on them in the literal sense of the term. But the hidden side of objects is left. For instance, just as we cannot see the far side of the moon from the earth, we cannot see every aspect of things. In other words, we cannot see things in themselves. We cannot support transcendental realism.

To perceive external objects through our inner perception is just like looking at one’s back in the mirror. But the figure in the mirror is flipped horizontally. Thus, the relationship between what exists outside our mind and what is perceived is not straight. As we shall see in Chapter 7, we take part in the process of producing phenomena. In other words, what we see is structured by ourselves. If so, to what extent is our knowledge of molecular structure relevant to reality?

6. The origin of structure

We find many structures around us: structures of computers, automobiles, houses, and so on. We can also identify structure in a variety of natural substances and phenomena: structures of animal bodies, geological strata, the earth, the atmosphere, the Galaxy, and so on. We see structure in non-physical objects as well: structures of literary works, musical compositions, societies, and so on. We also talk about economic, political and bureaucratic structures. What is structure? What is common to all of them, if anything?

Whether they are physical or not and whether natural or not, things are composed of parts. Structure may be defined in terms of a whole/part relationship. But the whole/part relationships of musical compositions are not as apparent as those of physical objects, for music is not an object to see but to hear. Music consists of temporal patterns of sounds. A musical score is a means of translating the temporal to the visual with musical notes. On the other hand, it is easy to show social structure schematically. Social structure is concerned with relationships between social entities such as people and organizations. But we are not sure whether it is proper or not to regard those relationships as structure.

We are not as careful in seeing as in hearing: we are more gullible with regard to TV than radio, for instance. Is it that we put too much trust in seeing? Probably. In addition, we tend to take the unobservable as being the same as the observable. We unconsciously apply concepts that have a proper use only within the bounds of the senses to what exists beyond those bounds. Kant says it is illegitimate to apply any concept whatsoever to objects existing beyond the bounds of the senses. The use of transcendental ideas without empirical premises inevitably leads us to empty sophisms and transcendental illusions. (A296/B352) Does the molecule really have structure? (Ochiai 2017, pp.197-207)

We cannot help looking for structure in everything. We find structure even in liquid water. Probably, we are so structured as to perceive structure in whatever we see. We want things to make sense. In order to make sense, they must have light shed on them and be displayed in order. What is hidden from the eye tends to be a threat. It makes us scared.

Remember the uneasy feeling we have when we see Escher’s trompe l’oeil. It does not make sense that going up a staircase leads to a lower floor. That nonsensical structure upsets us. A similar feeling is raised by Klein’s bottle, of which we cannot distinguish the inside from the outside. Both sides connect so seamlessly that they make one surface as a whole. Such is also the case with the Möbius strip. We cannot tell what is the outside and what is the inside. In Escher’s trompe l’oeil, too, the lower floor and the upper floor fuse together, so that which floor is upper or lower depends on how we look. Escher’s trompe l’oeil requires us to choose an aspect or a point of view from which to see it.

Atoms and molecules are in thermal motion. Therefore, the shape of the molecule varies with time. Atoms in molecules are changing their positions around the average. They are not of the same kind as things around us. Let us have a look at the matter from the opposite point of view. Since our universe is expanding at a tremendous speed, the relative positions of stars are changing accordingly. But because stars are very far from us, constellations look like they are standing still in the universe. Actually, the Great Bear is moving, though too sluggishly for us to discern it. It is the duration of measurement that determines the shape of an object. What we take as a definite shape is stable during our observation. It is that it fits in with our sense of space and time. But our sensible intuition is not everything.

CHAPTER 5

TRANSDICTION

Chemists deal with submicroscopic entities that exist beyond the boundaries of possible experience. They talk about molecular structure and explain reaction mechanisms as if they see what is happening at the molecular level. This mental habit is a source of a creative imagination which is characteristic of chemists. On the other hand, Kant says that a transcendental idea is likely to cause a transcendental illusory appearance. Is what a chemist imagines tenable? On what philosophical grounds is it possible to say that molecular structure is not a mere illusion?

1. What is transdiction?

Long before Western medicine had been brought to the Orient, empirical knowledge of acupuncture developed in China. Acupuncturists practiced based on a functional map of the human body showing, for example, the “meridian,” which was a network connecting the body’s acupuncture sites. Though their medical knowledge was quite different from that of Western doctors (for instance, anatomy was not distinguished from physiology), it was very effective and useful at least in a practical sense.

Chemistry, too, rests on chemists' imagination for its development. Since molecules are too small to see, what shapes and structures they have, how they interact with each other in chemical reactions, etc., are not as simple matters as those that can be observed. We conceive of these microscopic entities and events by projective inference: an inference based on circumstantial evidence and projected in the vertical direction to our empirical horizons. This is in contrast to extrapolation, which is a mere extension in the horizontal direction. This projective inference is called "transdiction" by analogy with prediction and retrodiction.

Prediction is about what will happen; retrodiction is about what did or did not happen. Both are concerned with things within experience. By contrast transdiction is "to use data in such a way as not only to be able to move back and forth within experience but also to be able to say something meaningful and true about what lays beyond the boundaries of possible experiences." (Mandelbaum 1966, p.61)

The epistemological technique of transdiction "was habitual with chemists long before physicists developed a similar art." (Rocke 1993, p.248) In chemical experiments a chemist manipulates compounds with her mind's eye being focused on molecules undergoing chemical reactions. It is no exaggeration to say that learning chemistry is to get accustomed to going back and forth across the boundaries of possible experience. An introductory chemistry course is taught by means of various models, including not only printed images of molecules but also hand-held physical models. By making good use of these models students come to understand what molecules are like. At the same time they have to learn how to do experiments: how to set up an apparatus, to cause reactions to occur, to purify reaction mixtures, to analyze reaction products, and so on. Each operation must be not only rational in itself but also consistent with what is supposed to be happening at the molecular level. In a theoretical as well as in a practical sense, students have to know why reagent A must be dropped into a solution of reagent B and not vice versa, why the temperature of a reaction vessel must be kept at around a certain temperature, why a reaction mixture must be washed first with acid and then with sodium bicarbonate solution, etc. Chemistry is not a collection of *ad hoc* knowledge and know-how but a science of molecules. Chemistry owes its success to transdiction.

Mandelbaum says, "any belief that ordinary material objects are actually composed of atoms, and the acknowledgement that these atoms are not capable of being perceived by our senses, commits one to a belief in transdiction." (ibid, idem., p.66) A question to be asked is whether or not this type of inference is legitimate.

2. Transdiction and Newton

"The whole burden of philosophy seems to consist in this—from the phenomena of motions to investigate the forces of nature, and then from these forces to demonstrate other phenomena." (Quoted in Mandelbaum 1966, p.71)

In this famous passage in the preface to the *Principia*, Newton is saying that "the explanation of phenomena involves not merely an extrapolation from past observations to future observations but also the discovery of the forces of nature," and that "the forces of nature are to be investigated by investigating motion and not by investigating other observable qualities of things." (ibid. idem, pp.68-69)

It is important to note that there is no evidence that Newton interpreted the notion of force in the sense that a body actually moves in a particular observable manner. Provided that Mandelbaum is correct, namely, if the notion of force is something more than a mere physical force, the above passage can be taken as an expression of Newton's metaphysical commitments, but not the expression of a positivistic theory of how science is to proceed. This is more evident in the third rule of the Rules of Reasoning in Philosophy prefixed to Book III of the *Principia*, as quoted below:

> "*The qualities of bodies, which admit neither intensification nor remission of degrees, and which are found to belong to all bodies within the reach of our experiments, are to be esteemed the universal qualities of all bodies whatsoever.* [...] and thence we conclude the least particles of all bodies to be also all extended, and hard and impenetrable, and movable, and endowed with

> their proper *vires inertia*. And this is the foundation of all philosophy." (Newton 1995, pp.320-321)

This seems to advocate using data within experience in order to make inferences about objects which not only have not been observed but also which cannot be observed.

The passage quoted below, which appears just before the passage quoted above, seems to claim that such a way of using data is valid so long as things which cannot be experienced are of the same kind as those found within experience. This assumption, as Newton suggests, can legitimately be made whenever we are dealing with characteristics which are found to hold without exception within our experience.

> "We no other way know the extension of bodies than by our senses, nor do these reach it in all bodies; but because we perceive extension in all that are sensible, therefore we ascribe it universally to all others also. That abundance of bodies are hard, we learn by experience; and because the hardness of the whole arises from the hardness of the parts, we therefore justly infer the hardness of the undivided particles not only of the bodies we feel but of all others. [...] The extension, hardness, impenetrability, mobility, and *vis inertia* of the whole, result from the extension, hardness, impenetrability, mobility, and *vires inertia* of the parts."

In relation to this, Newton claims that his laws of mechanics are not hypotheses because his laws are inferred from phenomena and afterwards rendered general by induction, whereas hypotheses are not so derived. This claim is evident in the fourth rule of Rules of Reasoning in Philosophy, as quoted below:

> "*In experimental philosophy we are to look upon propositions collected by general induction from phenomena as accurately or very nearly true, notwithstanding any contrary hypotheses that may be imagined, till such times as other phenomena occur, by which they may either be made more accurate, or liable to exceptions.* This rule we must follow, that the argument of induction may not be evaded by hypotheses."

Particular propositions inferred from phenomena and rendered general by induction are legitimate and universally applicable as well, because such propositions are closely tied to evidence and because "nature always acts in the same manner." (Mandelbaum 1966, pp.75-78) In those cases, says Mandelbaum, "transdiction is a form of simple inductive inference like extrapolation." (ibid. idem, p.62) But is it true that transdiction is a form of inductive inference?

3. Transdiction and inductive inference

Give an unknown term of a sequence such as 1, 2, 4, 7, 11, 16…. This is an example of mathematical induction. Any number can be known based on the regularity observed between known data. Similarly, we can classify chemical substances according to a law-like regularity. Mendeleev's prediction of unknown chemical elements is an example. It shows the effectiveness of extrapolation as well as interpolation in empirical science.

By contrast, to conceive of ideal gas (perfect gas) is not possible by simple inductive inference. It needs an insight into what is happening behind observed (or observable) phenomena. The concept of ideal gas is based on the idea that gaseous molecules under extremely low pressure behave as if there were no interaction between individual particles. Ideal gas is something like a limiting law which cannot be discovered by mere inductive inference but only by invoking transdiction.

Take Sadi Carnot's "caloric" as another example. When heat flows from a body of higher temperature to one at a lower temperature, work is done. Carnot discussed this by taking the analogy of a waterfall: as falling water performs work by turning a wheel without loss of water, heat falling from a higher to a lower temperature is able to produce work without loss of heat. Based on the mistaken conception that heat is a substance, Carnot arrived at many important conclusions such as why high-pressure steam engines are more efficient than low-pressure ones. "Their advantage lies essentially in their ability to utilize a greater fall of caloric. Steam generated at a higher pressure is also at a higher temperature and as the temperature of the condenser is nearly always the same, the fall of caloric is evidently higher." (Laidler 2001, p.91)

Thus, neither ideal gas nor caloric could be conceived of just by using data within experience. A creative imagination based on transdiction was necessary. They can be characterized as transcendental ideas. In fact, they are not without empirical content: the concept of perfect gas is derived from state equations of various kinds of real gas; the concept of caloric was derived through the analysis of internal combustion engines. The same is true of what we take as molecular structure. As we noted in Chapter 1 it is derived from accumulated knowledge about chemical reactions. It is based on an interpretation of chemical reactions from the standpoint of organic chemistry. We say that a structural formula is a map that shows "every possible site and every possible type of reaction for a given kind of molecule." (Ochiai 2013, pp.139-160) The localized bond is an ingenious creation that explains chemical reactions without the necessity of performing complicated quantum mechanical calculations for a given molecule.

Taking these examples into consideration, transdiction may be shown as a synthetic vector composed of two orthogonal vectors: one representing an inductive inference within experience, and the other the transcendental use of a concept, as is shown in Fig. 5-1.

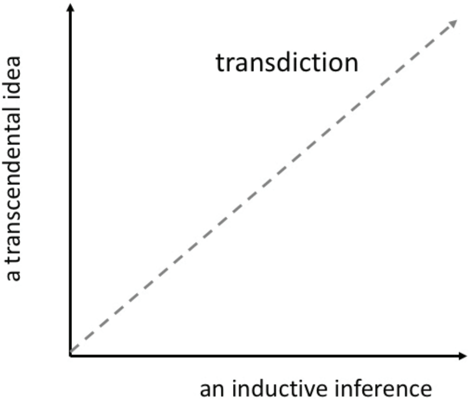

Fig. 5-1 Transdiction and inductive inference

The shorter the vector representing the inductive inference, the more imaginary what is conceived of by transdiction as was the case with caloric. Although Carnot conceived of caloric based on an analogy with falling water, there was no evidence that heat was a substance. Indeed, that was not the case. In general, when we make a transdictive inference, it is of critical importance to consider whether or not the same principle of nature holds equally beyond the boundaries of possible experience. The world of experience is governed by Newtonian mechanics, whereas the world of submicroscopic entities is subject to the laws of quantum mechanics. The concept of structure may not hold beyond those boundaries.

4. The principle of the uniformity of nature

As we noted in the previous section, the third rule of the Rules of Reasoning in Philosophy says, “The qualities of bodies [...] which are found to belong to all bodies within the reach of our experiments are to be esteemed the universal qualities of all bodies whatsoever.” The same rule also says, “because we perceive extension in all that are sensible, therefore we ascribe it universally to all others also.” Newton says that the qualities found to belong to all bodies within the bounds of the senses are to be found to belong to bodies existing beyond those bounds, and hence those qualities are taken as universal. Newton takes the principle of the uniformity of nature for granted and takes transdiction as justifiable by this principle. (Mandelbaum 1966, pp.83-84)

From the latter half of the same rule, it is evident that Newton takes transdiction as a very special use of the principle of the uniformity of nature: “Lastly, if it universally appears, by experiments and astronomical observations, that all bodies about the earth gravitate towards the earth, and that in proportion to the quantity of matter which they severally contain; that the moon likewise, according to the quantity of its matter, gravitates towards the earth; that, on the other hand, our sea gravitates towards the moon; and all the planets mutually one towards another; and the comets in like manner towards the sun; we must, in consequence of this rule, universally allow that all bodies whatsoever are endowed with a principle of mutual gravitation. For the argument from the appearances concludes with more force for the universal gravitation of all bodies than for their impenetrability; of which, among those in the celestial regions, we have no experiments, nor any manner of observation." (Newton 1995, p.321) Properties which are invariably associated with experienced objects are also the properties of all objects whatsoever, says Newton.

It is evident from expressions like "the least particles of all bodies" or "the hardness of the undivided particles" that Newton was referring to atoms (actually, corpuscles). If so, his arguments have a direct relevance to our problem, and questions immediately arise; 1) Can we rely on the principle of uniformity to discuss our problem of molecular structure? 2) Can the principle of uniformity be justified?

Instead of merely accepting such maxims as "Given the same effects we can assume the same causes," Newton extended the principle of the uniformity of nature and tried to justify those maxims. He says "because the hardness of the whole arises from the hardness of the parts, we therefore justly infer the hardness of the undivided particles not only of the bodies we feel but of all others." (ibid. idem, p.320) This suggests that Newton thought of the principle of uniformity as applicable across the boundaries of possible experience. As far as we know, however, such is not the case with submicroscopic entities: we cannot define the hardness and softness of atoms and molecules in the same way as we do those of tangible objects around us. Hardness and softness are concepts that hold for macroscopic entities, but not for submicroscopic entities.

As to the second question Newton was "uncommonly reticent," and the basis of the rule was never discussed. All we get is "a reference to the analogy of Nature, which is wont to be simple and always consonant to itself." (Buchdahl1969, p.339) As for Hume he treated the projective "act" of inductive generalization as "a spontaneous element, and an intimate part of the whole nature of scientific thinking." For Hume (and maybe for Newton as well) the process of inductive projection was "something that is altogether natural." Therefore, "all that is needed is a survey of its genetic condition, that is, the human frame of mind when it thus operates on the results of experiment and observation." (ibid. idem, p.340) In view of this, an interesting question is this: what makes induction a spontaneous element of scientific reasoning?

If most of the data obtained in an experiment come on a straight line, we expect that the next data will come around the line. We cannot help expecting tomorrow morning will be the same as this morning, day and night come alternately, seasons repeat over and over again, etc. The any kinds of regularity we observe in natural phenomena may be responsible for our feeling of the homogeneity of space and time. In fact we are under the influence of the natural environment. For instance, the four seasons in Japan, each of which is tasteful and beautiful, are taken to have nurtured sophisticated tastes for nature, as is exemplified by Haiku and the other traditional arts. Human beings are inseparable from their climatic environments, said Tetsuro Watsuji, a Japanese philosopher (1889-1960). Watsuji pointed out that the unique way of living observed in various regions of the world developed under the influence of the climate characteristic of each particular region. Cultural adaptation is as significant as biological adaptation. Culture in the anthropological sense consists in human behavioral patterns observed in a particular population, some examples of which are smoking, drinking, wearing glasses, shaking hands, taking off one's shoes in a room, etc. As is often the case with religious ceremonies, these patterns are socially defined and acknowledged. They are likely to have originated in particular social phenomena with adaptive implications.

For better adaptation we try to make sense of what we experience. To live in an adaptive manner is to make sense of the world, or in other words, to take the world as not just given but as structured by ourselves according to our intention. This might be a hint to answering the second question: we live in a world structured by ourselves in such a way that the principle of uniformity holds.

The world appears to us as what we take it to be. The principle of the uniformity of nature may not be an attribute of nature but an attribute of human nature. If so, what is reality? What is the causal structure of nature? Given that objective existence becomes reality for us only insofar as we can cognize it, reality might be something like yet-to-be-determined pure existence. In other words, reality is a kind of potentiality which manifests itself when conditions are met. It becomes actualized as an affordance in a phenomenal field, as we shall discuss in Chapter 7.

5. Transdiction and transcendental ideas

Kant says in the *Critique of Pure Reason* that “we cannot cognize objects as they might exist in themselves but only insofar as they appear to us spatiotemporally, and in accordance with our concept of them.” (Hall et al. 2010, p.3) Both intuitions and concepts are necessary for cognition, and “only through their unification can cognition arise.” (Kant 2007, A50-51/B75: Unless otherwise mentioned, quotations in this chapter are from Kant 2007.) In other words, “it is illegitimate to apply any concepts whatsoever to objects beyond the bounds of the senses.” (A63-64/B88) In fact, we are so accustomed and bound to the world of the senses that we uncritically believe that any object whatsoever can be referred to by means of the same concepts that have a proper use only within the bounds of the senses.

The transcendental use of concepts gives rise to transcendental ideas, or pure conceptions of reason, which represent objects antecedently to all experience. Transcendental ideas have “no application within the bounds of the senses but can only be understood as applying to things-in-themselves." (A321)

In addition, the transcendent use of concepts leads to transcendental illusions and to mistaking a subjective representation for an objective cognition. "[t]he illusion inherent in the proposition, the world must have a beginning in time. The cause of this is that there exists in our reason (considered subjectively as a faculty of human knowledge) fundamental rules and maxims of its use, which have the appearance of objective principles. And this leads us to regard the subjective necessity of a certain connection of our concepts for the benefit of the understanding as an objective necessity in the determination of things in themselves." (A296-7/B352-3)

Newton writes in the Scholium in Book I of *Principia* as follows: "Absolute space, in its own nature, without regard to anything external, remains always similar and immovable. Relative space is some movable dimension or measure of the absolute spaces; which our senses determine by its position to bodies." (Newton 1995, p.13) Based on this, absolute motion is defined as "the translation of a body from one absolute place into another." (ibid. idem, p.14) In Newtonian mechanics absolute space serves as a reference frame through which to determine true motions in the solar system.

This conception of absolute space is no more than a transcendental idea, says Kant, for an actual object of experience must be material. In *Metaphysical Foundations of*

Natural Science, Kant defines relative (empirical) and absolute space as follows: "Matter is the movable in space. That space which is itself movable is called material, or also relative space; that in which all motion must finally be thought (and which is therefore itself absolutely immovable) is called pure, or also absolute space." (Kant 2004, p.15) Absolute space "cannot be an object of experience, for space without matter is no object of perception, and yet it is a necessary concept of reason, and thus nothing more than a mere *idea*." (ibid. idem, p.98)

Characterizing absolute space as an "idea of reason," Kant shows a procedure for reducing all motion and rest to absolute space. That is to say, in order to determine the true motions in the empirically accessible material universe he considers our position on the earth and then "moves to the point of view of our solar system, then moves to the perspective of the Milky Way galaxy, and so on *ad infinitum* through an ever widening sequence of ever larger galactic structures serving as ever more expansive relative spaces." (ibid. idem, p. xiii; See also pp.16 and 98)

Then, Kant proposes an empirically meaningful surrogate for Newtonian absolute space, "the common center of gravity of all matter." (ibid. idem, p.102) Kant says that absolute space is necessary "not as a concept of an actual object, but rather as an idea, which is to serve as a rule for considering all motion therein merely as relative; and all motion and rest must be reduced to absolute space." (ibid. idem, p.99)

As is shown by the argument above, it is not easy to tell whether something is a transcendental idea or not. Newton maintains that his laws of mechanics are not hypotheses because they are inferred from phenomena. It might be that, if grounded in proper logic and observation, things conceived through transdiction are relevant to the world structured by we ourselves.

6. Transdiction as a source of creative imagination

“The essence of reason is its demand for the unconditioned.” (Rohlf 2010, p.196) “Reason is never satisfied with the understanding it currently has,” but always demands a more complete explanation. (The “unconditioned [condition]”is Kant’s term for a complete explanation.) For reason, “the questions never cease.” (Kant 2007, Aviii) Reason is just like “a child who is always asking why something is the case. For each answer the child will likely ask why it is the case until the series of questions comes to the point where one is sick of answering them.” (Hall et al. 2010, p.147) Thus, reason inevitably oversteps the boundaries of experience and gives rise to transcendental illusions. (A643/B671)

Kant says in the Appendix to the Transcendental Dialectic as follows: “Everything that is grounded in the nature of our faculties must be purposive, and be in harmony with their right use—provided that we can guard against a certain misunderstanding and can discover their proper direction. The transcendental ideas, therefore, will probably possess their own proper and, therefore, immanent use, although, if their meaning is misunderstood and they are mistaken for concepts of actual things, they can be transcendent in their application, and hence be deceptive. For not the idea in itself but merely its use can, in regard to the whole of possible experience, be either overflying (transcendent) or native (immanent), according to whether we apply them either directly to objects that supposedly to correspond to them, or apply them only to the use of the understanding in general with regard to objects with which it deals. All errors of subreption are to be attributed to a want in the power of judgement, never to the understanding or to reason." (Kant 2007, A643/B671)

After referring to the relation of reason to the understanding, Kant continues to explain the proper use of transcendental ideas as follows: "I maintain, accordingly, that transcendental ideas are never of constitutive use, so that thereby concepts of certain objects should be given, and that, if they are so understood, they are merely sophistical (dialectical) concepts. They have, however, a most admirable and indispensably necessary regulative use, in directing the understanding to a certain aim, towards which the directional lines of all its rules converge in one point. And although this point is only an idea (*focus imaginarius*), that is, a point from which, since it lies completely outside the limits of possible experience, the concepts of the understanding do not in reality proceed, it serves nevertheless to impart to these concepts the greatest unity and the greatest expansion. Hence there arises, no doubt, the illusion that those directional lines sprang forth from an object itself, outside the field of empirically possible knowledge (just as objects are seen behind the surface of a mirror). Yet this illusion (by which we need not allow ourselves to be deceived) is nevertheless indispensably necessary if, besides the objects which are before our eyes, we want to see also those which lie far away behind our back; that is to say, the illusion is necessary if, as in our case, we wish to direct the understanding beyond every given experience (as a part of the sum total of possible experience), and thus also to its greatest possible and most extreme expansion." (A644-5/B672-3)

A transcendental idea cannot be a constitutive principle, that is, it does not contribute to expanding our knowledge because it is a pure concept of reason and is formed without empirical basis. But it serves as a regulative principle to form the synthetic unity of empirical cognition. As to the latter, the common center of gravity we noted in the preceding section is an example. We can determine true motions in the empirically accessible universe relative to this center of gravity though it is unattainable forever.

It is the latter part of the quotation that is interesting to us in relation to the present argument: "this illusion [...] is nevertheless indispensably necessary if, besides the objects which are before our eyes, we want to see also those which lie far away behind our back.” We want to know what is happening at the molecular level, and hence make a transdictive inference. “The epistemological technique of transdiction was habitual with chemists long before physicists developed a similar art.” (Rocke 1993, p.248) “Ever since chemical atomism arose in the early years of the nineteenth century, chemists were comfortable in routinely inferring the atomistic compositions of molecules from macroscopic gravimetric measurements.” Liebig points out in his autobiography a characteristic that is found particularly in successful chemists. It is the ability to “think in phenomenon.” This talent can only be developed “by constant exercise of the senses, and it increased in him to the point of becoming a photographic visual memory of compounds and reactions.” (ibid. idem, p.33-34) On the one hand he was a student of the Kantian Kastner. On the other hand, he was the person who established the method of elemental analysis. Transdiction must have played a decisive role though molecular structure was not known in his days.

In reality, “as the [nineteenth] century progressed transdiction became ever more elaborate and inferences to composition were supplemented by inferences to molecular structure.” (ibid. idem, p.248) Chemistry exemplified Kant’s claim that “the illusion is indispensably necessary if we wish to direct the understanding beyond every given experience [...] and thus also to its greatest possible and most extreme expansion.” Concepts like chemical bonds and molecular structure became more and more important for organic chemists because such concepts helped them conceive of abstract ideas such as isomerism. They served as regulative principles for “the systematic unity of the manifold of empirical knowledge.” (A671/B699)

Since it was not until the middle of the nineteenth century that the structure theory in organic chemistry was established by Kekulé, it is not Kant’s fault that the central role of transcendental ideas and therefore the role of transdiction in chemical reasoning were not properly acknowledged. Although Kant described chemistry as “systematic art or experimental doctrine” in the preface to the *Metaphysical Foundations of Natural Science*, it turned out by the 1860s that laws of chemistry were not mere laws of experience. (Kant 2004, p.4; Friedman 2013, p.241)

In the nineteenth century “physics gradually became less concrete, more abstract, and more firmly based on an axiomatized mathematical foundation.” (Rocke 1993, pp.246-7) By the middle of the nineteenth century, a hypothetico-deductive approach became widespread in chemistry. Making a hypothesis was inseparable from substantiation, as was illustrated by Kolbe and Frankland in their research of radicals. Their works yielded not only theoretical progress but also a lot of practically meaningful results. Kolbe and Frankland are known, respectively, as a pioneer in electrolysis reactions and the founder of organometallic chemistry. Since then, for most chemists transdiction has been not only a mere tool for reasoning but also a tool for facilitating chemical practice. Today, “when the chemist adds methyl iodide to an ethereal solution of potassium ethoxide in a Williamson ether synthesis, her mind’s eye is focused on the activity at the molecular level.” (ibid. idem, p.248) We talk about molecular structure as if it were an object of immediate observation. Actually, no one has ever taken pictures of molecular structure because it is nothing but a theoretical construct. Pictures of the spatial arrangement of atoms or nuclei taken by electron micrograph or X-ray photograph are not taken as molecular structure, at least by organic chemists, because the term “molecular structure” connotes not only the linkage and spatial arrangement of atoms but also what is represented by chemical bonds, functional groups, curved arrows that show the movement of electron-pairs, and so on. In the end, molecular structure is an interpretation of chemical reactions from the viewpoint of organic chemistry.

7. A surrogate for transcendental ideas

Most chemists are realists, naïve or otherwise. However, it is one thing to be convinced of the existence of submicroscopic entities, and quite another to believe that every detail of those entities is accessible to us. It is not likely that our knowledge of those entities is the same kind as that of the palpable things around us. Critical realists admit the objective existence of reality which is inaccessible to us in direct experience.

As is shown in the next chapter in more detail, according to the tenets of critical realism the world can be classified into three ontological domains. (Denermark; Ekström; Jacobson; Karlsson 2002, p.20) The uppermost domain on the ontological map is the empirical domain, that is, the world as it appears to us. This domain contains data and facts, all of which arise in connection with some theory. In other words, our cognition of the world is theory-dependent, not to say theory-determined. On the other hand, it is because there exists something that makes things happen in the real domain that we observe those data and facts. Between the empirical and real domains is the actual domain.

Although naïve objectivism simply takes transdiction to refer to reality and is destined to fall into transcendental illusions, critical realism suggests an alternative approach. Since the causal structure of a real system is closed off to us forever, it is not an objective reality but a theoretical model that is responsible for our obtaining knowledge. By serving as a surrogate for what might exist, models play an essential role to expanding our knowledge. For instance, the ancient idea that matter can be divided into discrete units called atoms was so abstract and metaphysical that it could not be the object of scientific investigation. By contrast, Dalton's theory, in which an atom of each element is given a definite weight, is amenable to experimental tests and falsifiable. Though simple and primitive, Dalton's theory and his theoretical model transformed the metaphysical idea of atoms into an object of science.

The relationship between transdiction and the role of models is schematically shown in Fig. 5-2. In this figure we can see that models serve as an explanatory principle as well as a surrogate for things in themselves. Models also materialize transcendental ideas, as is the case with Dalton's theory. Though it is inevitable for human reason to transgress the boundaries of possible experience, this scheme helps us not to mistake subjective representations for objective ones. Thus, we can avoid falling into transcendental illusions.

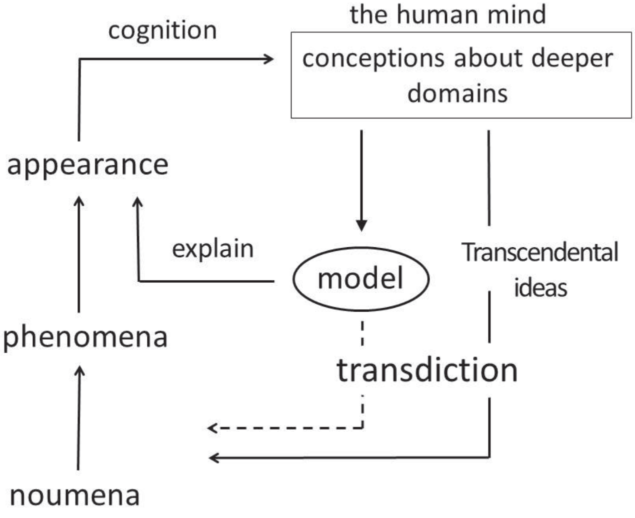

Fig. 5-2 The system of scientific representation

CHAPTER 6

KNOWLEDGE AND REALITY

Since molecules exist beyond the bounds of the senses, we cannot know by intuition what they are like. Therefore, we conceive of them and represent what we take them to be with various models. What we assume to be molecular structure consists of atoms, bonds, paired electrons, etc., and should be distinguished from tangible structures around us. Our problem in this chapter is to examine whether or not our notion of molecular structure can be understood within the scope of scientific realism.

1. Empiricists' view of the relation between knowledge and reality

Empiricism requires theories "only to give a true account of what is observable, counting further postulated structure as a means to that end." (van Fraassen 2011, p.3) Empiricism is a kind of realism that takes observable phenomena to be real. Empiricists say that we can affirm the reality of the objects of experience within the bounds of the senses and that only to those objects do our concepts have legitimate applications. Therefore, as van Fraassen says, "empiricists have always eschewed the reification of possibility." "They relegate possibility to relations among ideas or words, and regard these as devices to facilitate the description of what is actual." Empiricists go as far as to say that "postulates need not be true" except what is postulated is actual and empirically testable. A motto of empiricism is to "save the phenomena," namely, to reproduce what is observable. This is what Ptolemy did in predicting the motions of the planets with his geocentric model as is discussed below.

Chemists are always happy with creating new substances. It is said, no matter what the chemist says, what she creates shows what she is like. Then, is she an empiricist? She can be one at least in her lab, maybe. It is true that a chemist likes to say, "I have a working hypothesis." This is, however, taken by other chemists to mean that she will not investigate what is behind observation: a working hypothesis makes sense only insofar as it serves to produce something new. This attitude characteristic of chemists is not without reason. Before Kekulé established the theory of structure, what was assumed to be happening behind phenomena varied from person to person. As we saw in the preceding chapter, an impressive episode is known involving Liebig, who grew up in the Kantian philosophical atmosphere. He wrote in his autobiography that his ability to "think in phenomena" developed to the point of being able to make "a photographic *visual* memory of compounds and reactions." (Rocke 1993, pp.33-34)

Although experience is the firm grounds on which every scientific inference is made, science would be just an art of registering empirical data if inferences beyond the bounds of the senses were banned for the reason that they lack logical necessity. Chemical synthesis would be a collection of practical knowledge and know-how based on trial and error as it was in Liebig's day. In fact, the situation changed greatly with the advent of retrosynthetic analysis, by which the search for a feasible way of synthesis became logically guided. This suggests that we are on the right track even if what we are doing is not logically watertight. A hard-core empiricist, however, repudiates any theoretical entity which does not stand on empirical grounds.

However, it is not true that postulating theoretical entities is totally excluded from empiricists' arguments. On the contrary, as was exemplified by Ptolemy, any postulate is allowed, but if and only if it serves as an instrument to give an account of what is observed. Ptolemy said that not one but several mathematical models could equally save the appearance of planetary motions. For instance, he showed that the moving-eccentric model was mathematically equivalent to the epicycle-deferent model. What empiricists firmly hold is that we can never know whether or not unobservable things really exist as they are postulated.

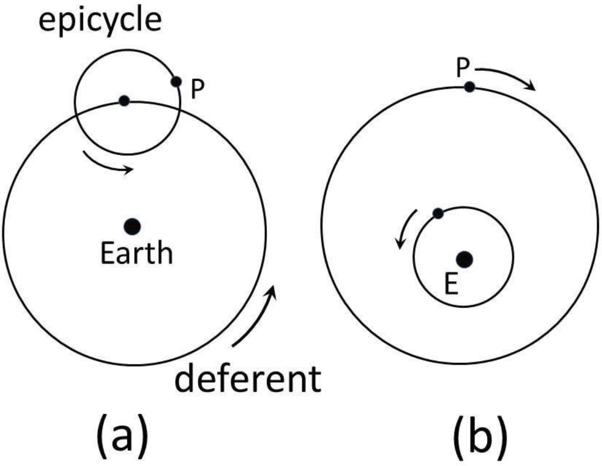

Fig. 6-1 (a) The epicycle-deferent model,
(b) The moving-eccentric model

Empiricists say that there is no way for beings like us to verify what is happening beyond the bounds of the senses. Agnosticism is the correct attitude to maintain in scientific arguments. In fact many theoretical entities have been proved to exist in the course of the ongoing pursuit of science. Atoms and molecules exist beyond all doubt. Hence the next question to be asked is concerning what they are like: for instance, what is molecular structure like? This may, however, never be asked, for molecules are not accessible to immediate observation. Empiricists say that talking about molecular structure is not philosophically grounded: such structure might be a figment of chemists' imagination.

Why are empiricists so nervous about making an inference across the boundaries of possible experience? Historically speaking, empiricists thought that natural science free from metaphysical impurities had to be based on the objective observation of nature. They emphasized sense data with which to register the observable. But their attempt ended up with the collapse of logical positivism after all.

Empiricists are cautious with metaphysical presuppositions in order not to enter into scientific arguments. Such an attitude is illustrated by Hume's arguments about inductive inferences. We think that the sun will rise tomorrow as it did this morning; autumn will come after summer; a stone thrown into the air will fall at last; our plane will safely bring us to our destination; a train will come on time as usual, etc. But is there any logical necessity to take the regularity of a series of events as grounds for thinking that a similar event will happen again? No. Hume flatly says. On careful examination of the operation of our reason, he noticed that there is no necessary connection between past events and future events. While our logical reasoning is internal and necessary, the relations between events are external and hence contingent. There are no rational grounds for connecting them. Therefore, it is illegitimate to expect something will happen again based on past experience even if it happens regularly and has never failed to happen up until now.

To empiricists there is no causality in nature but only regularity. Therefore, Newton, for instance, maintained that we ought to seek natural laws that connect phenomena. On the same line, positivists claim that certain (positive) knowledge should be based on natural phenomena and their relations. Information derived from sense data, which is interpreted through reason and logic, forms the source of all certain knowledge. It is a-posteriori knowledge systematized with logico-grammatical relationships between concepts that they have full confidence in.

Also, positivists once thought that all sciences would be unified in a single model through a hypothetico-deductive process. Mathematized physics was their favored model, under which all other sciences would be subsumed. From their point of view quantum mechanics was a promising candidate. (Dirac wrote as follows: "The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble.") (Dirac 1929, quoted in van Brakel 2000, p.120) However, is it not that relations represented by unsolvable equations are a mere possibility that empiricists never admit?

To rephrase the point, for empiricists, the notion of necessary connection between cause and effect is an example of an illegitimate application of ideas to an objective world. While it is tempting to think that causes necessitate their effects, effects are different events from their causes. There is no necessary connection between them. Causal inference is for the explanation of why particular outcomes occur; inductive inference is for a mere description. Though different in their purposes, both types of inference are based on external relations, and hence lack logical grounds.

There might be a point in what empiricists say. But we cannot be satisfied with their arguments, for we tend to take relations between events, if constantly conjoined, to be necessary. We have such a custom or mental habit to think that way, as was pointed out by Hume. In other words, we cannot escape from "projecting our felt associative propensity on to reality." (Hacker 2010, p.62) We cannot help thinking that the course of nature will not change, or that nature is uniform. This Principle of the "Uniformity of Nature" is paraphrased as "the future will resemble the past" (Oxford Dictionary of Philosophy, 3rd ed.) or "nature always acts in the same manner." (Mandlbaum 1966, p.78) This is none other than the manifestation of subjective judgement.

Why are we not happy with empiricists' arguments? Although relations between events may not be logically grounded, there must be something that makes events happen constantly conjoined. Otherwise, every scientific activity will be nothing but a miracle. Why do we take aspirin when we have a headache? It is because aspirin cures our headache. We cannot help thinking this way. Probably this is human nature. The world appears to us as such whether or not causal relationships are necessary. In other words, it might be that we structure the world as if there were a necessary connection between different events. This helps us predict what will happen in the future and cope with otherwise chaotic situations.

2. The observable/unobservable distinction

Empiricists tell us that we should remain agnostic about the unobservable region of reality. Accordingly, the distinction between the observable and the unobservable is of critical importance. It is central to the debate between realism and empiricism, for if such a distinction turns out to be groundless, empiricists' arguments collapse.

Let us consider the following—often cited—sequence of events: We are looking at something (a botanical specimen, for instance) with the naked eye. In order to make a careful examination we look at it through a magnifying glass. Then, we look at it through a low-powered microscope, then, through a high-powered microscope, and so on. Since this series of events seems to lie on a smooth continuum, it is unlikely that we can decide what is observable and what is not. A biologist would be happy to talk about what she *observed* with her high-powered microscope. (Okasha 2002, p.67)

What about the tracks of cosmic rays? When cosmic rays pass through a cloud chamber saturated with alcohol vapor, they collide with alcohol molecules and cause liquid droplets of alcohol to form. The liquid droplets can be seen to the naked eye as the tracks of cosmic rays. Most people who see this would not consider observation, but rather detection (of cosmic rays). In the same way we can detect a jet plane flying high in the sky by the vapor trail it leaves behind. On some occasions we can also see a jet at the beginning of a trail. On such occasions we say we are observing a jet. Change the point of view and we can get a different image of the same object: Europa is one of the satellites of Jupiter, which we can see with a telescope as Galileo Galilei did. If in the future we get closer to it on a spaceship, it will be observable to the naked eye.

In view of these examples, it is not clear where to draw the dividing line between the observable and the unobservable. Thus, empiricists' arguments collapse. This is the logical consequence of attaching too much importance to perception. But perception is none other than the activation of our sense organs. If a detector—instead of our sense organs—gets activated, there must be something that is responsible for that. Apart from the historical significance mentioned above, there is no reason to pay special attention to our sense data.

What matters more for us is where to place molecular structure: it is not just what is given, but what is theoretically constructed. Molecular structure is a sketch of what we conceive of, rather than a photograph. It is not an object of sensible intuition but an object of conceptualization.

3. Constructive empiricism

Bas van Fraassen claims that “science aims to give us theories which are empirically adequate”—what a theory says about the observable is true, or in other words, saves the phenomena. (van Fraassen 2011, p.12) Also, as a proponent of the semantic view of theories—i.e., the view that a theory is a collection of models—he says that “such a theory has at least one model that all the actual phenomena fit inside.” For him scientific activity is “one of construction rather than discovery”: science is the construction of models that are adequate to phenomena observed and not the discovery of truth concerning the unobservable. This is the reason why he names his doctrine constructive empiricism. (ibid. idem, p.5)

Constructive empiricism is a clever way of talking about science and reality. According to the doctrine, theories do not postulate what is beyond the bounds of the senses but only explain what is within those bounds. Then, there will be nothing uncertain about what theories say. Let us take Ptolemy’s system of planetary motion as an example. As we saw in the previous section, Ptolemy did not insist on his epicycle-deferent model being unique. On the contrary he maintained that, though it could simulate planetary motion, it was only one of the equally adequate solutions: the moving-eccentric model, too, could save the appearance of planetary motion. As long as it saves phenomena, a theory can be true whether or not it is relevant to reality.

Empiricism has something in common with the Aristotelian system of science described in Chapter 2. Just as Aristotle made his system consistent in the form of syllogism, so too empiricists make their arguments consistent in the empirical domain. No attempt is made to examine theoretical claims from a point of view outside a theoretical framework. To empiricists, and to constructive empiricists in particular, empirical adequacy (i.e., “save the phenomena”) is the unique criterion on which to decide whether or not a theory is tenable. In fact, a historical lesson we learned from Aristotle is that a self-consistent system can easily fall into nonsensical arguments. Even if Ptolemy’s model was not that bad, it was wrong after all.

There are lots of historical episodes which support constructive empiricism. As we saw in the preceding chapter, Carnot, who was one of the founders of thermodynamics and is famous for the Carnot engine, believed that heat produces work when caloric falls from a body of higher temperature to the one of lower temperature without loss of heat. Starting from such a wrong hypothesis, he arrived at the conclusion that the efficiency of ideal engine depends solely on the temperature difference between a supplier and an absorber of heat. It is interesting that Carnot did not himself know an indicator (pressure against volume) diagram, through which we are familiar with the Carnot cycle. Also, he did not know the concept of the absolute temperature, in terms of which efficiency is most easily expressed. To our surprise, he did not understand that work could be done at the expense of heat that disappeared. He did not imagine that the efficiency should be defined as the fraction of the heat absorbed at the higher temperature that was converted into work. (Laidler 2001, pp.87-93) There are many examples showing the usefulness of the notion of empirical adequacy for understanding the nature of scientific theories. We cannot flatly reject what van Fraassen says even if it seems strange at first glance. On the contrary, his doctrine has to be taken into consideration as much as possible, for every science—including quantum mechanics—is susceptible to constructive empiricists' interpretation.

4. Scientific realists' view of the relation between knowledge and reality

The Stanford Encyclopedia of Philosophy (SEP) tells us that "a general recipe for realism is widely shared: our best scientific theories give true or approximately true descriptions of observable and unobservable aspects of a mind-independent world." (Scientific Realism, Jun 12, 2017) Actually, the details of claims differ from person to person. The differences between their claims arise from variations in the particular aspects to which they direct their attentions. It is the difference in the sense in which they take themselves as a scientific realist.

Hilary Putnam says, "the sentences of scientific theories are true or false: what makes them true or false is something external—it is not (in general) our sense data, actual or potential, or the structure of our minds, or our language, etc."

(Quoted in van Fraassen 2011, p.8; Chakravartty 2010, p.4) Hacking puts it more simply as "the entities, states and processes described by correct theories really do exist." (Hacking 2008, pp.21-31) Bas van Fraassen, who takes the empiricists' claim about scientific theories into consideration, describes it as follows: "science aims to give us, in its theories, a literally true story of what the world is like; and acceptance of a scientific theory involves the belief that it is true." (van Fraassen 2011, pp.6-9) According to SEP, the dimensions of scientific realism are classified into, for instance, metaphysical, semantic and epistemological.

1) The metaphysical (or ontological) dimension: Scientific "realism is committed to the mind-independent existence of the world investigated by science." Actually, there are controversies about what is real: some people say it is entities that really exist and others say theories represent reality.
2) The semantic dimension: Scientific "realism is committed to a literal interpretation of scientific theories about the world." Scientific claims should be taken at face value. That is, unobservable entities, states and processes exist in the way theories say. In other words, theories are not mere instruments for the prediction of observable phenomena.

3) The epistemological dimension: Scientific “realism is committed to the idea that theoretical claims constitute knowledge of the world.” It presupposes that scientific theories will somehow become established as real, if not at once but in the future, in the course of the ongoing pursuit of science.

There are a lot of arguments among philosophers concerning the dimensions of scientific realism described above. Their claims are classified under the label of selective skepticism: explanationist realism, entity realism and structural realism. The classification is not exhaustive but conventional.

The first one, explanationist realism, is another name for scientific realism about theories. If theories are crucial in order to provide successful predictions, empirical success is the best explanation that theories are true or approximately true. But there are arguments that it is not theoretical laws but phenomenological ones that are successful in prediction and true of reality. Theoretical, “fundamental laws are true only of objects in theoretical models.” (Cartwright 2002, p.4)

In addition, theories are always open to correction, having been replaced one after another, whereas the entity responsible for the phenomenon under investigation is the same. Therefore, it is possible to be an anti-realist about theories and a realist about entities: entity realism is a kind of skepticism about theories. “If we can intervene in a certain phenomenon by exploiting the causal power of things responsible for the phenomenon, we do not doubt their existence.” (Chakravartty 2010, p.30)

A couple of weeks ago I happened to see an old friend who is a mathematician. He described his work. Although it was too technical for me to follow, I saw there was something in common with philosophy. Then, I asked, “Do you want to give a concrete shape to something like Plato’s Idea?” And he did. A proponent of structural realism says, “insofar as mature, non-*ad hoc* scientific theories offer approximately true descriptions of a mind-independent world, they do not tell us about its nature but about structure.” (ibid. idem, p.33) If the same equation survives from one theory to the next, we take the structure represented by the equation to be real. Such was the case with theories about the structure of light because Fresnel’s equations survived intact in Maxwell’s theory. In chemistry, the law of periodicity may be counted as an example: the periodic relationship between chemical elements is real and survives no matter what kind of table of elements is constructed.

There are a lot of arguments about the possibilities of science and scientific knowledge. We will examine in detail only those which are likely to be useful in resolving arguments about molecular structure.

5. Critical realism

Bas van Fraassen says that scientific realists, who on the one hand pointed out the extreme of positivism, on the other hand go too far in reifying whatever is unobservable. (van Fraassen 2011, pp.6-13) In fact, while most chemists are scientific realists, many of them are not so naïve as van Fraassen says. It is one thing to believe in submicroscopic entities, and another to think that every detail of those entities is accessible to us.

The existence of the molecule is an objective reality independent of the human mind. The molecule is inaccessible to immediate observation. Therefore, we conceive of it and represent what we take it to be with various models. What about molecular structure? As we noted in Chapter 2, it serves as “a map to show every possible site and every possible type of reaction for a given molecule.” (Ochiai 2013, pp.139-160) Thus, it is quite different in nature from tangible structures around us. Not only that, but in the ordinary sense of the term, “structure” concerns objects existing within the bounds of the senses such as the Eiffel Tower. It is not certain whether or not the word “structure” can be legitimately applied to objects beyond those bounds. Kant says in the *Critique of Pure Reason* that we are apt to impose subjective explanatory principles upon ourselves as objective. (Kant 2018, A293-4/B350) Can it be that molecular structure is a misapplication of the pure concept of reason? What we have to do is to examine how our notion of molecular structure is characterized and, in so doing, to show whether or not we can understand it within the scope of scientific realism.

According to the tenets of critical realism the world is classified into three ontological domains. (Bhaskar 2008, p.56) The uppermost is the empirical domain (i.e., the world as it appears to us). This domain contains data and facts, all of which arise in connection with some theory or concept because we can cognize objects only insofar as they appear to us in accordance with our concept of them. (A man from the Stone Age would not be able to tell what a computer was.) On the other hand, there must be something that is responsible for the data and facts. This is concerned with the real domain, which has powers to make things happen. (Critical realists oppose empiricists and maintain that things in the real domain cannot be reduced to empirical data.) Between the empirical and real domains is the domain of phenomena or the actual domain, where things are happening whether or not they are observed.

In Kantian terminology the real domain is concerned with noumena or things in themselves. (Of course Kant, who was an empirical realist, never took noumena as real.) The molecule, which is too small to see, is an example of a negative noumenon that is merely not an object of sensible intuitions. On the other hand, a positive noumenon is an object of non-sensible intellectual intuitions. Though it might be hard to imagine what it is, the omnipotence of God is an example. Since it is not given in sensibility, it must be given to the understanding via intellectual intuitions and thought by the understanding through concepts. But for beings like us it is impossible to have this type of cognition. We should be careful not to make the mistake of applying concepts that have a proper use only within the bounds of the senses to objects that exist in the real domain.

Since neither the actual domain nor the real domain is transparent to us, we have to do experiments to know what they are like. In other words, science is not a passive registration of empirical data but an action to dig into the hidden domains. (Danermark et al. 2002, p.20) Almost all scientists will agree with this. Bhaskar goes one step further and say that we can get to the real domain by sophisticating our models in the course of the ongoing pursuit of science. “The generative mechanism” of phenomena represented by models “may come to be established as real,” says Bhaskar. (Bhaskar 2008, p.56, p.45) Actually, submicroscopic entities are subject to the laws of quantum mechanics, and quite different in nature from things in the empirical domain. On the other hand, models are constructed by analogy with things within our experience. In what sense do models come to be established as real in the course of the ongoing activity of science?

This is not the only difficulty to be considered. A realist holds that “scientific theories correctly describe the nature of a mind-independent world.” (Chakravartty 2010, p.4) Bas van Fraassen cites the formulation given by Hilary Putnam: “a realist (with respect to a given theory or discourse) holds that

(1) the sentences of that theory are true or false; and (2) that what makes them true or false is something external—that is to say, it is not (in general) our sense data, actual or potential, or the structure of our minds, or our language, etc.” (van Fraassen 2011, p.8) Such cannot be the case, however. Admittedly, fundamental theories of physics such as Newton’s laws of mechanics may satisfy the requirement. But these are true of only objects in models. They are about the reality behind appearances, are given in the form of thoroughly abstract formulas, and do not describe particular circumstances. This is in marked contrast to phenomenological laws that provide detailed accounts of exactly how phenomena are produced. Though they are true of objects in reality, they have only a limited scope of application. (Cartwright 2002, pp.1-4) In either case, no single theory is a literally true description of the real world. We do not have a fundamental theory that describes the world correctly, nor do we have a phenomenological law that is true in all respects.

Giere says that a theory does not correspond to reality because a theory is a set of statements and different in nature from reality. Instead, he maintains that it is models that should be compared with real systems. In addition, given that each model has at best some similarity with a real system, it is a population of models that may link with reality. (Giere 1990, pp.80-85) Here again the question is in what sense models can be compared with reality. What similarity is there between a population of models and reality? As we noted above, models are made by analogy with things existing within the bounds of the senses, and the molecule exists beyond those bounds. Models cannot be similar to the molecule in the exact sense of the term.

Another point worth noting is that Bhaskar confuses reality with knowledge. He writes "according to Kant's transcendental idealism, the objects of scientific knowledge are models, […] the natural world becomes a construction of the human mind or, in its modern versions, of the scientific community." (Bhaskar 2008, p.25) In fact, Kant says that since space and time as well as categories (i.e., the *a priori* concepts of the understanding or the rules that the understanding uses to organize the representational content of sensibility) are contributions of the subject to her experience, "the objects of experience are nothing once we leave behind the sensible and conceptual conditions of the subject." (Hall 2011, p.139; Kant 2018, Bxxvi) It does not follow that the world is a human construction as Bhaskar maintains. Providing that the world is an objective reality existing independently of the human mind, it is not the world but our knowledge that is constructed.

It is said that "realism consists in a combination of a modest claim and a presumptuous one. The modest claim is that there is a subject-independent reality; the presumptuous claim is that we are capable of describing that reality accurately." (Mumford 2008, p.192) I lean toward the modest side.

6. Is Kant a scientific anti-realist?

Critical realism is a kind of transcendental realism in which the basic preconditions for our knowledge are taken to be found in reality. Bhaskar maintains that “it is necessary to assume for the intelligibility of science that the order discovered in nature exists independently of men.” “If there were no science there would still be a nature, and it is this nature which is investigated by science.” (Bhaskar 2008, p.27) Bhaskar criticizes Kant’s transcendental idealism. The truth is that “by an idealist one must understand not someone who denies the existence of external objects of sense, but rather someone who only does not admit that it is cognized through immediate perception and infers from this that we can never be fully certain of their reality from any possible experience.” (Kant 2018, A369)

Transcendental realism is the doctrine that “regards space and time as something given in themselves (independent of our sensibility).” The transcendental realist “represents outer appearances (if their reality is conceded) as things in themselves, which would exist independently of our sensibility and thus would also be outside us according to pure concepts of the understanding.” The transcendental realist considers all our representations of the senses as insufficient to render the reality of these objects certain. Hence it is “really this transcendental realist who afterwards plays the empirical idealist.” (ibid. idem, A370) This is the logical consequence of thinking that the external object of the senses must have an existence in themselves. It is far from certain that “if the representation exists, then the object corresponding to it would also exist; but in our system, on the contrary, these external things—namely, matter in all its forms and alterations—are nothing but mere representations, i.e., representations in us, of whose reality we are immediately conscious.” (ibid. idem, A371)

Then, is Kant a scientific anti-realist? To put it more specific, “does the role of reason in creating our scientific theories make Kant a scientific anti-realist?” (Rauscher 2010, pp.292-301) In the arguments about the relationship between the understanding and its objects, Kant explains that the understanding has only pure schema as a formal framework that provides for objectivity. Likewise, “pure reason has only its methodological principles (homogeneity, specification, and continuity) and the pure ideas of reason (soul, world, and God) as a formal framework to provide for objectivity.” Kant says that particular cognitions such as empirical laws and empirical concepts collected by the understanding are brought under these objective principles and ideas to create a system of science. “The principles of pure reason have objective reality in regard to this object of experience.” While reason does not determine particular objects in experience, and is therefore, not constitutive of experience, it provides a regulative systematicity to empirical cognitions. Reason neither determines any specific unity nor operates without any connection to the actual order of nature. Thus, Kant occupies “a middle ground between scientific realists and anti-realists.”

Although these arguments represent typical standpoints in Western philosophy, ways of seeing the world are not exhausted by them. According to the Teaching of Buddha, nothing ever exists entirely alone. “Everything is in relation to everything else. Wherever there is light, there is shadow; wherever there is length, there is shortness; wherever there is white, there is black. As the self-nature of things cannot exist alone, they are called non-substantial.” “Since things do not differ in their essential nature, there can be no duality.” It follows from this that “the important thing is to avoid being caught and entangled in any extreme, and to follow the Middle Way.” (The teaching of Buddha 2009, pp.114-120)

The Teaching of Buddha also says that “water is round in a round receptacle and square in a square one, but that water itself has no particular shape.” This is also expressed as follows: “Just as a picture is drawn by an artist, surroundings are created by the activities of the mind. While the surroundings created by Buddha are pure and free from deficiency, those created by ordinary people are not so. The mind conjures up multifarious forms just as a skillful painter creates pictures of various worlds. There is nothing in the world that is not mind-created.” (ibid., p.138)

We have much to learn from these passages regardless of our religious beliefs.

7. What is our belief grounded on?

If we can control things as we want, we are convinced that they are real. (Remember, say, riding a bicycle.) But Woodward points out that “what one needs for manipulation is information about invariant relationships, and one can identify invariant relationships even in cases in which one does not know laws, cannot trace spatiotemporally continuous processes, or unify and systematize.” (Woodward 2005, p.10)

In organic synthesis chemists identify reaction products by instrumental analyses. We interpret experimental data and become convinced that experiments went well. Actually, we simply associate signals with known structures registered in a database. We do not care about the principles on which the analysis works. But what if someone dares to ask about them? Of course, we explain, if we can. Then, another question is raised about it. We answer, but there are more questions and answers. Just as in the case of a child who is always asking why something is the case, such questions and answers never cease. This is the endless pursuit of the final grounds. It is not only practically impossible to perform but a wrong way to proceed.

Let us take another example. Someone asks me to make a document on a person I do not know. I interview his colleagues, his wife and kids about what he is like. Their reports will reveal his profile: what he is like as a researcher, husband and dad. We trust them if their descriptions make sense in the light of their experience. Even if their reports are at odds with one another, each description can be true in its own right, for what appears to each person depends on a particular context in which he or she is situated. Then, what generates the final document? If we are in an ordinary business setting, we have to make sure who needs the document for what purpose. We examine pieces of material from that point of view and arrange them to meet client's request.

We can describe one and the same object from various points of view. Each description may serve as a piece of jigsaw puzzle. Such is also the case with science. Every study has its own approach and result. It is the purpose and the context of study that provide a consistent picture of the object.

8. Constructive realism

Probably constructive realism will be beyond the scope of scientific realism. On the contrary, it may be better classified into anti-realism. Actually, whether it is realism or anti-realism, any standpoint we have examined thus far fails to give a convincing account of molecular structure. It may be that conventional classification is irrelevant to our problem. In view of this, constructive realism deserves consideration at the end of this chapter.

The world existing outside ourselves is independent of the human mind. We can cognize objects in the world only insofar as they are given in sensibility via intuition and thought by the understanding through concepts, said Kant. All that is known to us is processed through our cognitive activity. That is to say, our knowledge of the world is a human construction. This is the basic idea of constructivism.

Fritz Wallner, the founder and advocate of constructive realism, proposes to distinguish “Wirklichkeit” and “Realität”. (Wallner 2016, pp.9-26) The former is the world just given, or in other words, “a cultural as well as natural environment we live in.” Wirklichkeit is, in Wallner’s word, “just the necessarily presupposed world in which our Lebenswelt (environment) and the manifold Realität (realities) produced by different sciences are situated.” It is an object of mastering, not understanding. Realität is our cognitive world and an object of understanding. Thus, he makes a clear distinction between mastering nature (puzzle-solving) and understanding the world (getting knowledge).

The point is that to get knowledge we have to understand our cognitive world. And for understanding we need to integrate contents of information into our own linguistic frame: i.e., to translate it. In the context of scientific activity this is realized by “strangification”: namely, we take a proposition system out of its original framework and put it into another framework. This makes us free in respect to the specific language we are using. By doing this we can notice background information on which a proposition system works, and we can also get an insight into rules implicitly assumed in another science. Thus, “we get out of our scientific skin and become able to grasp the essence of a proposition system.” (http://www.bu.

edu/wcp/Papers/Sci/ScieWall.htm)

In science our cognitive world becomes known to us through construction of micro-worlds. This means that the objects of science (facts, concepts, theoretical entities, etc.) are not given but constructed through complicated scientific and technological activities. With the help of a framework (theories, hypothesis, explanatory principles, etc.) they are arranged and synthesized to give a proposition system in that framework, namely, a micro-world. Our cognitive world is given to us through such activities. It is the sum total of micro-worlds or the sum of all the scientifically structured aspects of Wirklichkeit.

For instance, the concept of atoms in molecules is a proposition system that holds in the framework of organic chemistry. It is one of those concepts (chemical bond, functional group, paired electrons, etc.) that underlie the notion of molecular structure. As is the case with other scientific concepts, this concept is based on various implicit assumptions, but it is by no means easy to tell exactly what they are. Therefore, instead of purifying the concept, we take it out of the original context (i.e., organic chemistry) and put it into a completely different context (e.g., density functional theory). Then, we will find background information about the former and rules implicitly assumed in the latter as is suggested by the following remarks: “One should not expect anything radically new (from the concept of atoms in molecules). […] Try to derive chemical bonding from the Schrödinger wave equation, the

Pauli principle and nothing else, and you will meet difficulties!"; "We are therefore compelled to ask, what is an atom in a molecule? How can we find it in the Schrödinger equation? Alternatively, how can we find it in density-functional theory?" (Parr and Yang 1994, pp.218-222)

Another example is provided by Woolley (Woolley 1978, pp.1073-1078) and Ochiai (Ochiai 2017, pp.197-207) in terms of a molecular shape and structure. By strangifying a molecular shape and structure and examining its compatibility between organic chemistry and quantum mechanics, Woolley concludes that a molecule has no shape when isolated in a stationary state because "a theory of space needs to be based on the evolution in time of interacting micro-systems." Molecular structure makes no appearance in a quantum treatment of molecules starting from first principles because the configuration space used in quantum theory is an abstract Hilbert space. Therefore, a quantum mechanical description of real molecules is given by assuming molecular structure and describing the situation in terms of a model time-independent Schrödinger equation by making use of the Born-Oppenheimer approximation. Molecular structure is taken as an ingenious model for describing molecular behavior in multi-molecular systems with strong interactions between molecules. Quantum mechanical calculations are likely to reveal spatial relationships between particles, but unlikely to derive structure. It is the subject who will find the meaning in structure in relation to the world of possible experience.

Understanding reality is only possible through construction of micro-worlds. To paraphrase it in terms of our problem, it is our conception of molecular structure that should be taken to be “Realität.” By contrast “Wirklichkeit” is the object of technical manipulation. We manipulate molecules and understand what they are through construction of various concepts and theoretical models. It is those concepts and models that create the contents of our knowledge. It may seem that we have arrived at the same conclusion as have constructive empiricists. But we do not go too far by claiming that the postulates need not be true if they save the phenomena. The process of strangification works as a filter to remove wrong postulates.

It is also through strangification that we can defend constructive realism against relativism. As we noted above “strangification is an effective way of understanding the philosophical as well as scientific grounds on which a proposition system holds. This understanding is essential for a proposition system to be able to claim legitimacy as a scientific claim.” On this premise we can assert that there are as many truths as viewpoints. Thus, “at least insofar as the method of strangification is applied in a proper way, there is no concern about relativism.” (Ochiai 2020, pp.457-465)

We get acquainted with the world outside ourselves through the appearance of an object, not the object itself. And the appearance of an object depends on how we are involved in a phenomenon. We are involved in a phenomenon as an agent essential for that phenomenon to make sense to us. That is to say, our cognition of the world becomes realized as a phenomenon. Making use of advanced instruments and devices, we produce novel phenomena and get to know the world we live in better than before.

CHAPTER 7

APPEARANCES, PHENOMENA AND REALITY

Kant says we cannot cognize objects as they might exist in themselves but only insofar as they appear to us in certain phenomena. Then, how does a phenomenon become cognized as an appearance? In other words, how is objective reality existing independently of the human mind transformed into what we experience?

We probably see the world as it is structured by ourselves based on our experience. To put it another way what we see is an affordance in a phenomenal field, of which we are an essential element. What is an affordance? What is a phenomenal field?

1. Is molecular structure real?

There are two things denoted by the term "molecular structure": the first is what we imagine to be molecular structure, the second, what is imagined. Since the molecule exists beyond the bounds of the senses, the latter is, if it exists at all, inaccessible to us in direct experience. Therefore, we talk about the former assuming that it represents the latter. What we imagine to be molecular structure consists of atoms and bonds. Despite its practical adequacy having been illustrated in organic synthesis (see, for example, Corey and Cheng 1989), its theoretical adequacy is not without disputes. For instance, quantum mechanical treatments of the molecule show that electrons in the molecule are not localized in bonds but delocalized over the entire space. (Dewar 1969, pp.140-143) Although there have been several attempts to prove the validity of the concept of atoms in molecules, these have disadvantages as well as advantages. For instance, Bader was able to derive atoms in a molecule by his ingenious mathematical method, but the overlapping of electron densities between atoms is forbidden, transferability is limited, and chemical bonds disappear into thin air. (Bader 2003; Parr and Yang 1994, pp. 216-238 and references cited therein) To what extent and in what sense can we take molecular structure to be real? The arguments in this chapter aim to answer these questions by relying on the concepts of affordances and phenomenal fields, which enable us to see molecular structure and quantum mechanical aspects of molecules as different outcomes of one and the same object. "Molecular structure is one of the dispositional attributes of a complex that includes a chemist who is engaged in organic synthesis." (Most of the arguments in sections 2 to 5 are based on Ochiai 2020, pp.77-86.)

2. Mereological fallacies

Since the molecule is inaccessible to immediate observation, our knowledge of the molecule is not only indirect but also likely to be imperfect. Both the classical and quantum mechanical concepts of the molecule should be seen as possible representations of what we take molecules to be. Therefore, we must not arbitrarily reject one or the other without considering the context in which each concept makes sense.

Although we are accustomed to separate a matter and the context in which it is involved, this way of thinking is neither logically necessary nor inevitable. On the contrary, it is unique to the Cartesian way of thinking, which assumes that the subject (cogito) is independent of the object (the external world). As is pointed out by Primas, "since the Cartesian way of thinking constitutes the basic structural pattern of scientific experience, every scientific theory mediates between a contemplating subject and the external world. We therefore have to consider two mapping processes; that is, (i) a mapping of the external world into the formal framework of a theory, and (ii) a mapping of the formal framework of a theory into certain psychic structures of the subject. In other words, mapping must involve three classes of referents: that is, objects, abstractions, and minds." (Primas 1983, p.18) Unlike the Omnipotent, human beings have bodies existing in the material world, so that the mediation function of theories cannot escape being influenced in various ways by individual circumstances.

Scientific theories should be evaluated not merely by their outcomes, but also taking account of the individual context in which they are derived. It is quite natural that Niels Bohr says the following: “Evidence obtained under different experimental conditions cannot be comprehended within a single picture, but must be regarded as complementary in the sense that only the totality of the phenomena exhausts the possible information about the objects.” (Quoted in Primas 1983, p.31)

In fact, submicroscopic entities such as electrons often give rise to not only a single perception but also to various ones depending on the contexts in which observations are performed. Therefore, the properties of these entities should be noted by taking all the possible perceptions into consideration (see, for example, the particle-wave duality of an electron). Otherwise, we are likely to commit mereological fallacies, the fallacies originating from mistaking a whole/part relationship. For instance, “we can say a man thinks, but cannot say the brain thinks because the brain is a part of a man and cannot be the subject.” (Bennet and Hacker 2003, p.73) That is, “the brain thinks” is an example of a mereological fallacy. “It is not the mind that thinks, any more than it is the brain. It is a human being that thinks.” Likewise, we are liable to commit mereological fallacies by referring to the attributes of submicroscopic entities based on some rather than all, of the affordances.

"The brain thinks" is a typical example of a misconception about the relation between the mind and matter. This idea, the Cartesian mind-body dualism, is derived from a misinterpretation of the Aristotelian concept of primary substance. A primary substance is "an individual thing of a given kind" such as Socrates. "Just as we cannot separate what Socrates is thinking about from Socrates himself, or Socrates from his appearance, for example, being snub-nosed, neither can we separate individual things and their properties." (Hacker 2010, p.31) Descartes mistook this concept in two ways: he took the mind and matter as two kinds of substances and took them as separable. Actually, "they are things which should be classified as sempiternal, and thus distinct in category from substances." Locke exacerbated this mistake by defining a substance as "something that possesses properties but is distinct from them." (For details, see Buchdahl 1969, pp.215-23) We will investigate this conception in some detail below in relation to the argument about chemical elements. To put things in a proper categorial framework, 1) neither minds nor bodies exist independently of human beings, and 2) bodies are no more bearers of minds than primary substances are bearers of properties. Since we are very liable to commit mereological fallacies, we need conceptual devices which make us aware of the whole picture of circumstances in which our cognition of the world arises.

3. Affordances

Since Gibson introduced the concept of the affordance into psychology in the 1950s, it has spread natural as well as social sciences. Gibson's basic idea is that we do not perceive a thing in general, but as an instrument for action: e.g., a knife affords cutting and a floor affords walking to people while a lake does not. As is suggested by these examples, this concept seems to be applicable to chemistry. Actually, it was not until the 1980's that it was first introduced into chemistry by Harré (see, for instance, Harré 2014, pp.77-91; Harré and Llored 2018, pp.167-186 and references cited therein).

Affordances are context-sensitive dispositional attributes of {agent-material world} complexes. Whether the agents are human beings or not, it is an agent-material world complex that has an affordance, so that "polar bear-walking" is an affordance of a local "polar bear-ice" system, but not of an "elk-ice" system. What the "polar bear-ice" system affords is not available to an elk.

To be more specific with regard to chemistry, chemical facts are not attributes of an independent world measured by means of instruments, but the dispositional properties of a complex such as {experimenter, devices, methods, chemicals, surroundings}. This means that the usefulness of experimental methods in science depends on thinking and acting within a certain kind of reality. A variety of historical episodes illustrate this. The optical resolution of racemic mixture of paratartrate by Pasteur is one of them. Legend has it that “Pasteur separated the racemic mixture of sodium-ammonium paratartrate by hand while looking through a magnifying glass. This was possible because each isomer of the mixture happened to have a distinct crystalline form, one displaying microscopic hemihedral facets on its right edge, the other on its left. It was lucky that he did a series of experiments in a cool environment in which paratartrate crystalizes into two distinct crystalline forms. If it had been above 28 degrees centigrade, both isomers would have crystalized together.” (Summarized and quoted from Geison 1995, pp.53-89) It is impossible to abstract the substance from the operative framework in which it is stored or used.

Another example is the simultaneous discovery of the tetrahedron by van ’t Hoff and Le Bel in 1874. While both scientists seem to have arrived at the same idea, what they achieved differs greatly in terms of affordances. Although van ’t Hoff focused on the relation between the asymmetric carbon atom and optical activity, Le bel directed his attention to the relation between the molecular type and optical activity. Le Bel’s study is an extension of traditional French crystallography since Pasteur, who maintained that “optical activity is the primary indicator of asymmetry at the molecular level.” (Ramberg 200, p.64)

The concept of the affordance seems to be rooted in the belief that the final arbiter of truth should have empirical grounds. We can make sure of the truth or falsehood of whatever is placed in concrete circumstances. This is the reason why we read an experimental section in an article with great care. (In contrast, transcendental ideas—such as the omnipotence of God—cannot be realized as affordances, for they have no application within the bounds of the senses.)

The concept of the affordance reminds us of the Aristotelian concept of first actuality. (Bennet and Hacker 2003, p.14) For instance, the first actuality of an axe is its power to chop wood inasmuch as its constituent matter has been appropriately fashioned into blade and handle. The form of an axe becomes actualized in matter appropriately fashioned into it. Likewise, chemical properties such as acid and base become actualized in terms of a {chemicals-surroundings} complex.

We should evaluate any chemical concept or theory as an affordance that becomes realized in a particular context in which an {agent-material world} complex is placed. Given this perspective, molecular structure may be the affordance of a complex that includes chemists who are engaged in organic synthesis, whereas a quantum mechanical molecule may be one of the possible affordances of a complex that includes quantum chemists who study electronic states of the molecule.

The intention as well as the ability of an agent to do something is an essential component of a complex that is responsible for the affordances of an agent. This suggests that the concept of the affordance may be compatible with Kant's theory of knowledge. Kant says the following: "If we call the receptivity of our mind to receive representations insofar as it is affected in some way sensibility, then on the contrary the faculty for bringing forth representations itself, or the spontaneity of cognition, is the understanding. […] Without sensibility no object would be given to us, and without understanding none would be thought. Thoughts without content are empty, intuitions without concepts are blind.” (Kant 2018, A51)

In order to understand this claim, the following two paragraphs, i.e., those in Bxxvi and A369, are worth noting both as the presuppositions and complements. That is, “it is proved that space and time are only forms of sensible intuition, and therefore only conditions of the existence of the things as appearances, further that we have no concepts of the understanding and hence no elements for the cognition of things except insofar as an intuition can be given corresponding to these concepts, consequently that we can have cognition of no object as a thing in itself, but only insofar as it is an object of sensible intuition, i.e., as an appearance; from which follows the limitation of all even possible speculative cognition of reason to mere objects of experience.” (ibid. idem, Bxxvi) From this it is evident that Kant’s theory of knowledge should be labeled as idealism, rather than constructionism, which does Kant explicate. “By idealist, therefore, one must understand not someone who denies the existence of external objects of sense, but rather someone who only does not admit that it is cognized through immediate perception and infers from this that we can never be fully certain of their reality from any possible experience.” (ibid. idem, A369)

Affordances are the context-sensitive dispositional attributes of {agent-material world} complexes. This means that the perception of affordances is “appearance” in Kant’s terminology. If so, we can say that a phenomenon becomes actualized as an affordance in a particular phenomenal field, as we shall argue in the next section.

4. Phenomenal fields

As we saw in the previous chapters, critical realists classify the world into three ontological domains: the empirical domain (i.e., the world that appears to us), the actual domain (where things are happening whether or not they are experienced), and the real domain (which has powers to make things happen). (Bhaskar 2008, p.56) Since the actual and real domains are not transparent to us, we have to do experiments to know what they are like. This ontological structure of the world is basically in accord with that of Kant. Actually, he writes that we cannot know an object as it might exist in itself but only insofar as it appears to us in a certain phenomenon. (Kant 2018, B295-325) A question worth careful consideration is in what sense a phenomenon is actual and in what manner it appears to us. We claim the following: as is shown in Fig. 7-1, physical matter falls into a phenomenal field and gives birth to a phenomenon just as a stone thrown into water makes waves around it. Physical matter is noumenal unless it gives birth to a phenomenon which is actual and the object of experience. Because we too take part in making phenomena, phenomena are accessible to us. That is to say, "phenomena are objects of experience only insofar as they appear to us in space and time and in accordance with the categories." (ibid. idem, B306; Hall et al. 2010, p.221) Phenomena belong to the actual domain. It is appearances, i.e., the perception of affordances, or in other words, the perception of phenomena actualized in pertinent phenomenal fields, that belong to the empirical domain. This is the reason why dispositional properties such as fragility are not observable. Given that the fragility of a wineglass is actual as a phenomenon, we cannot perceive it as it is because, as soon as we perceive the phenomenon, the phenomenon of our perceiving a wineglass causes a change in the original phenomenon, and different phenomena such as the breaking of the wineglass ensue. This is a logical consequence of the fact that we are embedded in phenomena as an agent.

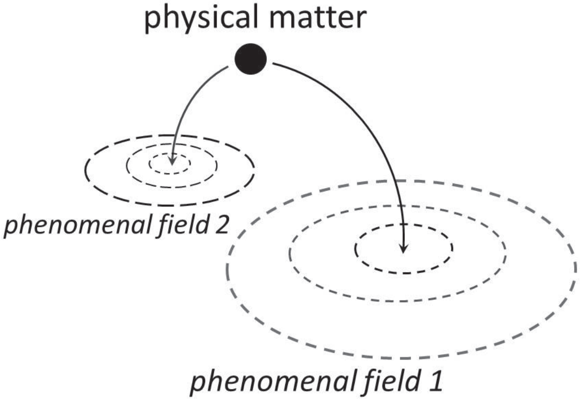

Fig. 7-1 Physical matter becomes actualized in phenomenal fields

What we see depends on how we are involved in a phenomenon. However, we habitually fail to remember this fact in everyday frames of mind and particularly in our scientific frame of mind. On the contrary, "we treat the world and the things and happenings in it as independently existing. That is, we focus on their relationships to one another and ignore the fact that they all alike stand to us as pegs upon which we are hooking our interests, attentions, queries, emotions, decisions and volitions. They are constituents of our variegated cognitive-cum-volitional-cum-emotional experiences." (Ryle 2001, pp.219-20)

Then, what is a phenomenal field? "Phenomenal field" is another expression for a particular context in which an {agent-material world} complex is situated. It is a conceptual device to schematize the contextual aspect of an affordance.

Emphasis is put on the relation between an agent's intention and the material world. Since material objects exist independently of the human mind, they remain potentially possible unless they somehow meet our consciousness. Material objects become realized for us as phenomena only insofar as they come in contact with us in phenomenal fields.

In a scientific investigation we take various approaches depending on our aims, our expertise and the material conditions under which research programs are performed. Various approaches, or in other words, different ways of cognizing the material world, are represented by different phenomenal fields. With this conceptual device we can realize that our cognitive activities, of which Kant's theory of knowledge serves as a guiding principle, are included in affordances as an essential constituent. The phenomenal field serves as a link between affordances and Kant's theory of knowledge, by which alone affordances are realized as dispositional attributes of {agent-material world} complexes.

The concept of the phenomenal field draws on the idea of "Fudo", which was first introduced by Japanese philosopher Tetsuro Watsuji in his famous book *Fudo* (1938). (Fudo is a Japanese word that consists of two Chinese characters: one denotes wind and the other denotes earth.) The phenomena of Fudo consist in cultural activities of human beings, the essence of which is biological adaptation to the natural environments specific to their lands. It was lucky for me that I had a chance to discuss the concept of Fudo and its implications for the philosophy of science with Augustin Berque at the Paris conference of the International Society for the Philosophy of Chemistry (ISPC) in 2017.

I would like to make one more comment about phenomenal fields: more often than not, philosophical questions become easy to tackle by drawing an analogy with things and events happening around us. To put it another way, it is by no means easy to figure out concepts that have no parallel in an empirical world. Hence Plato made use of the so-called "Allegory of the Cave" in order to explain his conception of Idea. He likens people who do not see real existence to prisoners chained in a cave. The prisoners cannot see anything but the wall of the cave. Behind them burns a fire. Puppeteers are between the prisoners and the fire. The puppeteers hold up puppets, which cast shadows on the wall. The prisoners unable to see the puppets—the real objects—take these shadows as real. Therefore, it is said, people who can see nothing but a phenomenal world are prisoners in Plato's cave. I hope the concept of phenomenal fields sheds light on the way we relate to the world.

Let us take the particle-wave duality of an electron as an example. The particle-wave duality can be taken as a pair of affordances linked to distinct world-apparatus set-ups. That is, when an electron falls into a phenomenal field which is suited to observing a diffraction phenomenon, we will see the wave character of electrons as one of its aspects. On the other hand, when electrons are studied in experimental set-ups suited to observing particle character, we will see phenomena showing the particle character of electrons. Being realized in different phenomenal fields, the particle-wave duality is not a contradiction but a pair of affordances.

In relation to the present argument the so-called Rubin's vase attracts our interest. It is a two-dimensional form in black and white. Depending on what appears to be a figure, the shape perceived by the viewer changes: a white vase on a black ground or the silhouette of two men facing each other. The reason why such illusory phenomena appear is that our perceptual experience is characterized by the shaping effect of the common border of the fields, with either black or white operating more strongly than the other. What we see depends on sensibility, understanding, what we intend to see or something else. It is phenomenal fields that actualize phenomena to give affordances.

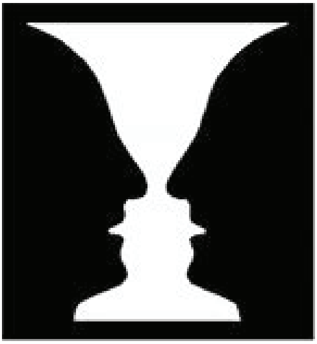

Fig. 7-2 Rubin's vase

In science as well as everyday life it often happens that one and the same object gives birth to various phenomena. The reason why this happens is that it is phenomenal fields that actualize phenomena. Let us take chemical elements as another example. We do not know chemical elements as they are in themselves but observe their properties as either simple substances or in compounds. In either case, material properties are determined not only by the attributes of the constituent elements but also by the conditions under which they are combined. We cannot imagine the properties of sodium chloride from the properties of metallic sodium and gaseous chlorine. Atoms in compounds are no longer the same as those isolated in atomic states. In addition, it may be a mistake to apply concepts of material properties to submicroscopic entities or vice versa. For instance, we can talk about the heat of reaction of chemical compounds, but cannot conceive of the heat of a single molecule, because heat is a statistical concept. In order to argue about heat we need a phenomenal field consisting of statistical amounts of molecules. Likewise, we need a proper phenomenal field that provides a convincing explanation for the relationship between substances and their properties.

5. Implications of affordances in science

We see different aspects of one and the same object depending on the conditions under which it and a subject are placed. This is a simple fact familiar to us not only in everyday life but also in scientific activities. Primas says in the argument about quantum mechanical behaviors of electrons that “each viewpoint creates its own reality.” (Primas 1983, p.30) While quantum physicists performing quantum mechanical calculations of the molecule see molecular orbitals delocalized over the entire space, organic chemists doing chemical synthesis conceive of molecular structure from information obtained during experiments. If what a physicist takes molecules to be is at odds with what a chemist takes them to be, it does not necessarily follow that one of them is mistaken. The number of possible affordances may not be boundless, however. It depends on the nature of an {agent-material world} complex, just like the number of surfaces is inherent to a polyhedron.

We cannot cognize material objects as they might exist in themselves. What is accessible to us is phenomena which become actualized as affordances in particular phenomenal fields, of which human consciousness is an essential part. It is the perception of affordances that is accessible to us in the empirical domain. The view of the world described here cannot be classified into either simple scientific realism or anti-realism. In a sense I agree with van Fraassen, who says that “scientific theories represent how things are, doing so mainly by representing a range of models as candidate representations of the phenomena, that is, observable objects, events, and processes.” (van Fraassen 2010, p.91) However, chemists will not agree with empiricists who reduce the real domain to the empirical domain.

In relation to the arguments described above, the following is also worth noting: van Fraassen writes that "perspectival drawing provides us with a paradigm example of measurement. The process of drawing produces a representation of the drawn objects, which is selectively like those objects; the likeness is at once at a rather high level of abstraction and yet springs to the eye. […] The example is paradigmatic also in that it shows very clearly that the representation shows not what the object is like in itself but what it looks like in that measurement set-up. The user of the utilized measurement instrumentation must express the outcome in a judgment in the form that is how it is *from here*." (ibid. idem, pp.91-92)

Whether or not we agree with the tenets of constructive empiricism, it is true that there are methodological limitations in science. Primas write as follows: "There are no entities in our world which have observable attributes independently of any abstraction. Observable phenomena are created, for instance, by abstracting from some Einstein-Podolsky-Rosen correlations. Using different abstractions, one observes different phenomena. Each abstraction creates its own reality." (Primas 1983, p.253) Does this mean that the truth of the material world is beyond our reach? Although Plato's "Allegory of the Cave" tells us that what we see is a shadow of reality, there must be some truth in a shadow. The shadow is the truth for us: in order to know what it is, we should reconsider the meaning of reality. The constructive realism we noted in Chapter 6 might be a possible solution.

Using various models, we describe possible aspects of molecules which appear to us as affordances. These models do not represent what might exist in the real domain but approximate to what we take molecules to be. Then, what is the real molecule? What is real structure?

Plato thought that reality consists in the idea of an object and is found in the world of Idea. Plato's Idea may look like the Kantian noumenon in the sense that neither of them is the object of sensible intuition. In fact Kant, who was an empirical realist, never took noumena to be real. If Plato is right, the ideal gas (or perfect gas) is real and the real gas is not real but actual. If Plato had been a chemist, he would have seen how inconvenient his ideal is. Actually, he was the last person to be a chemist. Chemists do not see any reality in what is nothing but a paper-and-pencil work.

Critical realists admit the objective existence of reality which is inaccessible to us in direct experience. The real domain has the power to make things happen. When we argue about the reaction mechanism, for instance, our mind's eye is focused on this domain. Given critical realists' ontological map, the answer to "what is the real molecule?" will be "what might exist in the real domain." Then, what is real structure? Molecules show a variety of qualities and properties, some of which are relevant to what we assume to be molecular structure. Probably, the truth is that the image of molecules has been so structured as to represent what we have experienced in organic chemistry, which needs the concept of structure.

6. Molecular structure and dispositions

Things have various qualities and properties: some are overt, others are covert; some are necessary, others are contingent. For instance, things are distinguished from one another by their shapes and structures: shapes and structures are necessary to individual things. They are overt and actual as well. They stand in contrast with properties such as fragility. A wineglass is fragile and it may shatter on the floor. But it may not shatter at all if kept in safety. Fragility is covert and becomes actualized when conditions are met. Solubility, inflammability, digestibility, etc., are covert properties similar to fragility. Like fragility, once actualized they are lost forever. By contrast, the tensile strength of an iron rod, the brittleness of an iron girder, the tolerance of stainless steel to acids, etc., though being covert like fragility, are not lost as long as objects exist.

The texture of silk seems to be distinct from the properties mentioned above. Silk manifests its texture in the eyes of a well-trained expert, whereas it does not to a lay person. It is a property contingent on the way it is observed, or in other words, a property whose manifestation depends on the condition of the subject. Another example of this kind is tasting wine. A sommelier with a sophisticated sense of taste, is able to appreciate a delicate flavor of wine which is not detectible to those who do not drink. (In relation to the present argument, it is worth noting that the ancient Greeks did not know the ocean as blue. As Homer described, they saw the ocean as black, or dark red like wine.)

Fragility, solubility and the like are called "dispositional properties" or just "dispositions". They are latent and seem to "lurk in a mysterious realm intermediate between potentiality and actuality." (Mumford 2008, p.4) Dispositional properties are posited as "explanations of past events and as the grounds for the prediction of future events." But the role they play in the production of events is not clear. Dispositional properties are distinguished from "categorical properties" such as shape and structure. Molecular structure, however, does not seem to fit well within this system of classification. Unlike the shape of an armchair or the structure of an engine, for instance, it is not accessible to us in direct experience. Our knowledge of molecular structure is indirect and based on theoretical models. Rather, molecular structure has similarities to dispositional properties. Molecular structure manifests itself if conditions are met. In addition, no current manifestation is necessary for it to be truthfully ascribed to things that allegedly possess this property. However, in contrast to fragility that would be lost once it becomes actualized, the molecule does not loose structure as long as it exists.

Molecular structure also resembles the texture of silk appreciated by silk experts and a delicate wine taste enjoyed by wine lovers. As the particular touch of a silk expert reveals silk's texture, the process of designing molecules reveals that molecules have definite structure. Molecular structure seems to be real to those who design molecules but does not to those who do not engage in such business.

There are similarities between dispositional properties and molecular structure. First, particular conditions or stimuli are essential to the manifestation of both such properties; second, a current manifestation is not necessary to ascribe such properties to things in which they are anchored. Molecules manifest their structural features only when they are designed.

(1) Dispositional properties:
    They are covert and unobservable (transcendental); a trigger is necessary for them to be realized; they are liable to a particular change in manifestation, etc.
(2) Silk texture & wine taste:
    They are covert but empirically accessible to a particular subject, of an intentional character, etc.
(3) Molecular structure:
    It is covert and empirically inaccessible, transcendental, amenable to chemical modification, etc.

Do fragility, solubility, brittleness, etc., have any ontological dimension? Take solubility for example. A sugar cube dissolves in water. The way it dissolves is explicable by the interaction between sugar molecules and water. But there are various chemicals that dissolve through a different mechanism. That is to say, what solubility is and how things dissolve should be distinguished.

As we have discussed above, things with dispositional properties are liable to undergo a particular change when a particular condition is realized: for example, when a wineglass manifests its fragility, this wineglass may have been lost together with its fragility. This does not go for a silk texture, for it is not the object (silk) but the condition of the subject (a silk expert) that changes. If mental attributes count as dispositions, the texture of silk appreciated by silk experts may well be included in dispositional properties. Certainly, just as a silk expert is disposed to use her fingers to sense the surface of silk, so too a sommelier is disposed to use her sense of smell to taste wine. If so, it might be better to put the subject and the object together and call them a “potentiality”, though it is nothing but an affordance.

7. Affordances, dispositions and possible worlds

An iron rod would not manifest its strength against tension without a chance to be strongly pulled toward both ends. Observed tensile strength is an affordance of a complex consisting of an experimenter, an instrument to measure tensile strength and an iron rod placed in a particular environment in which tensile strength becomes actualized. Silk would not manifest its texture without a characteristic surface or a chance to be touched by a silk expert. A silk texture is an affordance of a complex composed of a silk fabric and a silk expert placed in a particular environment in which silk texture is appreciated. A wineglass would not shatter if it has neither alleged fragility nor a chance to be dropped or accidentally struck. The actualized breaking of a wineglass is taken as an affordance.

The way physical matter manifests a dispositional property is schematically shown in Fig. 7-3. Phenomenal fields represent particular contexts in which physical matter becomes actualized as various affordances. A disposition can be represented by a possible fall of an object in a particular phenomenal field. Though a wineglass is regarded as fragile compared with a beer mug, it might be otherwise in other circumstances: for instance, in a phenomenal field in which there is nothing else but a wineglass and a piece of thin ice. This thought experiment suggests that the degree of a disposition is not intrinsic to an object but relative to conditions. This does not hold for categorical properties such as shapes and structure.

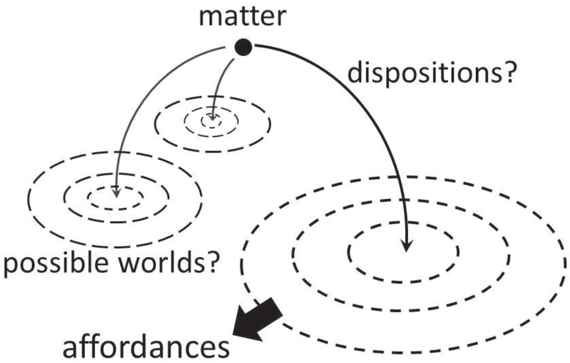

Fig. 7-3 Dispositions, possible worlds and phenomenal fields

There being possibilities is the same as there being as many possible worlds. Possible worlds represent all the possible scenarios we can imagine. "That a certain situation is possible is, in the language of possible-worlds theorist, that there is a world (a scenario) in which that situation is realized." (Summarized and quoted from Borghini 2016, p.87) As there is a world in which a wineglass shatters on the floor, there is a world in which it is kept in safety for centuries.

There is a possibility that a wineglass shatters because a wineglass is fragile or because there is at least one possible world in which the breaking of a wine glass happens. The scheme shown in Fig. 7-3 shows the relation between dispositions, possible worlds and affordances. It provides a meta-cognition over (the Humean) possible-world theorist arguments and (the anti-Humean) dispositionalist arguments, and possibly unifies them. It reveals that such latent properties as fragility and solubility are circumstantial, so that we have to take environment into consideration when we think about them. Otherwise, we might impose transcendental ideas upon ourselves as objective and take illusory appearances as real.

In saying that a wineglass is fragile, "we are not saying something about what it is actually doing, but it would or could do." (Vetter 2015, p.33) Then, how about talking about molecular structure? What we assume to be molecular structure enables transdiction across the boundaries of possible experience. What structure we regard as rational depends on what chemical phenomena we observe. Molecular structure is based on phenomenal fields in which it is realized as affordances.

8. The way theories become reality

Provided that the world is an objective reality existing independently of the human mind, we cannot cognize it unless it comes in contact with us in a phenomenal field. In other words, objective existence becomes a true object of cognition and reality for us only insofar as we are conscious of it. After all it is affordances that we take to be reality. If that is the case, theoretical entities that give birth to affordances count as real.

This is the reason why experimental confirmation of theoretical entities matters. The existence of submicroscopic entities such as atoms and molecules would not have been proved without Perrin's ingenious experimental work about

Brownian motion. It was his experiment that lent credit to Einstein's equation that reveals the stochastic nature of Brownian motion. Likewise, it was not until Millikan measured the elementary charge that the existence of the electron was proved. In order to demonstrate theoretical entities an experimenter creates phenomena in which theoretical entities play decisive roles. Demonstration experiments connect theoretical entities with known facts and incorporate them in the existing system of knowledge: that is, experiments make theoretical entities reality for us. (In this sense Wallner's micro-world, which we noted in Chapter 6 is almost the same as affordance.)

Remarkable achievements in organic synthesis over the last fifty years or so have made our knowledge of molecular structure more and more precise, and plausible to the extent that our knowledge of organic chemistry does not make sense without it. On the other hand, quantum mechanics has cast doubt on the concept of molecular structure. Quantum mechanical calculations on the electronic states of the molecule have undermined the notion that molecules have structure like the tangible objects around us. One and the same object has given birth to different affordances which are at odds with one another.

Various theories and concepts in chemistry have developed rather independently, as natural languages did. Chemistry is a mosaic of theories and concepts that have a variety of origins.

We say, for instance, that chemical substances consist of chemical elements. In fact, it is atoms that combine to form molecules. We say that there are atoms in molecules, whereas it is nuclei that exist in molecules. This is not a flaw but the fertility of chemistry, just as the existence of a variety of languages contributes to the cultural diversity of the world. There are as many realities as viewpoints.

CHAPTER 8

BEYOND CHEMISTRY

Dispositions are ethereal: we do not observe fragility, but rather the breaking of a wineglass; we do not observe solubility, but the dissolution of a sugar-cube. Are dispositions real? If so, why are they always latent? We seek to provide a clear insight into this long-standing problem.

Our approach is based on the comparison of various dispositional properties. In particular, the similarities as well as dissimilarities between physical dispositions (such as fragility) and handedness (enantiomorphism) are investigated in detail. The basis of the whole argument is Kant’s theory of knowledge.

Since chemistry is a practical science that engages in the transformation of matter, arguments based on chemistry are likely to provide a different point of view from familiar metaphysical arguments and are likely to shed light on the ontological grounds of dispositions.

1. Chemistry creates the world

The Japanese word for “human being” consists of two Chinese characters: one means “man” and the other “between.” The implication is that we cannot live alone. We become humans through interactions with others. To put it another way, we cannot see what we are by looking into ourselves, but by looking around us.

I am a chemist, and a philosopher of chemistry as well. I studied organic chemistry in my twenties and worked for the world's biggest pharmaceutical company as a research scientist. During those years I became acquainted with various chemists. Some of them were excellent as experimental scientists, others, like myself, not so much. I could not see a future there. I turned to biology and studied chemical interactions between plants and soil bacteria. Secondary metabolites such as caffeic acid deactivate certain kinds of soil bacteria that reduce the nitrates in soil to nitrogen gas. Deactivated bacteria exhale greenhouse gases such as nitrous oxide instead of nitrogen gas. Since caffeic acid becomes soluble due to the action of acid rain, the latter accelerates global warming. These studies made me realize how subtle and important the terrestrial circulation of chemical elements is for keeping our planet habitable.

My graduate school days, when I was in my thirties, were more rewarding than those of my twenties. The research group I was in consisted of biologists and geologists, who were studying the biological as well as geological evolution that had made the present global environment.

One geologist often said, "it happened recently."

I asked him how recent it was.

He replied, "maybe, one or two hundred thousand years ago."

"Oh, yeah? How recent it was!"

Since chemical reactions proceed in seconds, in minutes or in hours, the notion of hundreds of thousands or tens of millions of years was foreign to me. But, gradually, I became able to see things through the other's eyes, which made me rediscover chemistry. Then, I read Kant. The *Critique of Pure Reason* made a deep impression on me. It says that we cannot cognize objects as they might exist but only insofar as they appear to us spatiotemporally, and in accordance with our concept of them. That may be true of the molecule. Since then I had been a disciple of Kant.

I was also interested in the history of chemistry and read a lot of literature concerning how and in what contexts chemical concepts were constructed. Kant and chemistry combined in my mind. I felt that molecular structure was no longer just given but what should be conceived in a particular context.

Meanwhile, I happened to find a book about the philosophy of chemistry on the Internet. I bought it and read it through. My eyes became glued to the following sentence: "Although chemical synthesis is one of the most characteristic features that distinguish chemistry from other sciences, philosophers have paid virtually no attention to it since the nineteenth century interest in chemism." (van Brakel 2000, p.20)

"Who can do that?" I shouted in my mind. "Why, I can!"

This short story about me illustrates how we become ourselves. Chance and necessary encounters with people and writings of not only the current but also of past centuries, of not only domestic but also of foreign origin, shape our thoughts and make ourselves. Everything acts on everything else. Nothing takes shape by itself. It is chemistry that creates the world.

"The emergence from the night of nonbeing, the interconnection and fusion of generation and perishing of beings which mutually, in their binding interrelation, make room for each other and destroy each other in turn, this primordial happening, primordial movement, and primordial process are the way in which the world emerges." (Patocka 2018, p.8)

Nothing emerges from itself, of course. A disposition, if it exists at all, is no exception.

2. A mysterious realm between potentiality and actuality

A right hand is right and a left one is left from any point of view. It is too obvious to be questioned. But if there is only a single hand in a universe, what makes it either left or right? This is the question Kant posed about handedness. He wrote in the *Prolegomena* as follows: "the left hand cannot, after all, be enclosed within the same boundaries as the right (they cannot be made congruent), despite all reciprocal equality and similarity; one hand's glove cannot be used on the other. What then is the solution? These objects are surely not representations of things as they are in themselves, and as the pure understanding would cognize them; rather, they are sensory intuitions, i.e., appearances, whose possibility rests on the relation of certain things unknown in themselves, to something else, namely, our sensibility." "We can therefore make the difference between similar and equal but nonetheless incongruent things (e.g., oppositely spiraled snails) intelligible through no concept alone, but only through the relation to right-hand and left-hand, which refers immediately to intuition." (Kant 2004, 4: 286)

The argument concerning a single hand in a universe is interesting not only in its own right but also because it reminds us of dispositions such as fragility, solubility, inflammability, brittleness and the like. Just as we know nothing about what makes a right hand right or a left one left, we know nothing about what makes a disposition what it is. Nobody can tell what a disposition is, because once it manifests itself, it is lost forever. A dissolved sugar cube no longer has solubility. We take it for granted that a wineglass is fragile because of its fragility; a sugar cube dissolves in hot water because of its solubility. But we do not know whether dispositions are grounded on a firm philosophical as well as scientific basis or something as dubious as occult forces.

As we saw in the previous chapter, Harré and Llorde assert that every scientific fact is a contextually sensitive dispositional attribute of an {agent-material world} complex, i.e., an affordance. (Harré and Llored 2018, pp.167-186) Everything that appears to us is situated in a certain context in which we too are situated. If that is the case, is there any context in which a disposition can be made intelligible to us? In fact, dispositions are attributed to a wide variety of things regardless of the context in which those things are situated. For instance, petroleum is inflammable wherever and however it is stocked. A brave man is supposed to be brave in whatever conditions he may be placed.

In ordinary language dispositions are considered to be the properties of entities to which dispositions are attributed. “Dispositionalism adopts this tendency as its own and explains the meaning of modal sentences of ordinary language in terms of the dispositions of entities in the actual world.” (Borghini 2016, p.164) But we do not know whether dispositional properties are enough to explain the meaning of modal sentences. Does it make sense to say that a brave man behaves bravely because of his bravery? Is it not bravery but a particular situation that makes one behave bravely? Or is it not that “dispositional vocabulary has value only insofar as it refers to past actual and future possible events?” (Mumford 2008, p.v) A person who behaved bravely in the past is expected to behave bravely in the future because he is supposed to have bravery. In spite of their familiarity, the true nature of dispositions is hidden behind a thick veil.

3. Physical dispositions, their characteristics and likely explanations

As we have discussed above, certain mental concepts such as bravery are traditionally taken as the attributions of dispositions rather than the descriptions of present mental occurrences. For instance, the belief that eight eights are sixty-four is taken as dispositional because this kind of belief has typical manifestations (in verbal behavior) and typical stimuli (in questions), and can be truthfully ascribed even though there is no current manifestation. (Mumford 2008, p.7) But we will confine the arguments herein to physical dispositions such as fragility for ease of comparison with chemical properties.

Dispositions are properties with a particular characteristic: “to each disposition there corresponds a typical manifestation, but a dispositional ascription can be true even if no manifestation occurs.” (ibid. idem, p.5) A wineglass can be kept safely for centuries without manifesting its fragility; on the other hand, when it shatters due to a careless knock or an accidental fall, fragility is already lost. The same is true of the solubility of a sugar cube. Solubility disappears in hot water along with the dissolving sugar cube. Where does it reside, if it really exists? Why is it hidden from our senses? “Dispositions are considered ethereal: properties that somehow are not always manifest but which seem to lurk in a mysterious realm intermediate between potentiality and actuality.” (ibid. idem, p.4)

Because of this feature, dispositions are contrasted with categorical properties such as shape and structure, which are observable and always active, as it were. But the distinction between dispositional and categorical properties is far from lucid. The term “categorical” means unconditional and, if so, dispositions are categorical in the very sense that their ascriptions are true of their possessors unconditionally. “What is conditional (and potential) is not disposition itself but the manifestation of disposition.” “Dispositionalists claim that it is the breaking of a wineglass that is potential; the fragility of a wineglass is actual.” (ibid. idem, p.21) A wineglass put on the center of a large table is as fragile as one put on the edge of a small table. As we will discuss shortly, the manifestation of handedness is conditional: the notion of the right hand and the left one makes sense only insofar as both hands are present, whereas handedness itself seems to be possessed actually by each hand.

Moreover, it is not certain that the dispositional-categorical distinction is “anything more than a distinction in the way we talk about instantiated properties or states in the world.” (ibid. idem, p.195) Mumford maintains that “in order to be consistent in our claims about causation we can allow only one type of property or state to inhabit the world, but whether such properties are dispositional or categorical is a question we cannot answer.” (ibid. idem, p.195) All we can say is “whether or not dispositional and categorical concepts are applicable.” His claim is based on the fundamental idea that there are two senses of ontology that are relevant when we are considering the constitution of the world: the first concerns “how the world really is” and the second consists in “how we think the world is.” (ibid. idem, p.194) He accepts the division between the world and our conceptualization of it. “Whatever the world is actually like is unaffected by the way we conceptualize, describe, and think about it.” This view is consistent with the modest claim of realism (realism consists in the combination of a modest claim and a presumptuous one). “The modest claim is that there is subject-independent reality; the presumptuous one is that we are capable of describing that reality accurately.” (ibid. idem, p.192)

There are dispositional properties distinct in some respects from the physical dispositions described above. They are, for instance, the texture of silk and the taste of wine. As we have argued in Chapter 7, either of them manifests itself only through the action of particular stimuli, e.g., the special touch of a silk expert or the tasting skill of a sommelier. The rich taste of wine does not appear to those who do not drink, but only to those who know how to perceive it. Otherwise, there would be no need to improve one’s skill as a silk expert or a sommelier. But subject’s skill is not all that is needed to appreciate the dispositional property of the object. There must be something inherent to an object—silk is in any case silk, different from cotton. Some philosophers call a cape’s redness that provokes a bull a first-order property and the cape's provocativeness a second-order property. Mumford calls the latter "a judgement-dependent disposition" in contrast to "a non-judgement-dependent" property such as solubility and inflammability. (ibid. idem, p.204) We are not sure whether the texture of silk and the taste of wine can be classified as a judgement-dependent disposition.

The peculiarity of dispositions becomes clearer through comparison with well-known chemical properties. The characteristics of both dispositions and chemical properties may be summarized as follows:

C1: Every chemical fact is a context-relative dispositional attribute of an {agent-material world} complex, i.e., an affordance.

C2: As is shown by Kant's argument about the right hand and the left one (or enantiomorphism), chemical properties make sense only in terms of the relation between individual things to which such properties are ascribed. The relation between oxidants and reductants illustrates this.

C3: Chemical entities and their properties can be represented by various kinds of models such as the classical and quantum mechanical models of the molecule, which provide a basis for chemical practices.

These are in marked contrast to the following premises of dispositions (not only physical but also mental dispositions).

D1: Dispositions are unconditional, namely, they are conceived regardless of the conditions under which objects are placed.

D2: Dispositions are not likely to be the object of scientific modelling. This is because models representing things or events inaccessible to immediate observation are made by making an analogy with things and events existing within our experience, which consists in the relations between those things and events.

Kant says that “we cannot cognize objects as they might exist in themselves but only insofar as they appear to us spatiotemporally, and in accordance with our concept of them.” (Kant 2018, Bxxvi; Hall et al 2010, p.3) “The objects of cognition must be given in sensibility via intuition and thought by the understanding through concepts.” (ibid. idem, p.58) It is illegitimate to apply any concept whatsoever to objects beyond the bounds of the senses. (ibid. idem, p.136; A245, 246/B303, 304) Therefore, it is not certain whether or not it is legitimate to apply concepts such as shape and structure to things that exist beyond the boundaries of possible experience. If it is not, we cannot say whether concepts like shape and structure are conditional or unconditional.

Taking these claims into consideration, the reason why dispositions are latent is either that (1) dispositions are transcendental objects, (2) they are actual as phenomena though they are not realized as appearances, (3) they are noumena, or (4) they serve as a regulative principle. In the following arguments we shall examine these possibilities in terms of the five premises mentioned above.

4. Dispositions as transcendental objects

A transcendental object is a reference of objective reality which cannot be intuited by us. Kant says the following: "All representations, as representations, have their objects, and can themselves be objects that can be given to us immediately, and that in them which is immediately related to the object is called intuition. However, these appearances are not things in themselves, but themselves only representations, which in turn have their object, which therefore cannot be further intuited by us, and that may therefore be called the non-empirical, i.e., transcendental object = X." "The pure concept of this transcendental object (which in all of our cognitions is really always one and the same =X) is that which in all of our empirical concepts in general can provide relation to an object, i.e., objective reality. Now this concept cannot contain any determinate intuition at all, and therefore concerns nothing but that unity which must be encountered in a manifold of cognition insofar as it stands in relation to an object. This relation, however, is nothing other than the necessary unity of consciousness, thus also of the synthesis of the manifold through a common function of the mind for combining it in one representation." (Kant 2018, A109-110)

Let us say a careless knock of a wineglass or an accidental fall has smashed it. If other wineglasses, too, suffered similar results due to the action of similar stimuli, we would regard a set of similar stimuli and results as typical of a wineglass. The notion of fragility is, however, not derived directly from the observation of fragile objects. It requires us to make a leap beyond the boundaries of possible experience, i.e., transdiction, which is, as we saw in Chapter 5, defined as "to use data in such a way as not only to be able to move back and forth within experience, but to be able to say something meaningful and true about what lies beyond the boundaries of possible experiences." (Mandelbaum 1966, p.61) It is not certain whether transdiction gives "something meaningful and true," though. Actually, Kant describes in various places in the *Critique of Pure Reason* that the use of transcendental ideas (or concepts of pure reason) without empirical premises inevitably leads us to empty sophisms and results in transcendental illusions, which makes us mistake a subjective representation for an objective cognition. (e.g., Kant 2018, A293-97/B350-54)

Given fragility, it seems rational that a careless knock or an accidental fall brings about the breaking of a wineglass. The notion of fragility unites our various experiences of fragile objects to one and the same X and synthesizes our cognition of those objects and the related events. That is, the notion of fragility serves as a transcendental object. But we have no practical method for examining what underlies fragility, because it is conceived by transdiction and defined in such a way that it makes sense as it is in itself. This is in marked contrast to handedness. Given a single hand in a universe, we cannot say whether it is left or right. Neither can we say whether handedness is real or not. In such a world handedness would be a transcendental idea. In the presence of a mirror image, however, it is easy to distinguish the right hand from the left one, and hence handedness turns out to be real. Handedness has a material basis that underlies our observation. It is a context-relative dispositional attribute of an {agent-material object} complex, or in a word, an affordance. An affordance is falsifiable in terms of the material condition of an object. This is not the case with fragility.

Let us take molecular structure as another example for comparison. What we assume to be molecular structure is based on the concepts of atoms and bonds in molecules. It unites our experience of chemical practices and synthesizes our cognition of chemical compounds. It is responsible for logically guided chemical synthesis (See, for instance, Corey and Cheng 1989). Whether our notion of molecular structure is adequate or not is falsifiable in terms of what we achieve by relying on this notion. Molecular structure is, therefore, not only a transcendental object but also a representation of the contextually sensitive dispositional attribute of an {agent-material world} complex. (Ochiai, 2020, pp.77-86)

Molecular structure makes sense in relation to chemical practices such as designing molecules. The consistency of the relation is the ground on which to claim the validity of this notion. In general material properties make sense in terms of the relation between individual things to which they are ascribed, as is illustrated by oxidation and reduction, acid and base, electron-donor and accepter, R- and S-configuration, and so on. Such a relation is absent in fragility.

What we cognize as material properties are not the representations of things as they are in themselves but appearances, i.e., the perception of affordances. The basic idea of affordance is, as we have argued in the preceding chapter, that we do not perceive a thing in general but as an instrument for action. For instance, a knife affords cutting to a person who is a butcher. A floor affords walking to people but not to wild animals. Emphasis is put on the context in which an action is performed. Therefore, although we might even say that a wineglass affords breaking, we cannot say that a wineglass affords fragility because there is no context that affords what is merely potential. Fragility is not qualified as a material property.

An object that serves as an instrument for action is likely to be real and a possible object of scientific modelling. Even submicroscopic entities, if they serve as an instrument for action, can be represented with models by making an analogy with things that exist within the bounds of the senses. For instance, certain chemicals act on the human body as medicine. We account for the physiological action at the molecular level by making use of models. To put it another way, something that cannot be the object of scientific modelling may not exist. But, of course, ease of modelling does not prove the existence of theoretical entities, as is shown by many historic episodes. Caloric, a unit of heat, postulated by Sadi Carnot, is an interesting example, among others. (Laidler 2001, pp. 87-93) Fragility cannot be the object of scientific modelling.

Metaphysical supposition cannot be the object of scientific modelling. An example is the ancient idea of atoms, which is contrasted with Dalton's chemical atomism. As was referred to in the previous chapters, the former is without empirical premise and cannot be applied to science. In contrast the latter was applied to practical investigation of scientific problems and gave accounts of the laws of definite proportion and multiple proportions. By assuming a definite weight for atoms of each element Dalton made a link between a world of submicroscopic entities and laboratory work. (For the details, see, for example, Ihde 1984, pp.101-111.) That is to say, Dalton's atoms serve as a scientific model.

These arguments suggest that dispositions are not attributes of material entities but transcendental objects.

5. Dispositions are actual as phenomena

Kant says that "phenomena are the object of experience only insofar as they appear to us in space and time and in accordance with the categories." (Kant 2018, B306) It is possible that something is not the object of experience while actual as a phenomenon, for "there exists a domain that is not transparent to us." (Bhaskar 2008, p.13) Since the actual and real domains are closed off to us forever, we have to do experiments to know what they are like.

For instance, as is shown by the argument of a single hand in a universe, a right hand or a left one seems to be actual as a phenomenon, whereas neither of them can be cognized as right or left by itself. Handedness makes sense only insofar as both hands are present. It is the presence of both hands that makes handedness meaningful. This suggests the reason why enantiomers cannot be distinguished from one another in an abstract Hilbert space. Each enantiomer in a Hilbert space is comparable to a single hand in a universe. If, on the other hand, a universe were real and asymmetric as well, it would provide a context in which a single hand makes sense as a right hand or a left one. Of this possibility we know nothing, though.

Molecules are another example of a thing that is not the object of experience while actual as a phenomenon, for molecules are too small to be the object of experience. This suggests that a disposition, too, is actual as a phenomenon. Given that a disposition is actual as a phenomenon, we can explain the reason why fragility is latent: we cannot perceive fragility as it is because, once we perceive the fragility of a wineglass, the phenomenon of our perceiving fragility brings about a change in the original phenomenon and a different phenomenon such as the breaking of a wineglass ensues. (As we noted in Chapter 7, we are not passive observers of phenomena but essential components of phenomenal fields in which phenomena become realized as appearances. A phenomenal field is another expression of a context in which an {agent-material world} complex is situated. Since material objects exist independently of the human mind, they remain noumenal unless they somehow meet our consciousness. Material objects become realized for us as phenomena only insofar as they come in contact with us in phenomenal fields.)

If the argument above is relevant, fragility may be something like the limit of a change. But the notion of limit is unlikely to be the explanatory principle of material properties. Another problem is that it is not only fragility but also every disposition that we must account for. For example, we must account for both fragility and solubility based on a common explanatory principle. Moreover, it is not mechanism that accounts for what a disposition is.

Another possibility is that a disposition has no phenomenal field in which it becomes realized as an appearance. In comparison with molecules, whose essence is a negative noumenon, i.e., a non-sensible object, a disposition seems to be a positive noumenon that “exists beyond the boundaries of possible experience and independently of the relationship to other things.” (Hall et al. 2010, p.223) Kant says the following: “If by a noumenon we understand a thing insofar as it is not an object of our sensible intuition, because we abstract from the manner of our intuition of it, then this is a noumenon in the negative sense. But if we understand by that an object of a non-sensible intuition, then we assume a special kind of intuition, namely, intellectual intuition, which, however, is not our own, and the possibility of which we cannot understand, and this would be the noumenon in a positive sense." (Kant 2018, B306-307) That is, a positive noumenon can be cognized only by God or a being with a capacity for intellectual intuition, but not by human beings who possess only sensible intuition. Since a positive noumenon has no relation to other things and exists regardless of context, it has neither affordances nor phenomenal fields.

If something is not a mere transcendental idea, it must have a material basis in the actual domain as a phenomenon. Such is the case with molecules. (Something that is real and not actual as a phenomenon cannot be the object of scientific investigation. A possible example is the Omnipotent.) Provided that a disposition is a positive noumenon, it is not actual as a phenomenon, for a positive noumenon is supposed to exist independently of its relationship to other things, while on the other hand, phenomena potentially consist of {agent-material world} complexes. This conclusion is in contradiction with our premise in this section.

6. Dispositions are noumena

The molecule is a negative noumenon and actual as a phenomenon. By contrast a disposition might be a positive noumenon. Dispositions are not merely non-sensible but seem to be independent of other things. Provided that a disposition is a positive noumenon, it is real in the same sense as the Omnipotent being real, for neither is actual as a phenomenon. As long as a disposition is a positive noumenon, it cannot be the object of scientific investigation and it is not necessary to take this into further consideration.

Dispositions are not concerned with practical matters such as how a wineglass is broken or how a sugar-cube dissolves in water. To ask how things are disposed to act as they do is not the same as to ask why things have such dispositions nor to ask what dispositions are. (In contrast molecular structure is concerned with a how-question. What we assume to be molecular structure consists of atoms and bonds, and accounts for how a given type of molecule takes part in a given reaction and consequently, what kind of product is obtained.)

But does a why-question make sense in science at all? What can dispositions account for? (To be sure, without the notion of fragility it is hard to explain why a wineglass is easily broken or damaged. But does it make sense to account for fragility by relying on the notion of fragility? We should ask to what extent and by what mechanism a wineglass is easily broken or damaged.)

It seems that dispositions are more concerned with subjective judgement than with an objective description of the world existing independently of our consciousness. It might be the expression that a wineglass is fragile that invokes the notion of fragility. As we saw, when we say that a cape's redness provokes a bull, instead of saying that the bull rushes at a red cape, dispositions such as redness (a first-order disposition or non-judgement-dependent disposition) and provocativeness (a second-order disposition or judgement-dependent disposition) are invoked. Patocka says that words call our attention to things and through words we orient to them. Words are experienced as something external, something that is not the product of explicit activity; that is why words are so closely associated with things. (Patocka 2018, p.5) The first-order disposition is the material basis or the underlying mechanism of the second-order disposition.

The problems we have to consider are 1) as is pointed out by Mumford, the latter (second-order dispositions) adds no extra causal powers to their possessors over and above those causal powers of the former (first-order dispositions), 2) the former is as vague as the latter in what is really meant and 3) the mechanism of how things happen cannot account for why they happen.

The second point is evident in his claim that "the question whether it is first-order redness that causes the bull to be angry or second-order provocativeness appears to be the very same problem as whether it is a first-order molecular structure that causes sugar to dissolve or its second-order solubility." (Mumford 2008, pp.204-205) Unless the term "molecular structure" refers to chemical interactions between molecules, it would be a black box that associates what is merely conceivable (i.e., solubility) with what is observable (the dissolution of a sugar cube) through some unknown mechanism.

The notion of fragility enables us to explain why a wineglass smashes due to a slight knock that would never cause the breaking of a beer mug. Assuming dispositions is like assuming the absolute space in which true motions are described. In fact, Newton regarded it as an actual object of experience and as a reference frame to determine true motions in the solar system. (Kant 2004, p.xiii) Kant took this to be a transcendental idea and proposed, in *Metaphysical Foundations of Natural Science*, an alternative idea, namely, "the common center of gravity of all matter." (ibid. idem, p.102; the page number of the original text in volume 4 of the Akademie Edition of *Kant's gesammelte Schriften* is 563) This is a surrogate for Newtonian absolute space and an example of a regulative use of transcendental ideas. Although the common center of gravity is practically unattainable, it enables us to determine the true motions of objects in an empirically accessible universe.

7. Dispositions serve as a regulative idea

In view of the argument developed in the preceding section, it may be possible to see dispositions as a regulative idea. As to the regulative idea Kant writes as follows: "I assert: the transcendental ideas are never of constitutive use, so that the concepts of certain objects would thereby be given, and in case one so understands them, they are merely sophistical (dialectical) concepts. On the contrary, however, they have an excellent and indispensably necessary regulative use, namely that of directing the understanding to a certain goal respecting which the lines of direction of all its rules converge at one point, which, although it is only an idea (*focus imaginarius*)—i.e., a point from which the concepts of the understanding do not really proceed, since it lies entirely outside the bounds of possible experience—nonetheless still serves to obtain for these concepts the greatest unity alongside the greatest extension. Now of course it is from this that there arises the deception, as if these lines of direction were shot out from an object lying outside the field of possible empirical cognition (just as objects are seen behind the surface of a mirror); yet this illusion (which can be prevented from deceiving) is nevertheless indispensably necessary if besides the objects before our eyes we want to see those that lie far in the background, i.e., when, in our case, the understanding wants to go beyond every experience (beyond this part of the whole of possible and uttermost extension." (Kant 2018, A645/B673)

In another part of the *Critique of Pure Reason* he also writes as follows: "Now if one can show that although the three kinds of transcendental ideas (psychological, cosmological and theological) cannot be referred directly to any object corresponding to them and to its determination, and nevertheless that all rules of the empirical use of reason under the presupposition of such an object in the idea lead to systematic unity, always extending the cognition of experience but never going contrary to experience, then it is a necessary maxim of reason to proceed in accordance with such ideas. And this is the transcendental deduction of all the ideas of speculative reason, not as constitutive principles for the extension of our cognition to more objects than experience can give, but as regulative principles for the systematic unity of the manifold of empirical cognition in general, through which this cognition, within its proper boundaries, is cultivated and corrected more than could happen without such ideas, through the mere use of the principles of understanding." (ibid. idem, A671/B699)

A disposition may be only "an object in the idea" but serve as a regulative principle by virtue of which systematic unity is brought to our cognition. It is hard to imagine getting along without dispositions. It is just like living in a world in which the use of nouns is forbidden.

In science a why-question must be answered in the framework of affordance, or in other words, in a way that we can specify a context in which an {agent-material world} complex is situated. The question why a wineglass is fragile should not be answered by invoking alleged fragility but by taking into account the chemical constitution of glass, the particular shape of the wineglass, the way it is used, and so on. Why the bull rushes at a red cape should be accounted for by the situation in which the bull and the bullfighter are placed, the physiological as well as physical action of the red cape on the bull, and so on. A disposition is a kind of icon that lets us skip the necessary steps for identifying scientific experience. It is a transcendental idea. Kant says as follows: “there will be syllogisms containing no empirical premises, by means of which we can infer from something with which we are acquainted to something of which we have no concept, and yet to which we nevertheless, by an unavoidable illusion, give objective reality. In respect of their result, such inferences are thus to be called sophistical rather than rational inferences.” (Kant 2018, A339)

Unlike the Omnipotent, human beings are material objects placed in a phenomenal world, so that our scientific activities cannot escape the various influences of individual circumstances. This suggests that scientific knowledge is impossible without the viewpoint of affordance. It is neither possible nor legitimate to account for scientific experience without taking affordances into consideration. Dispositions, which have no affordance, cannot account for scientific experience.

Dispositions are either a transcendental idea (whether it be a transcendental object or a regulative principle of reason) or a positive noumenon: the latter cannot be an object of philosophical nor scientific investigation. Therefore, the fact that dispositions are latent should be accounted for by assuming dispositions to be a transcendental idea.

In an excellent overview of the history of the human mind Patocka points out that modern philosophy is characterized by "the abstract person." (Patocka 2018, p.13) In the 17th century modern humans came to understand their lives not from the perspective of integration in the harmony of the cosmic organism, but rather from a standpoint which seeks to transcend integration. Descartes discovered the role of self-confidence that inherits the role played by logos, mathematical entities, ideas and forms in ancient philosophy. Mathematics, too, became self-consciously formal and abstract, and incorporated physical reality within its scope. Continuing the trend of abstraction inherited from Greek mathematical philosophy, it rendered reality itself abstract: what it considers real is whatever corresponds to mathematical relations; overlooking their termini and their content, mathematics apprehends only the network of relations or only the structure of this web of relations.

The abstract person and its relation to the world are found in will, which shatters the ancient cosmos and all its legacy. The world is no longer an equal participant in a shared drama; rather, it ultimately figures as a mere subordinate component. The contradiction of this abstractly personal understanding of the place of humans in the world manifests itself in the theoretical self-objectification and practical self-reification of humans. The former is a contradiction which extends mathematical physics into an empirically causal theory of mind and of its cognition. Empiricism is a protest of human beings with their active integration in the world against mathematical metaphysics. But it is powerless because it is itself based on mathematical metaphysics.

According to Patocka, Kant is to be characterized as a figure who "uncovered the abstractly personal relation of humans to the world as a problem that needs to be resolved by a phenomenalization of the mathematical model of reality and by superordinating practical life, that is, the harmonic interaction of the will with all other will, to phenomenal nature." Not the psychological reflection that empiricists rest upon, but rather "a descent to the covert *logic of the constitution of objectivity* becomes the context of the world."

A revitalization of these withered human relations, namely, attaining a global construction of the meaning of the world and of being by unfolding a new logic, has been the issue for subsequent thinkers. This logic is one of the foci of present-day philosophical discussion. It concerns "the way in which each particular we experience acquires its meaning—how it appears to us, how it manifests itself, shows itself in what it is. Appearance, manifestation, *phainesthai* in Greek, will be its fundamental problem: hence the name, *phenomenology*." It seeks to "resolve philosophical problems on experiential grounds, *seeing* the things themselves, moving from abstract schemata to the fullness and depth of the sphere of life." It is about the meaning of existents and about beings as the presupposition for the description carried out by empirical science. The world appears to it as the foundation of that meaning. It discovers time and temporality at the basis of the world, “so that the meaning-bestowing ground of being itself in its nature becomes a temporal drama, a movement above which understanding cannot carry us since every understanding presupposes it.” (Summarized and quoted from Patocka 2018, pp.12-17)

How dispositions appear to the eyes of those who see the things themselves? This is an interesting question worth discussing if there is another opportunity.

CONCLUSION

Thinking about molecular structure has led us to the meaning of reality. The concept of molecular structure in organic chemistry involves atoms and bonds, showing the sequential connection and spatial arrangement of atoms in molecules. It has firm philosophical as well as scientific grounds. We assume it to be real as we take the objects we see around us for granted. We do not conceive that our perception is conditional. In fact, it is conditional and provisional. A moment's reflection is enough to understand that this is the case: we see a star twinkle in the sky, which may no longer exist. If we hesitate to accept what we assume to be molecular structure for the reason that it is conditional, nothing would be acceptable as real. Our belief in what we perceive probably comes from the fact that our perception is realized as an affordance which is defined as a context-relative dispositional attribute of an {agent-material world} complex. There is no reason to argue against what is afforded as a fact under well-defined conditions.

Reality as what is out there to be found may be a metaphysical fiction. Actually, what we take to be reality is the product of the mind and matter: things are nothing for us unless they become actualized as phenomena in phenomenal fields, of which we ourselves are one of the essential constituents. Therefore, neither transcendental realism (reality is a thing-in-itself) nor alleged constructivism (reality is our mental construction) is relevant. Since what is afforded from scientific activity depends on a {scientist-material world} complex, what is taken to be reality may be only one of many realities. This is often the case with submicroscopic entities, which are inaccessible to immediate observation. The way they manifest themselves depends on our approach: in what phenomena we are involved. It is therefore possible that what chemists believe is at odds with what physicists think due to their different theoretical models and that neither of them is irrelevant. It is in the context of organic chemistry that what we take to be molecular structure makes sense as reality.

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