VALERIA MOSINI (*)

Chemistry and Its Interpretation (**)

Riassunto - La questione riguardante l'interpretazione delle teorie scientifiche è stata recentemente collegata a quella dell'unità della scienza. In questo articolo discuto la validità di tale collegamento, per quanto riguarda la chimica e, più in particolare, la teoria della risonanza.

Introduction

The interpretation of scientific theories is at the heart of the controversy between realists and antirealists. The realist holds that science establishes an objective relation between the *explanandum* and the *explanans*. This claim is grounded on the view that the explanatory and predictive power of mature scientific theories ensure that these are true or approximately true, otherwise their success would be due to a mere coincidence or a to a 'miracle' (see, for instance, Worrall: 1989). By contrast, the antirealist holds that the relation between the *explanandum* and the *explanans* that science establishes is not an objective one, but represents an internal, functional link of logical, conceptual, or conventional character. This claim is grounded on a theory of knowledge according to which we can establish relations among perceptions, and yet these relations do not allow us to make definite claims on the world: "Outside these relations there is no reality knowable" (Poincaré: 1952, p. XXIV). As to the ontological status of the entities which appear in scientific theories, the realist holds that unobservable entities are ontologically on a par with observable entities, and that all terms which appear in mature scientific theories, no matter whether denoting observable or unobservable entities, are referential. The antirealist, in fact, holds that only those scientific sentences are meaningful that refer to observable entities and that existence claims

(*) Dipartimento di Chimica, Università degli Studi di Roma «La Sapienza».

(**) Presented at the VI National Meeting «Storia e Fondamenti della Chimica» (Cagliari, 4-7 october 1995).

for theoretical entities are illegitimate. Theoretical entities are just models, often far remote from the objects of the real world they purportedly represent, and scientific theories are true of the models, not of the objects in the real world. In other words, antirealism is the view that: "Theories can be used to relate and systematize observation statements and to derive some sets of observation statements (predictions) from other sets (data); but no question of the truth or reference of the theories themselves arises" (Edwards: 1972, p. 407).

The question concerning the interpretation of scientific theories has been recently connected to the question of reduction and unity of science (Rosenberg: 1995). Discussing the relationship between biology and physics, Rosenberg suggests that, beneath the level of generality of the theory of natural selection, biology is an instrumental discipline. The instrumental character of biology is testimony to the irreducibility of biology to physics, (which, so Rosenberg holds, is interpreted realistically) and hence, to the disunity of science, even though: "(T)here are neither differences in the epistemologies of the disciplines, nor differences in their subject matters, nor emergent differences in the levels at which their phenomena are organized" (Rosenberg: op. cit., p. 14).

Given the obvious connections between chemistry and physics and between chemistry and biology, it is interesting to investigate the controversy between realism and antirealism in chemistry. Chemistry is usually regarded as a phenomenological discipline which describes events whose explanation is to be seeked in physics' laws. The interpretation of chemistry is a wide question; this paper is a first attempt to address it by discussing the interpretation of the theory of resonance. Vermeeren (1986) claimed that no realist interpretation for the resonance structures is possible and hence that: "(T)he requirement of a realistic interpretation of theories at all times, as defended by a number of philosophers, is untenable" (Vermeeren: op. cit., p. 273). Contrary to Vermeeren's position, I claim here that the theory of resonance was interpreted realistically by its proponents. Yet my final conclusion will not be that the fact that a realist interpetation is possible for the theory of resonance supports scientific realism against antirealism. In fact, my conclusion will be that the theory of resonance differs in no respect from the other scientific theories for which both the realist and the antirealist interpretations have been given, and that the grounds to assess which interpretation is tenable for the theory of resonance are the same those used to assess which interpretation is tenable for any other scientific theory. In other words, I urge that, as fa as the interpretation of scientific theories is concerned, chemistry differs in no respect from physics.

The theory of resonance and its interpretation

The theory of resonance relates to the question of the nature of the chemical bond, usually defined as the sharing of two electrons between two atoms (Lewis: 1916 and Langmuir: 1919). The establishment of Lewis and Langmuir theory of the chemical bond on a quantum mechanical basis is due to Heitler and London (1927) who put forward the valence-bond theory. In the case of heteroatomic molecules, this theory was not totally satisfactory. For one thing, it led to cases of apparent shared valence, so that it seemed conceivable that the covalent bond could also consist in the sharing of one or three electrons (Sidgwick: 1927). For another thing, it created ambiguity as to what extent the bond in question was as to be regarded as covalent or valence-bond ionic. In other words, it appeared that more than one structure was required to describe all the properties of some compounds. At this stage the theory of resonance was put forward (see, for instance, Slater: 1931, and Pauling: 1931), which assumes that the structure of the compound is represented by an intermediate structure between two or more possible alternative valence-bond structures.

Vermeeren's claim (op. cit.) that the resonance structures could only be interpreted antirealistically is based on a distinction between theoretical entities introduced by Shapere (1969). On Shapere's account, one thing is to assert that a given theoretical entity exists, another thing is to attribute it certain properties which make the mathematical treatment of the problem under consideration possible. In the first case, the theoretical entity is given a realist interpretation, and is introduced through an existence term. In the second case, the theoretical entity is given an antirealist interpretation, and is introduced through an idealization term.[1]

Vermeeren's starting point in discussing the interpretation of the theory of resonance is Butlerov's principle (1879), which states that each chemical compound should be represented through one molecular formula. On Vermeeren's account, the theory of resonance violates Butlerov's principle and gives a purely instrumentalist interpretation of the resonance structures, viewed as idealizations. Vermeeren's second argument for his claim concerning the antirealist interpretation of the valence-bond structures was an analogous claim made in Soviet Union in the 1950s. According to the final resolution of the Conference on the theories of the

[1] Needless to say, if Vermeeren was right, classical mechanics and relativity theory, which make use of idealization terms like point masses and rigid bodies, could only represent marginal areas of scientific research. This is because For instance, classical mechanics describes bodies as mass points, and yet, the localization of a gravitational mass in a dimensionless point would result in an infinite gravitational potential that classical mechanics rules out. And the theory of relativity is based on the kinematics of rigid bodies, defined as bodies through which any force applied would be transmitted instantaneously, *i.e.* with infinite velocity. But the assumption of infinite velocity overtly violates one of the main tenets of the theory of relativity, that the velocity of all bodies is finite, and lower than the velocity of light.

chemical structure organized in Moscow in 1950, the theory of resonance makes use of ideal, ficticious, structures, seemingly suggesting that the 'real' structure of some chemical compounds is inconceivable. For the Soviet chemists, the theory of resonance represented an expression of the idealistic philosophy which rates the usefulness of a theory more than its plausibility.

Restating the resonance controversy

To discuss whether the introduction of the theory of resonance determined a definite shift towards antirealism in chemistry, as Vermeeren claimed, and whether the theory was a product of the idealist philosophy, as the Soviet chemists claimed, it is better to recall the terms in which the theory was actually put forward.

The concept of a system resonanting between two or more structures originates in quantum mechanics. If ϕ_1 and ϕ_2 are possible wavefunctions for a system in the same energy state, any linear combination of ϕ_1 and ϕ_2 is a possible wavefunction for the system in the same state, and the system is said to 'resonate' between ϕ_1 and ϕ_2. Notably, if the state is a stationary state, the wavefunction is obtained by solving the stationary Schrödinger equation, and is thus time independent. This means that the concept of resonance has no analogy with that of mechanical oscillation, in which the system is assumed to spend time in different situations. In the case of molecules, the theory of resonance assumes that the actual structure of a compound is not represented by any of the valence-bond structures conceivable, but results from a combination of them, the 'resonance structures'.[2]

It is true that considerations of convenience played a part in putting forward the theory of resonance, because: "By using valence-bond structures as the basis for discussion, with the aid of the concept of resonance, we are able to account for the properties of the molecule in terms of those of other molecules in a straightforward and simple way. It is for this practical reason that we find it convenient to speak of the resonance of molecules among several electronic structures" (Pauling: 1960, p. 186). Pauling also acknowledged that: "There is an element of arbitrariness in the use of the concept of resonance, introduced by the choice of the initial structures as the basis for discussion of the normal state of a system. (But all substances) *can be fitted* into a scheme of classical valence theory by the consideration of resonance among two or more such structures" (Pauling: 1960, p. 11, my emphasis).

The fact that convenience enters Pauling's considerations by no means imply

[2] Interestingly enough, the theory of resonance did not just play a crucial role in respect to the structure of a number of compounds, but also influenced nuclear physics. It was Wheeler who suggested that, pursuing the analogy between nuclear and molecular structures, any state of a nucleus should be regarded as a superposition of all possible nucleon clusters, and that the nucleus should be attributed a 'resonating group structure' (Wheeler: 1937).

that Pauling claimed that the valence-bond structures should be interpreted antirealistically. By contrast, Pauling meant something totally different, namely that the valence-bond structures could be used to describe the structure of compounds, despite the limits and flaws of the valence-bond theory.

Far from considering the real structure of some compounds beyond human reach, the theory of resonance was strongly concerned with the question of the real structure, as the following passages show: "The theory of resonance considered it possible for the *true* state of a molecule to be not identical with that represented by any single classical valence-bond structure, but to be *intermediate* between those represented by two or more different valence-bond structures" (Wheland: 1944, p. 2, my emphasis) and: "The two explanations constitute two unperturbed states, from which the *true* one is to be found by linear combination, so that the *real* situation is intermediate between the two" (Slater: op. cit., p. 487, my emphasis). For Wheland and Slater, the valence-bond structures were much more than ficticious structures of a compound whose real structure remained unknown: they were 'legitimate starting points' to try and get as close as possible to the real structure of the compound. Pauling gave a different interpretation of resonance, though not an antirealist one. In his (1960) book, he maintained that the question concerning the reality of the resonance structures originates in the difficulty to perform an experiment which would distinguish among the different structures, the difficulty being given by the fact that chemical methods which give information on bond type (Mills and Nixon: 1930) require that a reaction takes place, and reaction rates greatly exceed the rate of ordinary electronic resonance. The fact that Pauling mentioned an ideal experiment which would distinguish between the different resonance structures, suggests that he viewed the resonance structures as tautomers.

Clearly, Pauling's view of resonance structures differs from the standard view of resonance, defended by Slater and Wheland, that the real structure of the compound is intermediate between the resonance structures. At any rate, neither view is inclined towards antirealism. As to the standard view, it holds that the theory of resonance aims at getting 'as close as possible' to the real structure, where the limiting proviso, 'as close as possible', refers to the representation style avaliable. As to Pauling's view, it locates itself within the framework of scientific realism because regarding the resonance structures as tautomers means attributing them physical reality.

Scientific Realism and Dialectical Materialism

Before the controversy on the theory of resonance started, the theory had been well received in Soviet Union, to the point that it appeared in a book (Syrkin and Diatkina: 1946) which was to become the textbook adopted in the best Universities of the Country. The pubblication of the book followed Syrkin and Diatkina's

translation into russian of Pauling's *The nature of the chemical bond* and Wheland's *The theory of resonance and its applications to organic chemistry*. Around the end of the Fourties, the concept of resonance started to be viewed as being characterized by a strong implication with idealism, which in Soviet Union was identified with Mach's philosophy: "The theory of resonance may serve as one example of the Machist theoretic-perceptional tendencies of bourgeois scientists, which are hostile to the Marxist world view and which lead them to pseudoscientific conclusions concerning the solution of concrete physical and chemical problems". (Tatevskii et al.: 1949, quoted in Graham: op. cit., p. 303).[3] It was at the 1950 Conference that the opposition to the theory of resonance became the official standpoint of the Soviet chemists: on that occasion no-one (not even Syrkin or Diatkina) defended the theory, blaming their previous superficial interpretation responsible for its acceptance. As a matter of fact, it is the iterpretation of the theory of resonance given at the Conference which originated in a total misunderstanding. This is because it assumed that the theory of resonance used the resonance structures as explanatory devices, at the same time denying their existence. Clearly, this was not the gist of either interpretations of the theory (nor Pauling's or Slater and Wheland's).

Recall that, in the Thirties, Soviet Union had officially denounced quantum mechanics and relativity theory on idealistic charges, and that the rejection of the theory of resonance in the Fifties paved the way to the rejection of genetics, linguistics, and psychoanalysis. The reason for this is that, under Stalin, science, as anything else, was strongly politicized in Soviet Union and enjoyed very little freedom: the rejection of much of 20th century science on alleged idealistic charges was prompted by political reasons, and represented one among several: "Attempts to apply dialectical materialism to every kind of activity, from portrait painting to fishing. They produced a great deal of utter nonsense" (Haldane: 1939, p. 45). Thus it would be wrong to attribute the position of the Soviet scientists in the Stalin era to philosophical considerations intended to defend dialectical materialism. This is a complex doctrine and hosts highly diversified positions, none of which is similar to the extremely naive version of scientific realism defended at the 1950 Conference. Engels (1954), for instance, believed that human knowledge approaches the truth, but only through an asymptotic process. And Plekhanov claimed that: "Our sensations are sort of hieroglyphs informing us what is happening in reality. These hieroglyphs are not similar to those events conveyed by them. But they can completely truthfully convey both the events themselves and-and this is important-also those relationships existing between them" (Plekhanov: 1956, quoted in: Graham: op. cit., p. 41). Thus Plekhanov believed in a strict correspondence

[3] Interestingly enough, Mach's philosophy had been very influential in Soviet Union, especially because of the work of Bogdanov (alias Malinovskii). But, as early as 1908, Lenin set himself to the task of stopping the spread of Mach's philosophy by publishing *Materialism and Empiriocriticism*.

between external events and human sensations, but not in scientific theories providing faithful mappings of the world.

As far as the theory of resonance is concerned, it was not incompatible with dialectical materialism, as the final resolution of the 1950 Conference wanted, if an eminent dialectical materialist (though of the Western front) defined it as: "(A) brilliant example of dialectical thinking, of the refusal to admit that two alternatives (two contributing structures) which are put before you are necessarily quite exclusive" (Haldane: op. cit., p. 101).

Conclusions

There is no doubt that the theory of resonance represented a challenge to the Lewis-Langmuir theory of the chemical bond by proving it inadequate to account for the properties of a great number of compounds through a single structure. Thus what actually violated Butlerov's principle was not the theory of resonance but the Lewis-Langmuir theory itself. However, Butlerov's principle was established before the valence-bond theory was put forward, thus it could not possibly imply that each compound should be attributed one *valence-bond formula*. Moreover, most importantly, the extent to which the molecular formulas actually represent the structure of the compounds depends upon the system of representation, which is theory dependent and subject to change. Rather than a violation of Butlerov principle, the theory of resonance represented an attempt to bridge the gap between the need to satisfy the principle and the limits to representation imposed by the pictorial slyle available. It resulted in a step forward in the direction of providing a better understanding of the nature of the chemical bond and of the extent to which this can be pictorially represented: in 1931 Huckel vindicated Butlerov's principle by describing all the properties of benzene through *one* structure, which followed the representation style of the molecular-orbital theory.

The valence-bond theory and the molecular-orbital theory are based on mutually incompatible assumptions: the former attributes the bonding electrons to localized atomic orbitals, the latter to orbitals which extend over the whole molecule. The competition between the two theories promoted a re-thinking of the concept of chemical bond: despite the fact that this is currently described as the sharing of two electrons between two atoms, the conclusion emerged that: "From its very nature, a bond is a statement about two electrons, so that if the behaviour of these two electrons is significantly dependent upon, or correlated with, other electrons, our idea of a bond separate from, and independent of, other bonds must be modified. In the beautiful density diagrams of today the simple bond has got lost" (Coulson: 1970, p. 287). Nonetheless, the Lewis-Langmuir model of the chemical bond has not totally disappeared from the chemists' vocabulary, and the valence-bond theory is still used both for computational and, more often, for

teaching purposes. The reason for this is that the values of molecular parameters calculated according to the valence-bond theory are in striking agreement[4] with those calculated according to the molecular-orbital theory: "So long as the treatments are restricted to the ground states of the molecules, the two calculations lead to results of approximately equal accuracy, or inaccuracy" (Wheland: 1955, p. 655).

Is the survival of the valence-bond theory, and of the pictorial style corresponding to the Lewis-Langmuir model of the chemical bond, evidence that chemistry is an intrinsically antirealist discipline? Endorsing this view would be tantamount to claiming that the fact that Newtonian mechanics is still used (in a given range), because of its simplicity and accuracy, and despite its making use of the concepts of force, mass, energy, space, and time, that relativity theory has discredited, makes physics an intrinsically antirealist discipline. This consideration undermines the view that irreducibility and disunity of science can, *faute de mieux*, be attributed to a different intepretation for chemistry and for physics.

[4] This fact is further evidence in favour of the Duhem-Quine thesis concerning the underdetermination of theories by data.

REFERENCES

BUTLEROV A.M. (1879), «The Present Day Significance of the Chemical Structure», in: B.A. Kazanskii ed., *Centenary of the Theory of the Chemical Structure*, p. 85-102, Progress Publishers, Moscow 1961.

COULSON C.A., «Recent Developments in Valence Bond Theory», in: *Pure and Applied Chemistry*, *24*, 257-287, 1970.

EDWARDS P., *The Encyclopoedia of Philosophy*, Macmillan, New York 1972.

ENGELS F., *The Dialectics of Nature*, Progress Publishers, Moscow 1954.

GRAHAM L., *Science and Philosophy in the Soviet Union*, Penguin Books, London 1973.

HALDANE J.B.S., *The Marxist Philosophy and the Sciences*, Allen & Unwin, New York 1939.

HEITLER W. and LONDON F., «Wechselwirkung neutraler Atome und homoopolare Bindung nach der Quantenmekanik», in: *Zeitschrift fur Physik*, *44*, 455-472, 1927.

HUECKEL E., «Quantentheoretische Beitrage zum Benzolproblem», in: *Zeitschrift fur Physik*, *70*, 204-286, 1931.

LANGMUIR I., «The Arrangement of Electrons in Atoms and Molecules», in: *Journal of the American Chemical Society*, *41*, 274-292, 1919.

LEWIS G.N., «The Atom and the Molecule», in: *Journal of the American Chemical Society*, *42*, 762-785, 1916.

MILLS W.H. and NIXON I.G., *Journal of the American Chemical Society*, 2510, 1930.

PARTINGTON J.R., *A Short History of Chemistry*, London 1948.

PAULING L., «The Nature of the Chemical Bond I and II», in: *Journal of the American Chemical Society*, *53*, 1367 and 3225, 1931.

PAULING L., *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York 1960.

PAULING L. and WHELAND G.W., «The Nature of the Chemical Bond. V.», in: *Journal of Chemical Physics*, *1*, 362-74, 1933.

POINCARÉ H., *Science and Hypothesis*, Dover, New York 1952.

ROSENBERG A., *Instrumental Biology or The Disunity of Science*, University of Chicago Press, Chicago 1994.

SHAPERE D., «Notes Towards a Post-positivistic Interpretation of Science», in: P. Achinstein and S. Barker (eds.), *The Legacy of Logical Positivism*, John Hopkins, Baltimora, 115-160, 1969.

SIDGWICK N.V., *The Electronic Theory of Valence*, Oxford University Press, Oxford 1927.

SLATER J.C., «Directed Valence in Polyatomic Molecules», in: *Physical Review*, *37*, 480-489, 1931.

SYRKIN Ia. K. and DIATKINA M.E., *The Structure of Molecules and the Chemical Bond*, New York 1950.

VERMEEREN H., «Controversies and Existence Claims in Chemistry: the Theory of Resonance», in: *Synthese*, *69*, 273-290, 1986.

WHELAND G.W., *The Theory of Resonance, its Applications to Organic Chemistry*, J. Wiley and Sons, New York 1944.

WHELAND G.W., *Resonance in Organic Chemistry*, J. Wiley and Sons, New York 1955.

WORRALL J., «Structural Realism: the Best of Both Worlds?», in: *Dialectica*, *43*, 99-124, 1989.