

## Is there a quantum definition of a molecule?

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The paper surveys how chemistry has developed over the past two centuries starting from Lavoisier's classification of the chemical elements at the end of the eighteenth century; the subsequent development of the atomic–molecular model of matter preoccupied chemists throughout the nineteenth century, while the results of the application of quantum theory to the molecular model has been the story of this century. Whereas physical chemistry originated in the nineteenth century with the measurement of the physical properties of groups of chemical compounds that chemists identified as families, the goal of chemical physics is the explanation of the facts of chemistry in terms of the principles and theories of physics. Chemical physics as such was only possible after the discovery of the quantum theory in the 1920's. By then the first of the sub-atomic particles had been discovered and seemingly it is no longer possible to discuss chemical facts purely in terms of atoms and molecules – one has to recognize the electron and the nucleus, the parts of atoms. The combination of classical molecular structure with the quantum properties of the electron has given us a tremendously successful account of chemistry called 'quantum chemistry'. Yet from the perspective of the quantum theory the deepest part of chemistry, the existence of chemical isomers and the very idea of molecular structure that rationalizes it, remains a central problem for chemical physics.

*The rabbi spoke three times. The first talk was brilliant – clear and simple. I understood every word. The second was even better – deep and subtle. I didn't understand much, but the rabbi understood all of it. The third talk was by far the finest – a great and unforgettable experience. I understood nothing, and the rabbi himself didn't understand much either.*

A favourite story of Niels Bohr, quoted from *Niels Bohr. A Centenary Volume*, eds. A.P. French and J.P. Kennedy (Harvard University Press, Cambridge, MA, 1985) p. 299.

### 1. Introduction

In the nineteenth century Dalton's atomic hypothesis was used to give the chemical elements a microscopic interpretation; the atom was conceived as the ultimate building-block of matter. Compounds came to be thought of in terms of definite combinations of atoms that we now call molecules. Subsequent developments in physics revealed the existence of the electron and the nucleus as a sub-atomic structure that

required a completely new physical theory, quantum mechanics, for its description. The application of the quantum theory to the electrons in molecules is the cornerstone of the modern understanding of chemistry, and everyone will assent to the following quotation ([2]): “Today we realize that the whole of chemistry is one huge manifestation of quantum phenomena.” Paradoxically, it turns out to be very difficult to formulate a coherent quantum theory of chemistry. What we have at the moment is a subtle mixture of classical and quantum concepts; the paper reviews this situation in three short sections. The classical framework of chemistry is laid out in section 2, and the way these concepts were built into the applications of quantum theory to chemical problems from the outset is reviewed in section 3. Finally, in section 4 the possible application of quantum theory to chemical theory is discussed.

## 2. The classical context

The modern scientific attitude that emerged in the seventeenth century aimed to describe the natural world through analytical procedures of classification and systematization; the underlying mechanical philosophy was grounded firmly in a picture of the world as a world of physical objects endowed with well-defined fixed properties that can be described in mathematical terms – shape, size, position, number and so on. It can be seen as a return to the mathematical ideals of the Pythagoreans, and of Plato, and a renewal of the ideas of the early Greek atomists, for example, Demokritos. The prime movers of this revolution were René Descartes and Isaac Newton; both sought to found physics on mathematics rather than a philosophical tradition that had originated in Antiquity.

This ancient tradition is derived from a perception of material bodies as possessing inherent qualities that govern their chemical and physical behaviour; alchemy, for example, belongs to this human mythical tradition which is directly contrary to the analytical, scientific approach. Things have dynamic qualities that can be accounted for by analogy with human emotional states, or through personification; the mythical account of the physical world may be seen as an extension of human life in the world, and is based on perceptions totally alien to the modern world of science and technology. The mythical perception of the world is synthetic in outlook, seeing the world as a dynamic living whole, without distinction between living things and the inanimate. In short, the scientific revolution represented a fundamental shift from the organism to the machine as the model in terms of which the natural world would henceforth be understood. As far as chemistry is concerned, this shift in outlook did not take place until more than a century later. Although alchemy was regarded with increasing scepticism throughout the eighteenth century due to the accumulation of empirical evidence that spoke against transmutation of metals, the decisive break in favour of the modern approach to chemistry can be associated with the publication in 1789 of the book *Traité Élémentaire de Chimie* by the French aristocrat Antoine Lavoisier [3,8].

Chemistry is concerned with the composition and properties of matter, and with the transformations of matter that can occur under the action of heat, radiation or other sources of energy. The characteristic chemical notion of a *pure substance* is based on an ideal conception of the chemical and physical properties of matter and their change. Physical properties belong to materials in isolation from other materials, and are those properties that can be observed without conversion of the material into other substances, whereas chemical properties refer to the chemical reactions that materials undergo. There we have a fundamental distinction between the goals of chemistry and physics. From the results of chemical experiments the chemist singles out a particular class of materials that have characteristic and invariant properties. Such materials are called pure substances and may be of two kinds, viz. *compounds* and *elements*. After Lavoisier, elements were to be characterized by their gravimetric properties: an element is a pure substance that forms products of greater weight than itself in all chemical changes which it undergoes. Compounds are formed from the chemical combination of the elements, and have properties that are invariably different from the properties of the constituent elements. Lavoisier produced a reasonably correct and extensive list of elements. Most importantly, he introduced their modern names and much of the terminology we still use in chemistry, and at a stroke killed off alchemy by abolishing its old obscure language.

In the nineteenth century the chemical elements were given a microscopic interpretation in terms of Dalton's atomic hypothesis that marks the beginning of chemical theory. Henceforth the elements were to be regarded as being composed of microscopic *building-blocks*, atoms, which were indestructible and had invariable properties, notably weight, characteristic of the individual elements. Similarly, compounds came to be thought of in terms of definite combinations of atoms that we now call molecules. Atoms and molecules are microscopic in an obvious sense; they are not visible to the naked eye nor directly accessible to any of our other senses. Dalton's idea is different from historically earlier interpretations of the atomic concept such as that of early Greeks, like Demokritos, or of Robert Boyle and Newton who believed there was *one* fundamental microscopic particle – one Catholic matter, as Boyle said. Nearly 50 years of confusion followed Dalton until, in 1858 the Sicilian chemist Cannizzaro outlined a method whereby one could reliably determine the relative weights of different kinds of atoms and he used this to define the atomic composition of molecules. This account of stoichiometry is the first significant theoretical achievement in classical chemistry based on the atomic/molecular conception of matter; we shall need to revisit it in the light of the quantum theory [9].

Having sorted out ideas about elements and compounds in terms of atoms and molecules, attention shifted to *synthesis* – the making of new compounds, and progress thereafter was rapid, especially in the chemistry of compounds containing the element carbon, what we call organic chemistry. In order to keep track of the growth of experimental results, more and more transformations of compounds into other compounds, some kind of notation was needed. In mid-nineteenth century chemists hit on a highly original conception – *molecular structure*. Over a period of many years chemists de-

veloped a kind of chemical language – a system of signs and conventions for their use – which gave them a representation of their fundamental postulate that atoms are the building-blocks of matter; molecules are built up using atoms like the letters of an alphabet. A molecule in classical chemistry is also seen as a *structure*, as a semi-rigid collection of atoms held together by chemical bonds. So not only do we count the numbers of different kinds of atoms in a molecule, but also we say how they are *arranged* with respect to each other, and so we can draw pictures of molecules. To each pure substance there corresponds a structural molecular formula, and conversely, to each molecular formula there corresponds a unique pure substance. The laws that govern the relative dispositions of the atoms in ordinary 3-dimensional space are the classical valency rules which therefore provide the syntax of chemical structural formulae. *Valency*, the capacity of an atom for stable combination with other atoms, is thus a constitutive property of the atom.

It is absolutely fundamental to the way chemists think that there is a direct relationship between specific features of a molecular structure and the properties (chemical and physical) of the substance to which it corresponds. Of especial importance is the local structure in a molecule involving a few atoms coordinated to a specified centre, for this results in the characteristic notion of a *functional group*; the presence of such groups in a molecule confers specific properties to the corresponding substance (acid, base, oxidant, etc.). Moreover, each pure substance can be referred to one or several categories of chemical reactivity, and can be transformed into other substances which fall successively in other categories. Thus the classical structural formula of a molecule summarizes or represents the connection between the spatial organization of the atoms and a given sequence of chemical reactions that the corresponding substance participates in, notably but not only, the reactions required for its analysis and for its synthesis.

The development of the interpretation of chemical experiments in terms of this molecular model was a highly original step for chemists to take for it had nothing to do with physics. In the nineteenth century the only known forces of attraction that might hold atoms together were the electromagnetic and gravitational forces, but these were seen to be absolutely useless for chemistry, and so were given up in favour of a basic *structural principle*. This obviously marked a break with the then known physics, a rupture that could not be healed until the development of the quantum theory. On the other hand, chemists had made a change that brought their thinking much more into line with the customary approach in physics; from the 1860's onwards inductive argument was replaced by a deductive model based on the formulation and testing of hypotheses. A final important point to keep in mind is that chemistry at the start of the nineteenth century was a science of the transformation of *substances* (Lavoisier) whereas by the end of the century it had become a science of the transformations of *molecules* (Van't Hoff), so much so that practitioners now of the chemical sciences – parts of material science and biochemistry as well as chemistry – scarcely distinguish between substances and molecules [8].

### 3. Quantum chemistry

There had of course already been fruitful interactions between chemistry and physics, for example, from the mid nineteenth century onwards, physicists and chemists conducted some interdisciplinary studies of groups of compounds that chemists identified as *families* – measurements of boiling points, melting points, refractive indices, solution electrical conductivities, densities, vapour pressures, etc. – and both contributed to the development of the science of thermodynamics. Physical chemistry as such can be said to have been founded by Wilhelm Ostwald, a great entrepreneur for the subject; he became the first director of the Physical Chemistry Institute in Leipzig (1887) and founder editor of the first journal specifically concerned with physical chemistry, the *Zeitschrift für Physikalische Chemie*. Chemical physics, properly speaking, came later with the rise of quantum theory.

In the years immediately before World War I, the atomic theory finally became universally accepted; among the highlights of its mature conception before the rise of quantum theory we can mention Perrin's investigations of Brownian motion and Ostwald's conversion to atomistics (from Machian positivism), both in 1908, and the Braggs' 'proof' of the atomic constitution of matter demonstrated through their analysis of the X-ray diffraction pattern of alkali halide crystals (1913) [8]. Just as the atomic theory matured, a radical change in the idea of molecular structure arose with an unexpected input from physics. The X-ray diffraction experiment opened the way to a completely new route to determining molecular structures that broke the link with chemical reactions described earlier; henceforth molecular structure was to be a physical observable. X-ray diffraction is applicable in principle to any substance that forms regular crystals including, of course, biologically important compounds. Today, every chemist and biochemist learns his or her trade using molecular models of structures that are routinely obtained from X-ray measurements – most famously (though not routinely!) the structure of DNA, 'the molecule of life', an icon of the twentieth century, which is perhaps the best known molecule ever.

As chemistry made rapid progress in the late nineteenth century, physicists began to unravel sub-atomic structure, and so undermine the position of the atom as the ultimate building-block of matter, even if it remained the ultimate unit in chemical transformations. A hundred years ago this year, J.J. Thomson announced in a lecture at the Royal Institution (London) that cathode rays were electrically charged particles carrying a mass only 1/2000th of the mass of the hydrogen atom. With the discovery of the electron as a universal constituent of matter came the recognition that atoms must also contain positive charge in order to maintain their electroneutrality. Its distribution in the atom was settled by Rutherford's interpretation of his celebrated experimental study of the scattering of  $\alpha$ -particles by gold foil in terms of the nuclear model of the atom. Perhaps the most important idea that followed from the early investigations was that the understanding of the structure of the atom would inevitably require the solution of a problem in dynamics. This process of finding new 'fundamental particles' has gone on throughout the whole of the twentieth century – seemingly ever more exotic

and mysterious. Increasingly, physics is seen as being reduced to invisible ‘particles’ and their interactions.

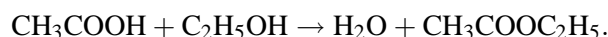
Classical mechanics does not work for the electrons and nuclei in atoms and so something new was needed. Over a twenty five year period from 1900 a new kind of mechanics, *quantum mechanics*, was devised and applied to these new areas of physics. The prototype theory that emerged slowly in the first quarter of the twentieth century is now called the *old quantum theory*, to distinguish it from *quantum theory* proper, discovered in various forms by Heisenberg, Schrödinger and Dirac (1925/1926). Essentially, all the basic concepts used in structural molecular spectroscopy today were developed within the framework of the old quantum theory and are firmly based on the classical concept of molecular structure; they were taken over with little change when the modern quantum theory was discovered. Examples are well known: the separation of molecular energies into electronic, vibrational and rotational contributions (Schwarzschild (1916), Heurlinger (1919)) which provides the basis for the analysis of molecular spectra in terms of bond-lengths and bond-angles; the use of potential energy surfaces for describing chemical reactions, and the Franck–Condon principle. We also find the beginnings of electronic structure theory in this period, for example, the angular momentum classification of molecular electronic *orbitals* of diatomic molecules (Hund, Mulliken (1925/1926)), subsequently reinterpreted using Schrödinger’s form of quantum theory as the molecular orbital model of diatomic molecules (Hund (1928), Mulliken (1931/1932)). Moreover, although the applications of the old quantum theory to the problem of the chemical bond were not very successful, the subsequent quantum-mechanical ‘valence bond’ calculation on the hydrogen molecule due to Heitler and London (1927) was based on the same general idea that the nuclei provide an effectively fixed framework of charges about which the electrons moved, so that the dynamical problem was to determine the electron distribution appropriate to a specified arrangement of the nuclei. Even the separation of electronic and nuclear motion which underlies the modern theory of the chemical bond and valency was first formulated in terms of the old quantum theory and subsequently reworked by Born and Oppenheimer (1927) using the new quantum mechanics [7]. Chemistry, without molecular structure would be unintelligible, and so, the application of quantum mechanics to chemical problems had to preserve that feature; this set the style for what has become known as *quantum chemistry*. The details are well known and need not be elaborated here; suffice to say that the electrons and nuclei are treated differently through the Born–Oppenheimer or adiabatic approach, notwithstanding subsequent inclusion of ‘non-adiabatic’ effects, for only through a classical treatment of nuclear positions does molecular structure become meaningful.

#### 4. Chemistry and quantum theory

If one approaches chemistry from the perspective of quantum theory there are two problems that stand out as fundamental questions:

- (a) The equilibrium problem – what are, and what is meant by, the *structures* of the molecules of stable chemical substances?
- (b) The kinetic problem – how do these stable substances *change*, one to another, in a chemical reaction and finally reach an *equilibrium state*?

The second problem is part of a bigger question in physics concerned with irreversibility. There are many different approaches to the problem; one well-known one due to Prigogine and collaborators argues that in certain kinds of quantum theories there are representations in which there are initial states (density matrices) which evolve into the future ( $t \rightarrow +\infty$ ) towards an equilibrium state, even though the initial state did not develop from an equilibrium state in the remote past ( $t \rightarrow -\infty$ ). Thus the time-evolution is non-unitary and  $t = -\infty, +\infty$  play different, inequivalent roles. The essential feature of such theories is that the Hamiltonian,  $\hat{H}$ , for the system that evolves towards an equilibrium state must have the purely continuous spectrum associated with an infinite number of degrees of freedom [4]. Thus for the description of chemical reactions one must suppose that  $\hat{H}$  refers to the *substances* in the reaction vessel, rather than their molecules. To take a familiar example, the mixing of ethanol with acetic acid leads eventually to a different, equilibrium mixture that contains water and ethyl acetate as well as ethanol and acetic acid:



We may ask, without pausing here to answer, what is actually meant by the Hamiltonian for these substances; what *is* the Hamiltonian for water or ethanol?!

Faced with such an horrendous question, we retreat and focus instead on equilibrium mixtures. One of the first topics met that gives chemistry its characteristic flavour is the subject matter of classical stoichiometry, i.e., the laws of chemical combination that describe the mass relationships between substances in closed equilibrium systems. These experimentally derived relationships can be expressed formally as a system of linear equations that exhibit a remarkable feature, namely the occurrence of *integers*; in the classical account of Cannizzaro this feature is rationalized by reference to the atomic theory in terms of molecular formulae, like  $\text{H}_2\text{O}$ . However, the mathematical structure of stoichiometry can be set up without appealing to the notion of atoms, and one is led to ask, *why integers?* The integers enter as matrix elements ( $-m_{ij}$ ) in the linear equations that specify the contributions of elementary substance  $j$  to compound  $i$ . From the point of view of a classical theory their occurrence seems to be miraculous.

Quantum theory puts an entirely different perspective on this issue. It would seem natural to suppose, quantum mechanically, that ( $-m_{ij}$ ) could be constructed from the Abelian algebra formed by the *number operators* of the elementary substances. A similar viewpoint has been developed in statistical dynamics which deals with the statistical averaging required for the description of a many-body system at finite temperatures based on the number operators for the chemical species involved, without reference to a Hamiltonian theory, as in a fully microscopic quantum field

theory [5]. Stoichiometry however is an incomplete account of chemical reactions in that it does not recognize the occurrence of *isomerism*; the formula  $C_3H_4$ , for example, is associated with three distinct chemical substances: allene, cyclopropene and methyl acetylene yet there is only one entry in the stoichiometric matrix ( $-\mathbf{m}$ ) for this formula. This mass degeneracy must be accommodated in other ways; the classical answer of Van't Hoff is through embedding atoms in three-dimensional space which results in the possibility of topologically inequivalent arrangements of the atoms and their 'bonds'. Whether a natural topological structure can be associated with an algebra of number operators to give the same effect is an open question [9].

A characteristic feature of chemistry is that the atom is the smallest particle that needs to be considered. Not much can be usefully said about quantization based on atoms beyond the idea of number operators touched on above. In order to develop a Hamiltonian theory it seems that one has to recognize sub-atomic structure in terms of electrons and nuclei. There are two possible ways to approach this: 'top-down' or 'bottom-up'. The 'top-down' approach aims to describe matter in bulk (substances therefore). Much of the modern theory of condensed matter is concerned with a quantum theory of electron and nuclear fields and could be expected to have some relevance to chemical theory [1]. The precise chemical nature of materials has usually not been of much interest in general theories of some physical property which is exhibited by different materials. For a quantum description of the physical properties of bulk matter – diffraction experiments, electrical conductivity, ferroelectricity, magnetism, optical properties, superconductivity, etc. – it is not necessary to take the further step to the classical picture of matter based on atoms and molecules. Consequently, the issue of isomerism, which is of fundamental importance to the chemist, is not confronted in such discussions. Nevertheless, quantum field theory may well provide the basis for a future theoretical chemistry; it leads one to expect the existence of long-lived composite quasi-particles (elementary excitations) possessing centre-of-mass motion *and* internal excitations that can be described in terms of the quantum states of a system with a *finite* number of degrees of freedom (corresponding to a definite number of particles); these states can be used to build a Fock space as a tensor product. The relevance of this approach to what we ordinarily call an atomic or molecular gas is obvious [8].

In the 'bottom-up' approach we start with the notion of atoms and molecules as given; they are interpreted as collections of specified numbers of electrons and nuclei and there is a corresponding Hamiltonian operator to use with the Schrödinger equation. A fundamental account of this Hamiltonian recognizes that electrons and nuclei carry *electric charge* and must be described by electrodynamics. If one chooses to present electrodynamics with the Coulomb gauge condition imposed, so that the vector potential is purely transverse, the energy carried by the longitudinal electric field (due to the charges) is just the Coulomb interaction; having chosen a particular gauge, however, it is difficult to show that the physical predictions of the model are independent of the choice of (Coulomb) gauge, i.e., *gauge-invariant*. A more general Hamiltonian that does not require a specific choice of gauge to be made at



the outset can be developed; this, however, no longer contains an explicit Coulomb interaction [10]. In gauge-invariant quantum theory interactions between charges are mediated by the exchange of virtual photons. Bound states involving a given number of charged particles are associated with poles in the scattering amplitudes (calculated for the same number of particles) for which *non-perturbative* calculations are needed [6]. These can be achieved through summation of whole classes of Feynman diagrams, for example, summation to infinite order of the ‘ladder diagrams’ leads to an equation for bound states which can be interpreted as though it arose from an effective potential which in lowest order (in  $v/c$ ) is the Coulomb interaction, and has the Breit interaction as its contribution of order  $(v/c)^2$ . So the  $N$ -particle Coulomb Hamiltonian which is the usual starting point in discussions of non-relativistic quantum chemistry is an effective Hamiltonian derived from quantum electrodynamics by integrating out some of the effects of the radiation field vacuum; processes involving real photons have to be dealt with subsequently by perturbation theory. The origin of the Dirac–Breit Hamiltonian for relativistic quantum chemistry is essentially similar [6].

Finally, we return to the example of  $C_3H_4$ ; in the present terms this represents a collection of 3 carbon nuclei, 4 protons and 22 electrons. For quantum chemistry we easily imagine the nuclei to be placed in the arrangements corresponding to the three distinct stable molecules of this formula, and then apply quantum mechanics (the Schrödinger equation) to the electrons to obtain the total electronic energy in the three cases. Other nuclear arrangements lead to different electronic energies and we represent the whole set of such energies as a potential energy surface (including of course the classical Coulomb energy of the nuclei). Suppose we apply quantum mechanics to *all* the particles in one go, what do we get? It is easier to say what we have never found so far – no suggestion of three distinct isomers for the molecules of allene, cyclopropene and methyl acetylene. This negative result does not mean that either quantum mechanics or chemistry must be ‘wrong’ – it does mean that we do not know how to formulate the quantum mechanics (i.e., *write down explicit equations*) so that the theory predicts, in this case, three isomers. Lacking that we have had no choice but to put the molecular structure in by hand. This is not a problem of not having a big enough computer; rather it is the problem of not knowing what to compute. That means we need a new idea.

## References

- [1] P.W. Anderson, *Basic Notions in Condensed Matter Physics* (Benjamin, Cummings, 1984).
- [2] C.J. Ballhausen, *J. Chem. Ed.* 56 (1979) 357.
- [3] A. Lavoisier, *Traité Élémentaire de Chimie, Oeuvres de Lavoisier* (Imprimerie Imperiale, Paris, 1864).
- [4] I. Prigogine and C. George, *Proc. Natl. Acad. Sci. USA* 80 (1983) 4590.
- [5] R.F. Streater, *Statistical Dynamics* (Imperial College Press, 1995).
- [6] S. Weinberg, *The Quantum Theory of Fields*, Vol. 1, *Foundations* (1995) chapters 10, 13.
- [7] R.G. Woolley, *Adv. Phys.* 25 (1976) 27.

- [8] R.G. Woolley, in: *Molecules in Physics, Chemistry and Biology*, Vol. 1, ed. J. Maruani (1988) p. 45.
- [9] R.G. Woolley, *Mol. Phys.* 85 (1995) 539.
- [10] R.G. Woolley, *Mol. Phys.* 88 (1996) 291.