

The Nature of the Chemical Bond —1992

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Much of my life has been devoted to study of the nature of the chemical bond. Accordingly I read with much interest the paper by J. F. Ogilvie with the title "The Nature of the Chemical Bond—1990" (1), which contains errors and logical flaws, some of which I discuss here.

The Fundamental Structure of Quantum Mechanics as a Basis of Chemical Applications

Quantum theory began in 1900 with the discovery by Max Planck of his radiation law, which introduced a new physical constant, called Planck's constant. Within a few years Albert Einstein had used this theory in explaining the photoelectric effect, the photochemical equivalence law, and the low-temperature heat capacities of solids, and Niels Bohr had used it in interpreting atomic spectra. Many physicists contributed to improving the understanding of physical phenomena by applying the old quantum theory, with considerable but not complete success. By 1920 it was recognized that the old quantum theory needed to be revised.

This revision was accomplished in 1925 and 1926 by the discovery of quantum mechanics by Werner Heisenberg, Paul Dirac, and Erwin Schrödinger. It is now generally accepted that quantum mechanics is reliable in its application to all problems in chemistry and to nearly all in physics.

I arrived in Germany in 1926, just when Schrödinger was publishing his papers on his wave equation. By the end of 1926 I had written two papers, applying quantum mechanics to certain physical properties of atoms and monatomic ions (X-ray fine structure, electric polarizability, diamagnetic susceptibility, and electron distribution), and had begun work on applying quantum mechanics to the problem of the nature of the chemical bond.

Since I was part of the process that refined quantum theory, I feel I must take issue with several of Ogilvie's statements and conclusions. My impression is that Ogilvie seems not to have a good understanding of quantum mechanics, as is illustrated by the following examples.

Editor's Note

In this issue we bring to closure the current discussion of the nature of the chemical bond. Readers will recall the paper by Ogilvie [*J. Chem. Educ.* **1990**, *67*, 280–289] giving one modern point of view of the chemical bond. In this issue, we publish another modern point of view by Pauling together with three letters (page 600) that the Ogilvie paper engendered. These letters have been selected from a larger number (which we are unable to print) and are representative of the kinds of responses that the paper generated. Since both Pauling and Ogilvie use the photoelectron spectra of methane to provide evidence for their (divergent) views, we also publish in this issue (page 522) a paper by Simons on photoelectric spectroscopy of methane.

The Planck Radiation Law

Ogilvie states that it is possible to derive Planck's radiation law from classical statistical mechanics without any quantum assumptions whatsoever. This statement is clearly false. Planck's radiation law involves a new physical constant, called Planck's constant, unrelated to other constants. Every derivation of the radiation law must include a quantum assumption, introducing Planck's constant.

The Bohr Atom

Ogilvie states that the great physicist Niels Bohr made two errors, which fortuitously cancelled one another, namely, treating circular orbits and using quantized angular momentum to evaluate the energy. Bohr, in his remarkable contribution to quantum theory, introduced two innovative ideas. One idea is that only a few of the infinity of states of a system according to classical dynamics are allowed: these are the quantized energy levels. He also stated that a transition between two allowed energy levels can occur with the emission or absorption of a photon with frequency equal to the difference in energy of the two levels divided by Planck's constant. Moreover, Bohr calculated the energy levels for H and He⁺ by a quantum method (quantizing the angular momentum) that he had devised. Wilson and Sommerfeld soon showed that for an elliptical orbit in H and He the energy is independent of the eccentricity. Bohr had taken the eccentricity to be zero (spherical orbits), and had got results in essentially exact agreement with the spectra. When quantum mechanics was developed, 12 years later, it was found that the eccentricity is never zero. This fact does not justify the derogation of Bohr as having committed errors.

Nickel and Electron Repulsion

Ogilvie states that the fact that nickel is not a gas shows that quantum mechanics fails for atoms with atomic number greater than 10 because the orbital picture of the atom is based on electrons that do not repel one another, and that this is "just one logical fallacy of many that abound in the typical discussions of the 'chemical bond'." This statement is quite false. I do not know of any quantum theoretical or quantum mechanical calculations in which the mutual repulsion of electrons was ignored. For example, in 1926 I published the first quantum mechanical treatment of the properties of atoms containing many electrons (2), based upon ideas formulated by Gregor Wentzel (3); electron-electron repulsion was taken into account in this treatment, as it has been in all later quantum mechanical treatments of all systems containing two or more electrons.

Chiral Molecules

Ogilvie states that "Pioneer quantum mechanics provides no explanation of optical activity." This statement is not true. Schrödinger's original equation, 1926 ("pioneer quantum mechanics"), included a time-dependent term. Ogilvie may know this fact, but not be aware of its significance. Consider a molecule of alanine, H₂NCH(CH₃)-

COOH; the solution of the Schrödinger equation over an infinite time would show the normal state to have no chirality, but the quantum mechanical treatment suitable to a few years of observation would show the normal state to be chiral, either L or D.

Several of Ogilvie's other arguments seem to show that his understanding of quantum mechanics is at best superficial. An example is his statement that "the very notions—entirely of a classical nature—of vibrational and rotational motion, in which the positions of nuclei relative to the center of molecular mass vary with time, seem inconsistent with the molecules existing in eigenstates having properties independent of time."

The Relationship of Quantum Mechanics to Atomic and Molecular Structure

The initial quantum theory was successful with only the simplest atoms and with no molecules. In the years before 1925 leading physicists, such as Heisenberg and W. Pauli, tried to apply it to He and to H_2^+ (the simplest molecule, with a one-electron bond), but they failed. However, quantum mechanics was successful in this regard. Heisenberg soon applied his theory of resonance to explain the helium spectrum and Burrau made an accurate calculation of the bond energy in H_2^+ . These steps forward were soon followed by W. Heitler and F. London's treatment of the electron-pair bond and by many other applications of quantum mechanics to chemistry.

The concept of quantum mechanical resonance and the theorem that in quantum mechanics the actual structure of a system has a lower energy than any other structure have turned out to be especially important in chemistry. The energy could be calculated for an assumed wave function for a molecule. Any change that lowered the energy indicated some addition to the picture of the chemical bond. The polarization of bond orbitals and the partial ionic character of bonds were discovered in this way. The minimum-energy theorem led to the formulation of the electronegativity scale. Modern chemistry and molecular biology are the products of quantum mechanics. Chemistry has been changed by quantum mechanics even more than physics.

Quantum mechanics has also contributed to chemistry in other ways; for example, the properties of moderately simple molecules that are not available for experimental study can now be reliably calculated.

The modern theory of the nature of the chemical bond is the product of the thinking and experimental observations of chemists of past generations, refined in recent decades by new experimental observations and quantum mechanics.

A number of Ogilvie's statements about molecules and the chemical bond can be criticized. Here are some more examples.

Molecular Structure

In several places Ogilvie makes statements such as

The existence of classical properties, such as molecular structure or shape, is in direct contradiction to the superposition principle of pioneer quantum mechanics.

This statement is clearly not correct and I can only surmise that it was made because of his misunderstanding of quantum mechanics, as illustrated by the example dealing with chirality.

Orbitals

The subheading of the Ogilvie paper, "There Are No Such Things as Orbitals!" is based on a misconception of the meaning of the word "thing". One of the dictionary defini-

tions of thing is "Anything that is or may become an object of thought;" in other words, a thing need not be tangible, but it could be represented by a symbol. Ogilvie quotes Robert Mulliken's definition of the word that he had invented: "something as much like an orbit as is possible in quantum mechanics." Quantum mechanical expressions for orbitals, such as those that Mulliken and I and scores of other theoretical physicists have formulated, are clearly objects of thought, and hence are things. An equation for an sp^3 hybrid orbital printed on a sheet of paper in an issue of the *Journal of the American Chemical Society* in 1931 might even be considered to conform to another definition of thing, "a material object without life or consciousness, an inanimate object." Ogilvie has surely shown that orbitals are objects of thought.

Methane

Ogilvie makes several nearly equivalent statements such as the following: "That this [tetrahedral] structure implies sp^3 hybridization is a common, but fallacious, assumption" and "Despite the fact that many authors of textbooks of general chemistry have written that CH_4 has a tetrahedral structure because of sp^3 hybridization, there neither exists now, nor has ever existed, any quantitative experimental or theoretical justification of such a statement." I, of course, had written in 1928 (4) that as a result of the resonance phenomenon (that is, sp^3 hybridization) a tetrahedral arrangement of the four bonds of the quadrivalent carbon atom is the stable one; that is, has a lower energy than other arrangements, corresponding, for example, to a bond formed by a 2s electron and three bonds formed by 2p electrons. I made this statement on the basis of a quantum mechanical calculation that I had carried out. Later I formulated a useful and powerful way of simplifying the quantum mechanical calculations (5). This simple method of discussing relative bond energies leads to the quantitative theoretical conclusion that in the normal state the methane molecule is tetrahedral and, to the degree of approximation involved, has sp^3 bond orbitals. The tetrahedral structure is verified experimentally. Other, more detailed theoretical calculations, do not invalidate this conclusion. It is my opinion that the contrary arguments invoked by Ogilvie have little merit.

Ogilvie makes use of the following argument in an attempt to show that there is something wrong with sp^3 hybridization in methane; I believe this argument to be illogical. With four equivalent sp^3 C-H electron-pair bonds, there are eight equivalent electrons in these bonds, as well as two electrons in the inner shell of the carbon atom. Hence experiments should reveal only two kinds of electrons. However, the photoelectron spectrum of methane reveals

three separate systems, corresponding to adiabatic (first) ionization energies/ 10^{-18} J about 2.0, 3.6, and 47.6. ...We deduce from these experimental data that there are three distinct bands of energy for the electrons in CH_4 , not just two that might be supposed on the basis of (eight) 'valence' and (two) 'core' electrons...All we can deduce therefrom is that the primitive model of eight equivalent 'valence' electrons in CH_4 is not supported by this experimental evidence.

This argument is, of course, completely illogical and without merit. The observed ionization energies are the difference in energy of CH_4 and CH_4^+ (plus e^-). CH_4 has only one energy value, but CH_4^+ has three: one corresponds to a hole in the core, and two to a hole in the sp^3 set (three electron-pair bonds plus one one-electron bond). These two are split because there are two different resonance structures for the hole among four tetrahedral positions. The observed ionization energies do not invalidate but, instead it

can be argued, support the allocation to CH_4 of four equivalent electron pair bonds.

Electronegativity and Carbon Monoxide

Ogilvie begins his brief discussion of electronegativity by saying that I introduced it (in 1932, ref. 6). He then discusses the electric dipole moment of CO in an incorrect way. The relation between electric dipole moment and electronegativity for both single and multiple bonds is discussed at length in my book *The Nature of the Chemical Bond* (ref. 7, 3rd ed., p 97), and the structure and dipole moment of carbon monoxide are analyzed there also (p 266). I pointed out that for the structure corresponding to $\text{C}=\text{O}$ a large dipole moment would be expected, but that in fact the normal state of the molecule involves also the triply bonded contribution $\text{:C}\equiv\text{C}^+$ (as well as the single-bonded contribution), which neutralizes the others, leading to a quite small dipole moment value, with oxygen at the positive end of the dipole. Ogilvie simply assumes that the greater electronegativity of oxygen than of carbon requires that oxygen be at the negative end of the dipole, and that accordingly the concept of electronegativity is flawed. He is clearly mistaken.

Ogilvie also advances another argument, pointing out that during vibration of the molecule the dipole moment fluctuates from :CO^+ at small values of the internuclear distance to $^+\text{CO}^-$ at large values of this distance, and asks

How can any simple concept as embodied in an electronegativity scale lead in general to the reliable prediction of such varied behavior within a particular electronic state or for different electronic states of a given molecule?

This is an interesting question, and the answer to it is obvious to anyone who has studied my book. At the average internuclear distance I assign to the CO molecule the contributing structures $\text{:C}\equiv\text{O}^+$, 50%; $\text{C}=\text{O}$, 40%; and $^+\text{C}-\text{O}^-$, 10%, giving (with correction for the polarization of bonds as determined by the electronegativity difference) a value for the dipole moment that is close to zero. At smaller interatomic distances the contribution of the structure $\text{:C}\equiv\text{O}^+$ increases, as does also the dipole moment, with oxygen positive. At large interatomic distances the structures $\text{C}=\text{O}$ and $^+\text{C}-\text{O}^-$ predominate, and the dipole moment reverses. The theory of resonance accordingly ac-

counts for the observed relation between dipole moment and internuclear distance.

The Consequent Implications for Chemical Education

The concept of the chemical bond is the most valuable concept in chemistry. Its development over the past 150 years has been one of the greatest triumphs of the human intellect. I doubt that there is a chemist in the world who does not use it in his or her thinking. Much of modern science and technology has developed because of the existence of this concept.

The really great discoveries about the chemical bond were made by great chemists of the 19th century: Berzelius, Butlerov, Frankland, Couper, Kekule, Van't Hoff, and, LeBel. G. N. Lewis and Irving Langmuir made significant contributions during the period 1916-1920. Then quantum mechanics came along, making the chemical bond more useful and helping to systematize and simplify chemical science.

Beginning courses in chemistry should emphasize the simpler aspects of molecular structure in relation to the properties of substances. These aspects include the electronic structures of atoms, with emphasis on the noble-gas structure, the shared electron-pair bond, the tetrahedral carbon atom, the electronegativity scale, partial ionic character of bonds, and the idea of resonance as applied to the benzene molecule. I agree with Ogilvie that some things, especially molecular orbitals, should be left out, but in my opinion the classical concept of the chemical bond, together with its recent refinements, must be included in the course, together with a good bit of descriptive chemistry. During recent years much more information about molecules and crystals and their reactions, both experimental and theoretical, has become available, but this information has not decreased the value of the concept of the chemical bond. I am pleased and gratified that in 1992 the chemical bond is alive and well.

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