The Nature of the Chemical Bond—1990

There Are No Such *Things* as Orbitals!

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In 1931, Pauling published a theory (*1*) that has had during the intervening years great influence on the thinking of chemists. That paper, actually the first of seven under the general title "The Nature of the Chemical Bond", was followed by a monograph (*2*) based on lectures given at Cornell University, but the paper (*1*) refers to an earlier publication (*3*) under the title "The Shared-Electron Chemical Linking" that was stated to contain several original ideas greatly amplified and extended both in papers in the series and within the monograph. The remainder of the title of the initial paper (*1*) of the series is "Application of Results Obtained from the Quantum Mechanics and from a Theory of Paramagnetic Susceptibility to the Structure of Molecules". During the six decades since the appearance of the root paper (*3*), great advances in the understanding of properties of chemical substances have naturally resulted from both experimental and computational means. Because among these experiments spectral measurements of simple compounds under conditions of negligible intermolecular interactions have been especially important, we illuminate our discussion with the results of the interpretation of selected spectra. As a consequence of the various developments, one can now critically appraise the ideas that were generated during the early years of the quantum era; at that time the hopes and wishes for a quantitative understanding of the fundamental principles of chemical structure and reactions exceeded the then current ability to test their correctness or objectivity.

In this essay we are concerned with three particular aspects of quantum mechanics in modern chemistry, namely the fundamental structure of quantum mechanics as a basis of chemical applications, the relationship of quantum mechanics to atomic and molecular structure, and the consequent implications for chemical education. In so proceeding, we generally adopt a historical perspective for the context of our present state of development. We incorporate several original ideas and unfamiliar interpretations as well as naturally to recall pertinent recent results from the research literature. First we distinguish between quantum laws and quantum theories, and then discuss the most fundamental principles of quantum mechanics. Because chemists have been traditionally exposed to only one approach to quantum theory, they have become misled about the generality of certain concepts, such as orbitals and electronegativity; the objective of the discussion of quantum theories is to distinguish between what is fundamental and what is artifact. The structure of the methane molecule occupies a central position in the teaching of much chemistry; we contrast the qualitative and obsolescent ideas with the more quantitative information now available from spectral measurements. Because photolectron spectra have been taken (*4*) to prove the "existence" of molecular orbitals, we devote particular attention to an alternative interpretation that we apply specifically to CH_4. As diatomic molecules are relatively simple systems, a fully quantitative analytic (algebraic) treatment of their spectral properties is practicable; we cite evidence that structural information can be derived just as well by approaches based on classical mechanics as by various quantal approaches. With this background we finally advocate a more intellectually honest approach to both the thinking of chemists and the teaching of chemistry that recognizes chemistry to be a science of materials as well as a science of molecules. A principal objective of all this discussion is a critical assessment of some qualitative concepts of quantum theory, such as atomic and molecular orbitals and electronegativity, that have evolved since Pauling's paper (*3*) to become established in the fabric of modern chemical education.

Quantum Laws and Quantum Theories

A half century after Dalton's atomic hypothesis about 1807, Couper proposed (*5*) the first enduring notions about molecular structure, reinforced by Kekule, van't Hoff, and Le Bel within the next two decades. Thus was formed a century ago the fundamental *classical* idea of a molecule as a fairly rigid arrangement of atoms in three-dimensional space; between certain adjacent pairs of atoms a chemical bond was supposed to exist. In the formation of these ideas the phenomenon of optical activity played an important role. The organic chemists, and later the inorganic chemists after Werner, developed a profound though intuitive idea of the existence of molecules to which were attributed structures in great variety although based on a simple framework of a few chemical bonds about each atomic center. During the 19th century many physical chemists (mostly electrochemists) remained skeptical of the atomic hypothesis, until Ostwald's eventual capitulation about 1900, but the spectroscopists such as Dewar at Cambridge entertained no such doubts. Although the basic idea, albeit based entirely on inference from experiments on a macroscopic scale, that the structure of a molecule consisted of a system of chemical bonds spatially distributed about and between atomic centers was thus widely accepted by the end of the 19th century, the quantitative experimental proof had to await the 20th century.

The dawn of this century also coincided with the birth of the quantum era, based upon Planck's explanation of the spectral distribution of radiant energy from a black body. Planck's basic hypothesis was that light of a particular frequency ν could be radiated not continuously, but only with energy in integer multiples of $h\nu$; however, it is possible (*6*) to derive Planck's radiation law from classical statistical mechanics without any quantum assumptions whatsoever. Hence, even though quantum theories flourish, their historical foundation has been largely superseded. Before we proceed further to consider the development of quantum theories, we outline the quantum laws most significant for chemical purposes.

We summarize in the table some fundamental physical properties of molecules and photons. Free molecules may exist in states of quantized total energy, but radiant energy exists in quanta called photons. A photon as the discrete unit of monochromatic radiation characterized by frequency ν and wavelength λ (related by $\lambda\nu = c$ in vacuo) has neither net electrical charge nor rest mass; its energy W is given by the Planck relation $W = h\nu$, h being the Planck constant. The photon has both a definite linear momentum $|\mathbf{p}| = h/\lambda$ and a

Physical Properties of Molecules and Photons

Property	Molecule	Photon
Charge	0, ±1 e, ±2 e, . . .	0
Mass (rest)	$M > 0$	0
Energy	$W \approx W_{tr} + W_{el} + W_{vi} + W_{rot}$	$W = h\nu$
Linear momentum	$\lvert\mathbf{p}\rvert > 0$	$\lvert\mathbf{p}\rvert = h/\lambda$
Angular momentum	$\lvert\mathbf{J}\rvert = [J(J + 1)]^{(1/2)}\hbar$	$\lvert\mathbf{J}\rvert = \hbar$

definite angular momentum $|\mathbf{J}| = h/2\pi$. In contrast, a free molecule may be electrically neutral or may carry a net electrical charge in units of the protonic charge. Although no quantum theory so far developed seems to require that molecular mass be quantized, it remains true that the mass of any known stable molecule (having a specific isotopic composition) is almost an integral multiple of the mass of the hydrogen atom $^1{}_1$H. Likewise, the magnitude of the protonic charge lacks theoretical justification. The total energy of a molecule that can move freely within some confining space is the sum of discrete contributions arising from the translational motion of the center of mass (relative to a coordinate system fixed in space), the nuclear motions (vibrational and rotational about the molecular center of mass), and the electronic motions about the nuclei; the quantum number for total angular momentum (apart from nuclear spin) has the symbol J. Thus the quantities energy, linear and angular momentum, mass,[1] and charge that during the 19th century were the subjects of laws of conservation are recognized to be ultimately discrete or quantized at the microscopic level. We may thus consider the experimental proof of the discreteness of these five quantities under appropriate conditions to constitute the quantum *laws* of nature.

The first attempt to construct a quantum *theory* of atoms or molecules was made by the chemist Bjerrum, in 1912, in relation to the vibrational and rotational motions of diatomic molecules; this theory was unsuccessful in explaining the then known infrared spectra. Bohr's theory of the one-electron atom, based on Rutherford's model of the nuclear atom, seemed more successful. In summary, the restriction of the angular momentum of the electron moving in a circular orbit about the nucleus (or rather the center of mass of the two-body system) to integer values of the Planck constant led to the energy of the atom assuming only values proportional to the inverse of the square of the same integer; moreover, the radius of the orbit was directly proportional to the square of the same integer, the proportionality factor being (approximately) the Bohr radius a_0. We know now that the energy of the one-electron atom has essentially no direct dependence on the state of the angular momentum of the atom; in other words, the energy of such an atom having a particular value of the quantum number n for energy remains essentially degenerate for different values of the quantum number l ($l < n$) for orbital angular momentum. Thus this apparent success of the Bohr theory depends on the fortuitous cancellation of two errors, namely circular orbits and the dependence of energy on the quantum number for angular momentum; one may scarcely wonder that the theory fails entirely to explain quantitatively the spectra or properties of atoms containing two or more electrons, or even the one-electron molecule H_2^+.

Enduring quantum theories began with the pioneer *(6)* quantum mechanics of Heisenberg and Schrodinger; created between 1922 and 1927, and digested between 1927 and 1933, during which period they were applied to atoms and molecules, these are generally the only quantum theories that chemists have encountered. After Born recognized *(7a)* the necessity for a mechanical theory, i.e., one that treats the positions and momenta of elementary particles, Heisenberg *(8)* discovered the noncommuting property of these quantities, that Dirac *(9)* immediately understood to be the fundamental postulate of quantum mechanics. If we represent a component of the position of a particle by the quantity q_k and a component of the momentum by p_j, each subscript j or k denoting one of the x, y, or z axes in a Cartesian system for instance, we may write compactly this fundamental principle of commutation:

$$[p_j, q_k] \equiv p_j q_k - q_k p_j = -i\hbar\delta_{jk}$$

here i means the square root of -1, the Kronecker delta function δ takes the value 1 if $j = k$ and 0 otherwise, and $\hbar = h/2\pi$. Although it is well known (cf. Landau and Lifshitz *(10)*, for instance) that one can derive from this equation Heisenberg's principle of indeterminacy, that one can also derive[2] the de Broglie relation $\lambda = h/p$ is not so widely appreciated. De Broglie postulated this relation in 1923, but it was not widely known until later. Learning of this relation in 1926, Debye commended *(12)* to Schrodinger the search for a wave equation to take account of the wave effects associated with moving particles.

What kinds of quantities may be subject to this possible failure to commute? Obviously mere numbers are not subject to such a restriction. Two kinds of quantities do, however, qualify, and each kind is the basis of one form of pioneer quantum mechanics. In general matrix multiplication is not commutative; matrix mechanics was developed by Heisenberg, Born, and Jordan. An algebraic quantity, for instance x, also fails to commute with the differential operator with respect to the same quantity, thus d/dx; Schrodinger developed wave mechanics on this basis. Because we can choose either a coordinate representation with the quantity q_k and the corresponding operator for momentum $-i\hbar \mathrm{d}/\mathrm{d}q_k$ (so as to be consistent with the commutation law), or a momentum representation with the quantity p_j and the corresponding operator for position $i\hbar \mathrm{d}/\mathrm{d}p_j$, two possible approaches to wave mechanics are possible; generally the former is preferred because potential energy is more easily expressed in terms of position coordinates than in terms of momenta. Obviously the operands of the operators $\mathrm{d}/\mathrm{d}p_j$ and $\mathrm{d}/\mathrm{d}q_k$ must be different functions, i.e., being dissimilar in both algebraic form and hence graphical representation. Furthermore, despite the then-known requirements of the theory of relativity, the time-dependent Schrodinger equation embodies second-order derivatives for space coordinates but a first-order derivative for time, in contravention of their equivalence. First Schrodinger in a formal way, then Pauli in a much more precise proof, demonstrated the equivalence of matrix mechanics and wave mechanics; later Dirac and von Neumann produced further proofs within more general formalisms. Nevertheless, Dirac *(11b)* concluded that Heisenberg's approach is more fundamental than Schrodinger's in quantum field theory. Dirac *(11c)* described a third approach to quantum mechanics in terms of a relativistically correct wave equation containing matrices as coefficients of the first derivatives with respect to both time and space coordinates; for the one-electron atom this approach leads

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[1] Although the equivalence of mass and energy recognized by Einstein has eliminated mass as a separately conserved quantity, for operations in the chemical laboratory the conservation of mass is still an exceedingly useful rule.

[2] The proof is implicit in Dirac's book (*11a*), to which the reader is referred for the details of the notation. We take as the starting point the transformation function $\langle q|p\rangle$ connecting the momentum and coordinate representations, in which $|p\rangle$ are the basis kets of the momentum representation. Briefly, this transformation function must be the solution of the differential equation resulting from the replacement of p by the corresponding differential operator $-i\hbar \mathrm{d}/\mathrm{d}q$; hence

$$\langle q|p\rangle \approx e^{2\pi ipq/h}$$

If we replace q in the exponent by $q + nh/p$, n being any integer, then the right-hand side remains unchanged in magnitude, because $e^{2\pi ni} = 1$. Because h/p has the significance of a wavelength λ, the desired result is obtained.

naturally to a fourth quantum number for electron spin. This equation must be considered one of man's supreme intellectual triumphs in that it led to the prediction of the existence of antimatter, specifically the positron, a few years before its experimental detection. Despite this achievement, for systems containing two or more electrons the Hamiltonian in the Dirac equation has no true bound-state solutions (*13*). Dirac also developed another approach (*11d*) in terms of operators for the processes of creation and annihilation; these ladder operators, however, apply not to mechanical variables, but rather to the populations of energy states between which the occupation numbers change as a result of transitions.

What we have endeavored to demonstrate within this section is that there exist quantum laws, essentially experimentally based like all other scientific laws; these laws express the discreteness of certain physical quantities at the microscopic or molecular level. There also exist many quantum theories, two in particular being collectively termed the pioneer quantum mechanics (*6*); these, the matrix mechanics of Heisenberg, Born, and Jordan and the wave mechanics of Schrodinger, are absolutely equivalent methods and therefore have correspondingly equivalent limitations of applicability. By these means one can calculate the values of certain observable properties of, for instance, molecular systems. The unavoidable conclusion of the recognition of the equivalence of these two distinct methods is that any particular feature of either mathematical method is an artifact peculiar to that method, thus merely a parochial description and accordingly not a universally meaningful or valid physical (or chemical) property of the molecular system.

Application of Quantum Mechanics to Molecular Structure

Quantum Methods and Atomic Structure

Although in his first paper in the specified series (*1*) Pauling alluded to the matrix mechanics, thereafter he, in common with virtually all other chemists, ignored its existence, despite the fact (*14*) that Pauli achieved the first quantum-mechanical solution of the one-electron atom according to matrix mechanics, not wave mechanics. The first computation in quantum chemistry is generally attributed to Heitler and London (both physicists), who in 1927 attempted to solve the simplest molecule H_2 according to wave mechanics. This computation is based on the separation of the electronic and nuclear motions; during the same year, Born and Oppenheimer justified the latter procedure (*15*) that introduces into—indeed imposes upon—quantum mechanics the classical idea of molecular structure. Strongly influenced by the apparent success of this calculation on H_2 (actually the accuracy of the results was poor even in comparison with the then-known experimental data), Pauling, Slater, and others initiated the so-called valence-bond approach and applied it to many molecules. Pauling also placed much emphasis on the idea of resonance and on hybridization—the formation of linear combinations of atomic wave functions assigned to the same atomic centre. About the same time, Hund, Lennard–Jones, Mulliken, and others developed an alternative approach with linear combinations of atomic wavefunctions on different atomic centers. Mulliken invented the term orbital, defined with characteristic obfuscation in his review "Spectroscopy, Molecular Orbitals and Chemical Bonding" (*16*) as "something as much like an orbit as is possible in quantum mechanics". An orbital is precisely a mathematical function, specifically a solution of the Schrodinger equation for a one-electron system, thus an atomic orbital for the H atom or a molecular orbital for H_2^+. Although the atomic wave functions are comparatively easy to use in calculations, the solutions for H_2^+ have a more complicated form in general; hence a linear combination of atomic functions on different centers serves as an approximation to a molecular orbital.

Before proceeding to consider molecules, let us first devote some attention to the structure of atoms. First of all, it should be quite clear to us that no atom exists within a molecule (*17*) and hence by implication in other than an isolated condition (such that interactions with either other matter or intense electromagnetic fields are negligible). This statement is quite independent of the utility of the approximation of atomic functions in the construction of a molecular wave function for the purpose of some calculation. If we define a molecule as a stationary collection of nuclei and the associated electrons in an isolated condition, then a practical definition of an atom is a molecule having only one nuclear center. The periodic chart serves as a basis of classification of various chemical and physical properties of elementary chemical substances. Following many less successful attempts at the classification of the chemical elements, Mendeleyev based the periodic chart on experimental evidence, the periodicity of chemical and physical properties as the atomic number is increased from unity, although there were of course recognized to exist more or less gradual trends or variations of properties within a given family or column of the chart. The common approach to the teaching of the electronic configuration of atoms of the elements is based on the solutions of the Schrodinger equation for the one-electron atom. Based in fact on the existence of these periodic properties of the chemical elements, Pauli had already in 1925 shown the necessity for a quantum number for electron spin. In practicing the aufbau procedure, we include this fourth quantum number in an entirely ad hoc way because Schrodinger was unable to render any account of this in the solution of his equations (dependent or independent of time). If we associate chemical inertness and resistance to liquefaction with an electronic configuration known as a "closed shell", then we predict that an atom of the first three noble gases would contain 2, 10, or 28 electrons, that is, corresponding to the elements helium, neon, or nickel. Although the first two results are correct, clearly the prediction fails for the atomic number Z greater than 10. The reason for this failure is the lack of account of interelectronic repulsion; in other words, the orbital picture of an atom (or molecule) is based on electrons that do not repel one another, an entirely unphysical condition. The error of this predictive process is obviously extrapolation from a single point, just one logical fallacy of many that abound in the typical discussions of the "chemical bond". Of course, one may introduce ad hoc rules to correct for this drastic simplification, such as the $(n + l)$ or diagonal rule, but such rules are of quite limited utility. In this regard Millikan (*18*) has described his generation of two computer programs (in BASIC) to reproduce the electronic configurations of atoms of the first 106 elements, one incorporating all the rules and exceptions, and the other simply a list of the "correct configurations" to fit the available experimental evidence. Which program was the shorter (i.e., having the smaller number of statements)? The latter! Clearly recognized by Millikan (*18*), the significance of this result is that the aufbau principle is merely an illusion: the periodic chart is not a theoretical result but rather the product of experiment not derivable by means of a physical theory.

On the other hand, there have been developed methods to calculate atomic energies and transition frequencies. The procedure due to Hartree (1928) and Fock (1930) has been almost universally employed for calculations on not only atoms but also molecules. In this procedure according to common descriptions, one forms a basis set of one-electron functions (possibly atomic orbitals) and then takes into account the interelectronic repulsion by selecting one electron and calculating the average field of the remaining electrons; the wave function of the selected electron is then calculated in the field of both the nucleus and the remaining electrons. This process is repeated for each electron in turn until all the resultant wave functions, and consequently the total (approximate) statefunction that is their product, are negligibly altered in consecutive iterations.[3] Under these conditions of the "self-consistent field", the energy of the atomic system converges to a finite value. However, this value is, even with the disregard of relativistic effects, not correct; due to the use of an average field of the "other" electrons in the Hartree–Fock procedure, error arises because of inadequate account of correlation between electrons. This error is taken into account in a further stage of computation beyond the Hartree–Fock limit by procedures known as configuration interaction and many-body perturbation theory. The important conclusion from the brief outline of this algorithm is that, although one may start the calculation with a basis set of orbitals, such as the simple solutions of the Schrodinger equation for the one-electron atom, by the time that one reaches the Hartree–Fock limit, or beyond, the nature of the initially chosen one-electron functions is (within limits) irrelevant. Thus, only at the beginning of the calculation do the orbitals have any meaning, and then only in a mathematical sense.

A new approach to the Dirac–Hartree–Fock equations with a finite basis set has been recently claimed (19) to be suitable for both atomic and molecular calculations with no problems of spurious roots, variational collapse, or continuum dissolution that have plagued the conventional Dirac equation for many-electron applications; this development permits in principle the calculation of atomic and molecular properties that do not suffer from the neglect of relativistic effects (the variation of mass with velocity). Thereby chemists may be enabled to escape from the (self-imposed) tyranny of the Schrodinger equation.

Molecular Structure, with Particular Reference to Methane

We state first the conventional definition that molecular structure signifies at least a fairly rigid arrangement of atomic nuclei (surrounded by their associated electrons) in three-dimensional space. There are, of course, several further aspects of molecular structure. Topology is concerned with the order of connection of the atomic centers. Conformation relates to the shape of the structure and the relationship of one portion of the structure to other segments with intermediate atomic centers in a line of connectivity ("chemical linking"); the existence of structural and rotational isomers is associated with conformational features. Configuration pertains in part to the spatial arrangement at chiral centers in molecules of compounds exhibiting optical activity (the ability of substances or their solutions to rotate the plane of linearly polarized light); the existence of enantiomers and diastereomers is associated with configurational features. The geometric attributes of molecules are the bond lengths (distances between nuclei or atomic centers considered to be connected by a chemical bond) and the angles between bonds. Further structural aspects include any quantity that may be represented as a function of distance with respect to nuclear coordinates: for instance, the potential-energy function of which the geometric structure represents a set of values of nuclear coordinates at which the energy has an absolute or relative minimum (or at least a point of inflection in a so-called transition structure), and any other radial function (such as for the dipole moment, spin-orbital interaction, etc.) that may be determined either by theoretical calculation or indirectly from experimental data.

Because the study of diatomic molecules (i.e., containing two atomic nuclei but obviously not two atoms) reveals less information about certain qualitative aspects of molecular and electronic structure than the study of polyatomic molecules that appear to have some characteristic shape, we consider first methane (in its ground electronic state). A molecule of CH_4 has a tetrahedral shape; explicitly, we mean that four planes, each defined by a set of three hydrogen nuclei (at their equilibrium positions relative to the carbon nucleus), define a tetrahedron in three-dimensional space; the carbon nucleus lies at the geometric center of the regular tetrahedron. That this structure implies sp^3 hybridization is a common, but fallacious, assumption. (At this point let us be clear that such a description is valid only within the valence-bond model, in turn within the approximation of nonrepelling electrons treated according to the Schrodinger equation, thus only within wave mechanics, and specifically the latter in the coordinate representation.) This notion of sp^3 hybridization persists despite Pauling's acceptance (2, 20) that such a description is inaccurate even within the narrow confines of the model just specified. Chemists have been long accustomed to understand from their experiments that the methane molecule contains four equivalent C—H bonds; according to a tradition also of long standing, each bond is associated with one pair of electrons to which the connected atomic centers each contribute generally one electron. Is there any experimental evidence pertinent to the latter attribute? Before one attempts to seek an answer to this question, one must understand that a molecule of CH_4 contains 10 electrons that are fundamentally identical and indistinguishable. Any question that we pose must be expressed in a physically meaningful manner so that we can seek an answer consistent with general physical and chemical principles; merely to invent or to invoke some tautological explanation is a futile exercise. Secondly, to interpret an experimental observation requires some model, and hence some hypotheses or theory either explicitly or (more hazardously) implicitly. Thus we are prepared to examine the photoelectron spectrum of CH_4; we describe in the appendix an objective method for the interpretation of the data from such an experiment, illustrated by reference to the spectrum of H_2 (21).

In examining the entire range of the photoelectron spectrum of CH_4, we find three separate systems (22, 23), corresponding to adiabatic (first) ionization energies/10^{-18} J about 2.0, 3.6, and 47.6. The presence in the first region of three overlapping features is attributed to a Jahn–Teller distortion of CH_4^+ (in this electronic state CH_4^+ is deduced to have nonzero orbital angular momentum), which removes the degeneracy that would otherwise exist; the (more or less diffuse) vibrational excitation in these three components extends over the range $(2.0–2.6) \times 10^{-18}$ J. The ionization energy in this range is comparable with the first ionization energies of both the C and H atoms. The transition energy in the second region, extending from $(3.6–3.9) \times 10^{-18}$ J, is similar to that of the first excited state of the atomic ion C^+ (relative to the ground state of C). The third region is characteristic of carbon, the energy of this feature varying only slightly in different compounds. 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; in other words, this deduction *would be* entirely consistent with the association of only effectively six electrons with the first band of energies, and then two further electrons with each of the two further bands, *if* we could distinguish electrons in this way. However, because electrons are absolutely indistinguishable, 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. Alter-

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[3] In fact, and contrary to the impressions given in practically all accounts of the Hartree–Fock procedure, all the electrons are fit simultaneously, not iteratively from one to the next. Furthermore, for a system of N electrons and M basis functions one could solve the Schrodinger equation in one step by solving a matrix problem of size N^M; such a solution would automatically include configuration interaction. Because for any but the simplest molecule the quantity $N^M \approx N^{2N}$ implies a very large matrix, then the Hartree–Fock approximation provides a more tractable starting point for the full computation.

natively, we can try to apply the two relations to which allusion was made above in relation to the Bohr theory of the H atom. Although these equations are not rigorous in their original form, they are in fact found to be approximately correct by the more accurate quantum-mechanical theory; the average or most probable distance between the nucleus and the electron replaces the exact radius of the circular orbit in the second equation. Taking these two relations together, we can conclude that the greater the ionization energy corresponding to a particular band, the larger the average distance from some nucleus of the remaining electrons. Because the second and third ionization energies of CH_4 are much larger than the ionization energy of atomic H but comparable with ionization energies of atomic C to known states of C^+, the nucleus with respect to which one must consider the average distances must be that of C. The implication is that, of the 10 electrons in the CH_4 molecule, only six are on the average about as close to the C nucleus as to any of the four H nuclei. In agreement with the lack of support for the attribution of eight "valence" electrons discussed just above, this conclusion is also entirely consistent with Pauling's (*20*) acceptance that the s^2p^2 atomic configuration of C is important, although this choice of electron description merely marks an initial stage of a prospective calculation.

Let us consider the calculation of the energy and structure of CH_4. The calculation is called *ab initio*—from first principles, even though the magnitudes of the charges of the nuclei and electrons and of the mass of the electron are in fact assumed to have experimental values. The process of the calculation then begins with the choice of basis functions, such as two 1s and four sp^3 hybridized atomic orbitals for the electrons contributed by the carbon atom and one 1s orbital for the electron contributed by each hydrogen atom. The next stage is the calculation of the self-consistent field for each electron according to the procedure due to Hartree and Fock, essentially as outlined above for the atomic calculation. When convergence is achieved, then the energy of the system is determined. If this process is repeated with variation of the relative nuclear positions (held fixed during the calculation according to the Born–Oppenheimer method), then the set of internuclear distances and interbond angles for which the energy is a minimum corresponds to the (Born–Oppenheimer) equilibrium molecular structure; alternatively the determination of the gradients of the energy with respect to internuclear distances and angles may also lead to the same ultimate structure. In this case the calculated structure corresponding to the minimum of energy is the regular tetrahedron with the distance about 1.1×10^{-10} m between the C and H nuclei. Such a computed bond length is roughly correct, but certainly not extremely accurate. Quantum-mechanical calculations are a valid and useful method for the prediction of molecular energies and, by means of the Born–Oppenheimer procedure, for the prediction of other molecular properties, among which the geometrical structural parameters are important. However, in those cases for which experimental data of high quality are available, the latter data are generally more accurate than the prediction. For instance, even for the small molecule HCl the best theoretical (*24*) value, 1.277×10^{-10} m, of the equilibrium internuclear separation differs from the experimental value, $(1.274603 \pm 0.000003) \times 10^{-10}$ m, derived from an analysis of spectra data (*25*) by about 800 times the experimental standard error (including that in the pertinent physical constants).

The important conclusion about such an ab initio calculation for methane is that, whether one assumes, in addition to the four 1s orbitals of the H atoms and the 1s orbital of C, four sp^3 tetrahedral hybrids, or three sp^2 trigonal hybrids plus one further 2p orbital, or two diagonal sp hybrids plus two further 2p orbitals, or one 2s and three 2p (unhybridized) atomic orbitals, precisely the *same* value of the energy and the *same* values of the geometric parameters define the equilibrium structure (*26*). This conclusion is true if one uses only a small basis set limited to the atomic orbitals that pertain to the ground-state description of the constituent atoms. A fortiori this conclusion is true at the Hartree–Fock limit attained by means of an augmented basis set sufficient to yield an exact solution of the Hartree–Fock equations for the self-consistent field. In other words, hybridization is at least irrelevant; moreover, the use of hybridized atomic orbitals in a (necessarily) approximate molecular calculation can even be a detriment as a result of error due to the neglect of certain terms (*26*). According to *Coulson's Valence* (*27a*), "hybridization is not a physical effect but merely a feature of [a] theoretical description"—hybridization is in the mind of the beholder! 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. For instance, in a recent edition of a popular textbook of physical chemistry (*28*), we find the argument "These four atomic orbitals may form sp^3 hybrids directed towards the corners of a regular tetrahedron. Therefore the structure of methane . . . is a regular tetrahedron"; in the latest edition, the question "Why is CH_4 tetrahedral?" once again evokes an answer by reference to orbitals and hybridization, although the causal relationship is not so succinctly stated. Gillespie (*29*) quoted an example of a textbook of general chemistry in which the author wrote that the structure of methane is tetrahedral because of sp^3 hybridization and a few pages later that the hybridization is known to be sp^3 because the structure is tetrahedral—a completely and explicitly circular argument! But is Atkins's argument (*28*) less circular because it is merely implicit? Again we quote from *Coulson's Valence* (*27b*): "It would be quite wrong to say that, for example, CH_4 was tetrahedral because the carbon atom was sp^3 hybridized. The equilibrium geometry of a molecule depends on energy and energy only . . . ". In a recent collection of papers to mark the anniversary of Pauling's paper (*3*), Cook (*30*) has agreed that "hybridization cannot explain the shapes of molecules". He also argued that "hybridization is not arbitrary" and is "something which happens"; the former attribute is logically meaningful only within the valence-bond approach to the solution of the Schrodinger equation within the coordinate representation—obviously a parochial context, and the mysterious connotation of time in the latter description is an obvious mistake.

How then can we know that methane has a tetrahedral structure? van't Hoff and Le Bel inferred that shape in 1874 from chemical information. The structure deduced from electron diffraction experiments is fully consistent with that conclusion. Finally we may do calculations of the so-called ab initio kind that also yield that result, regardless of the nature of the basis set of one-electron functions (orbitals) that is chosen as the starting point, within sensible limits as described above. Such computations may even be done directly by means of electron densities and the Schrodinger equation, without invoking orbitals[4] as a starting point (*32*). We emphasize that orbitals *have no physical existence;* they are merely mathematical functions according to one particular approach (i.e., namely wave mechanics, within its coordinate representation) to the mathematical solution, by ana-

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[4] For many years "molecular-orbital" calculations have been done without the use of atomic orbitals as basis functions, but the functions of the Gaussian type (*31*) that have been used—for convenience of evaluation of integrals—have been chosen in sets essentially to mimic atomic orbitals, even though in only some restricted region of internuclear separation.

lytic or numerical means, of a particular differential equation. In other words, there are no such *things* as orbitals. Again in quotation from *Coulson's Valence* (*27c*), "... orbitals do not exist! They are artifacts of a particular theory, based on an independent particle model ... ", that is, based on nonrepelling electrons. For this reason also, we have refrained from the interpretation of photoelectron spectra as involving the ionization of electrons from (or even associated with) particular molecular orbitals, despite the widespread practice of this fallacy (for instance, *4*, *33*).

Similarly, the classification of electrons as bonding, nonbonding, or antibonding is a logical fallacy, because electrons are fundamentally indistinguishable. Careful computations of the electron density in molecules have been made; the objective was to determine whether electrons may be considered to be "localized". The essential idea is that one might specify within molecules a certain region of space, called a loge (*34*), in which to find one, but only one, pair of electrons has a large probability. If such a loge were located centrally between two nuclei, then it would correspond to a pair of bonding electrons; if it were near a particular nucleus or situated of the order of half a bond length from a nucleus but in a direction away from other nuclei, then it might be considered a nonbonding pair, classified as core or lone pair, respectively. Although the criteria of localization produced somewhat distinct regions of bonding and nonbonding pairs in BH (*34*) and BH_4^- (*35*), in CH_4, NH_3, H_2O, and HF the electrons were found to be increasingly delocalized (*35*). Such details of the electron density were found (*36*) to be much more sensitive to the quality of the basis set than to the total energy (and therefore to any structural parameters deduced from the energy gradients); specifically, an increase in the quality of the basis set in general produced a decrease in localization. Although the presence, within a system of a photoelectron spectrum, of either extensive vibrational excitation or a large difference between the vertical (corresponding to the most intense line in the system) and adiabatic (at the onset of the system) ionization energies, has been commonly supposed to indicate the ionization of a, for instance, bonding electron, even the large ionization energies measured by means of X-rays for photoionization have accompanying vibrational structure (*23*); such a supposition leads unnecessarily to even "core" electrons being considered bonding (or possibly antibonding). Furthermore, because the formation of a cation from a neutral molecule is known to enhance delocalization of the remaining electrons (*37*), one must draw only with great care any deductions from a photoelectron spectrum that inherently involves an electronic transition from a neutral molecule to a cation. We conclude that the either experimental or computational evidence for localized electrons within a molecule is in general not strong, in particular not for CH_4.

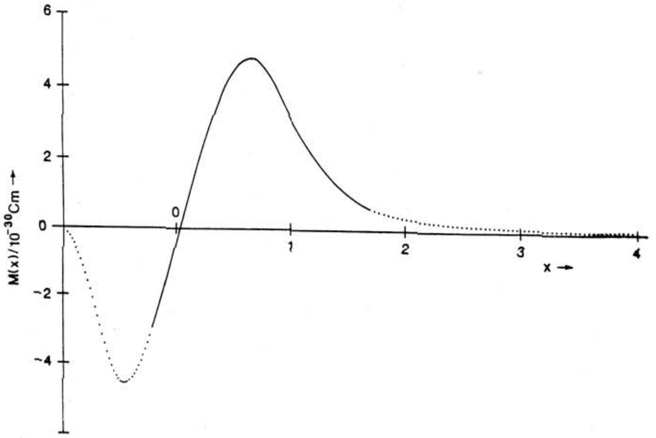
One enduring notion about the chemical bond has been that it is characterized by the accumulation of electronic charge in the region between the nuclei. Recent accurate measurements (*38*) of electronic density be means of X-ray crystallography have indicated that such an accumulation may not in every case accompany bond formation. Whether such a conclusion is also required by the results of calculations in which multiple "bent bonds" between the carbon atomic centers in FCCF (*39*) and C_6H_6 (*40*) and between the C and O atomic centers in CO_2 (*41*) are found to be favored over the conventional "sigma" and "pi" description remains to be seen.

Electronegativity

The concept of electronegativity (*2*) was introduced by Pauling to signify the power of an atom to attract electrons. Thus one might reasonably expect that the difference, if not too small, of electronegativities of two atoms might reliably indicate the relative electric polarity with respect to the internuclear vector of a diatomic molecule containing these same atomic centers. As electronegativity is not a directly measurable quantity, such as ionization energy or electron affinity, different definitions (*27*) give rise to different scales. Some scales are based directly on a combination of measurable properties, but the scale due to Hinze et al. (*42*) depends on hybridization—one arbitrary quantity based on another! Of the several different scales of electronegativity that now exist (*27*), all appear to concur that the difference between the electronegativities of C and O atoms is moderately large, about one-third that between those of Li and F, with O being more electronegative than C. Therefore, one might be misled to expect the polarity of CO in its most stable electronic state to be in the sense $^+CO^-$, but the experimental evidence (*43*) for the ground state unequivocally indicates $^-CO^+$; similar anomalies exist for other molecules. In fact the magnitude of the electric dipole moment of CO at its equilibrium internuclear separation is comparatively small, only about 3×10^{-31} C m; the variation of the dipole moment with internuclear distance is, however, somewhat complicated. Unlike the dipole-moment functions of the hydrogen halides that have a single maximum near the equilibrium distance R_e (*44*), the function of CO displays two extrema (*45*), shown in the figure. At internuclear distances R larger than R_e, the polarity is $^+CO^-$, whereas at $R \ll R_e$ the polarity is $^-CO^+$, with the dipole moment approaching zero toward both limits of the united atom (Si) and the separate (C and O) atoms. 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?

Further Aspects of Molecular Structure

Excluding from our consideration electronically excited molecules (*46*), there exist in their ground electronic states (*47*) some stable molecules that lack the rigidity taken to characterize molecular structure, apart from less stable molecules (complexes) such as H_2Ar within which the H_2 moiety seems to rotate almost freely. Some instances of stable molecules are NH_3, classified according to the Born–Oppenheimer method to be pyramidal even though (classically) it passes through the (average) planar conformation between opposite pyramids 10^9 times per second; PF_5 and $Fe(CO)_5$, which have nominally distinct equatorial and axial bonds to the central atomic center but which interchange these bonds fairly rapidly (pseudo-rotation); XeF_6, which seems to have a structure describable only as a distorted octahedron; and bullvalene $C_{10}H_{10}$, which at 373 K shows by both ^1H- and ^{13}C-nuclear magnetic resonance spectroscopy that all the H



The electric dipole-moment function of CO in the ground electronic state; the full curve represents the function defined by experimental data, and the dotted curve represents the theoretically inferred approach to the known limits; $x \equiv (R - R_e)/R_e$.

atomic centers are structurally equivalent to each other and all the C atomic centers are in turn structurally equivalent to each other; the latter property is unexpected from the nominal formula with a tricyclic structure based on cycloheptadiene. Quantum-mechanical calculations of these structures and the associated molecular properties made in accordance with the Born–Oppenheimer method may produce misleading results. An attempt *(48)* to surpass the limitations of the Born–Oppenheimer approximation in a calculation of the structure of NH_3 using "orbitals" for the protons as well as the electrons led to the interesting (and physically meaningful) result that the structure was planar, but with a large amplitude of vibration of the protons perpendicular to the plane; there may have been flaws in the computational procedure, but a corrected calculation seems never to have been undertaken. On the other hand, it may be possible to use spatial distributions for protons while continuing to implement the Born–Oppenheimer procedure. The conditions according to which the Born–Oppenheimer approximation is most valid are clear, namely for ground or other electronic states of diatomic molecules separated by relatively large differences of energy from adjacent states; in these cases the adiabatic and nonadiabatic corrections to the Born–Oppenheimer potential energy may be relatively small *(49)*. Conversely, the approximation is of questionable validity in the following conditions: for electronically excited states of polyatomic molecules not well isolated; for "transition structures", which are not true eigenstates at all; for stable ground electronic states near the dissociation limit (and therefore necessarily having energies close to those of other electronic states); for states having both potentially high symmetry and degeneracy as a result of net orbital angular momentum (giving rise to first- and second-order Jahn–Teller effects); and for exotic molecules containing particles of mass smaller than that of the proton.

According to rigorous quantum mechanics, a molecule lacks extension in space or time *(6, 46, 50, 51)*; if a description of a given experiment uses molecular eigenstates, then no structural interpretation is possible. When in the course of a molecular quantum-mechanical calculation taken to completion the integrations are done over the coordinates of all the constituent particles (both electrons and nuclei), the result of the calculation is only an energy. The existence *(6)* of classical properties, such as molecular structure or shape, is in direct contradiction to the superposition principle of pioneer quantum mechanics. Being a classical concept, molecular structure is thus extraneous to pioneer quantum mechanics *(6)*. Therefore, to seek a quantum-mechanical explanation of molecular structure is logically inconsistent. Which is more important to the chemist, quantum mechanics or the concept of molecular structure? Furthermore, although a probability distribution of nuclear positions—or even electronic positions—relative to a set of axes fixed in the molecule may be determined by means of some appropriate quantum-mechanical calculation, we must take care to distinguish, in the nuclear case, between such a probability distribution and the molecular structure according to the classical idea *(46)*.

Because molecular structure is a classical concept, the structure of molecules and crystals may be experimentally determined by purely classical means. In the experiments of electron diffraction of gases at small densities, or X-ray diffraction of suitable crystals, or of neutron diffraction of crystals (in the absence of anomalous magnetic effects), no information whatsoever about the quantum numbers pertaining to the diffracting objects is obtained. In fact, the electron density probed by X-rays and the field of the electrical potential sensed by diffracted electrons are characteristic of continuous distributions of matter with local maxima and minima. Molecular spectroscopy, well known to be a powerful experimental method for the determination of molecular structure, has been considered by some authors to be "experimental quantum chemistry", but a careful analysis of the content of such discussions reveals that the essential quantum nature is a consequence of the quantum *laws* specified above, rather than any particular quantum *theory*. To be precise, for stable molecules the structural information (geometrical parameters) from molecular spectra is deduced almost entirely from the rotational fine structure; the associated attribution of moments of inertia to a molecule is, however, an entirely classical concept *(50)*.

Let us consider briefly diatomic molecules in which the nature of the structural deductions is most clear. A quantitative analytic theory to take account of all the effects *(52)* observable within a particular electronic state has been developed *(47)*. Three different approaches to the derivation of the algebraic expressions in this theory have been developed: classical mechanics using Fourier series, of course assuming the quantum *laws* of discrete energy states, etc.; quasiclassical mechanics using the action integrals of Bohr's quantum theory,[5] as extended by Wilson and Sommerfeld, in the formalism due to Jeffries, Brillouin, Kramers, and Wentzel; and a formal quantum-mechanical approach, specifically through Rayleigh–Schrodinger perturbation theory, of course assuming the Born–Oppenheimer separation of electronic and nuclear motions. The notable feature of these three different methods is that they each yield the same results *(47)* in analytic form.[6] In other words, in order to provide a quantitative treatment of vibration-rotational energies from which can be derived the structural information desired by chemists, quantum mechanics is unnecessary. One might almost have anticipated this result, because 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. In contrast, no quantitative physical theory of electronic spectra of molecules, diatomic or polyatomic, has been developed, although methods to calculate the required properties are certainly practiced.

Because molecular structure is a classical concept, we might seek classical theories to describe it. One such classical theory, to which reference is commonly made according to the initials of its name the "*V*alence-*S*hell *E*lectron-*P*air *R*epulsion" theory owes its development *(27)* to Sidgwick, Powell, Gillespie, and Nyholm. Not only are its predictions prone to error, but also—and more importantly—its basic premises of more or less equivalent localized electrons as lone or bonding pairs are not justified; the reasons have in general been discussed above. After a quantitative assessment of the foundations of this theory, Roeggen *(53)* concluded that "the VSEPR model can no longer be considered a valid framework for the discussion of molecular equilibrium geometries". To find a more acceptable classical theory of molecular structure remains a challenge to the ingenuity of chemists.

Implications for Chemical Education

In the preceding sections, we have discussed the fundamental principles of quantum mechanics, the laws and the theories, and then the relationship of quantum-mechanical methods to atomic and molecular structure. These concepts

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[5] For this reason, the old quantum theory, that is, the one due to Bohr, Wilson, and Sommerfeld, is worthy of inclusion in courses on quantum mechanics in chemistry and physics but not in general chemistry in relation to the H atom or spectrum.

[6] Agreement is exact for at least the leading terms; some differences in higher order terms are found between the classical method and the other two (which, however, agree completely with one another to all orders), but the classical formulation has not been refined sufficiently to permit a decision whether these differences need to exist *(47)*.

have relevance to the ways that all chemists think about their subject, but naturally the implications of these topics are most significant for chemical education. Here we proceed to draw some conclusions about the relevance of quantum mechanics, quantum-mechanical methods and their properties and attributes to the teaching of chemistry. In so proceeding, we must distinguish between molecules and materials so as to avoid a *category fallacy*. Molecules and substances belong to categories of different logical types, as do analogously molecules and mathematical functions such as orbitals; as Primas has argued (*6*), a category fallacy results when categories of different logical types are treated on a par.

Formally a molecule consists of only electrons and nuclei, certainly not orbitals or even atoms (*17*). The properties of charge densities calculated by means of the molecular-orbital approach have been used (*54*) to define an "atom". Evidently such a hydrogen "atom" in HF has properties (size, electronic charge, etc.) greatly different from those of the H "atom" in LiH or even from those of one of the four purported to be in CH_4; each is far from sharing the well-documented spectral properties of the free H atom. Clearly it would be preferable to devise a name other than atom for such portions of molecules so as not to distort the meaning of a well-established term. In isolated conditions (within the gaseous phase at small densities) stable molecules may exist in quantum states. In dense phases (compressed gases, liquids or solids), by definition free molecules no longer exist, but, if the intermolecular interactions are relatively weak, then some properties, such as spectroscopic, of these phases may resemble to some extent those either measured for the ensembles of free molecules in dilute gases or calculated by so-called ab initio methods. When we make certain types of measurements, such as spectral, on sufficiently dilute gases, then to a useful approximation we may take the measurements to relate directly to molecular properties; for other types of measurements or for less dilute conditions, then the measured property pertains to the aggregate or medium, the totality of all the interacting nuclei and their electrons, rather than to individual molecules. Moreover, as we make such spectral measurements on substances as a function of increasing density, the changes may seem to be continuous in the range from the dilute gaseous to the bulk liquid phase, for instance; this behavior should not be taken to imply logically that the material simply consists of the molecules on which we might practice our calculations. With the possible exception of atmospheric gases, almost all the matter on which chemists ply their craft belongs to the category of material rather than molecule, and therefore belongs outside the realm treated by the methods of, for instance, quantum mechanics or statistical mechanics. Thus just as there exist no atoms within molecules (*17*), in a certain sense there exist no molecules within dense materials. There are extreme cases of crystalline materials such as diamond or sodium chloride for which the nominal formula C or NaCl denotes the structural unit; in these cases the change of most physical or chemical properties from the dilute gaseous phase to the bulk solid is not gradual. There are further cases such as amorphous mixtures, polymeric materials, and solutions or suspensions in strongly polar solvents for which the molecular notion is quite inapplicable. Even though we might develop some approximate procedure (because of simplifications, much more approximate in principle than the ab initio methods for small molecules) in order to make calculations on models of condensed phases, we should expect that any predictions of effects applicable to the surface, or even to irregular portions of the interior, may be inherently unreliable. In their obsession with the molecule, many chemists, especially chemical educators, have lost sight of the chemical reality of the material world in which we exist.

What then is the status of the chemical bond in 1990? We know what it is not: it is not a stick between two balls as the organic chemists of the 19th century might have imagined. It is certainly not orbitals; how can the cause of an observable property of a *physical* object be a *mathematical* artifact, such as the solution of a certain differential equation? In particular, an equation as singularly flawed as that due to Schrodinger, lacking, as it does, direct provision for electron spin and other relativistic effects, is objectively unattractive. Even Schrodinger himself admitted "rather lamely, [that he could not] see how . . . to account for particle tracks in track chambers, nor, more generally, for the definiteness, the particularity, of the world of experience, as compared with the indefiniteness, the waviness, of the wavefunction" (*55*). From a more chemical point of view—but intimately related to the same problem, is it intellectually satisfying to the reader (certainly not to this author) to be informed (*56*) that "planarity at N in di- and trisilylamines has been correlated with (p → d) pi-bonding from N to Si", especially because the primary evidence for such (p → d) pi-bonding is the selfsame planarity—another circular argument? Moreover, from the evidence of both photoelectron spectra and the results of quantum computations, the chemical bond, at least in the case of methane, appears not even to be necessarily associated with one (or more) pair of electrons, according to the prequantal model of Lewis and Langmuir. If we know what the nature of the chemical bond is not, can we state what the nature is? Of course we know in general that the chemical bond reflects electrical forces originating from small charged particles of which the coordinates and momenta may be subject to the commutation law. The chemical bond exists to some extent in all neutral diatomic molecules from the most weakly bound He_2 (which may have not even a single bound vibrational state in its ground electronic state) to the most strongly bound CO. Does it matter what is the nature of the chemical bond? What is of great importance to chemists is the substance of not the words, "The nature of the chemical bond", beginning the title of Pauling's paper (*1*) but the final words, "the structure of molecules" and also of matter. Since 1928 we have developed powerful experimental methods to determine the structure of molecules and matter, for instance by diffraction, microscopy, and spectroscopy. We have at the same time developed powerful mathematical algorithms to calculate such structure that like the experimental methods suffer however from limits of accuracy and applicability. All these methods permit us to exploit the many and diverse chemical properties and reactions the study and application of which make chemistry both fascinating and useful.

Why do we say that the CH_4 molecule has a tetrahedral structure? The reason must be that the experimental evidence clearly yields that result; our computations, applicable to and accurate for such a simple system, also concur in that structure, providing that experiment has directly or indirectly supplied that evidence. In a thoughtful essay titled "The invincible ignorance of science", Pippard (*57*) has pointed out that even a single helium atom cannot be predicted purely mathematically from the starting point of two protons, two neutrons, and two electrons. Why do we then tolerate the myth, expressed according to Primas (*6*) as "We can calculate everything", that the Schrodinger equation, leading to orbitals, the misleading aufbau principle, etc., is the fundamental basis of chemistry?

Traditionally, the prototypical reaction to illustrate first-order chemical kinetics is, paradoxically, not primarily a chemical reaction at all but rather the radioactive decay of some unstable nucleus. This decay has been tested experimentally (*58*) over half-lives having a very broad range, namely 0.01–45. Throughout this range no deviation was found from the exponential decay characterized by Rutherford (*59*). However, this exponential behavior is formally incompatible with quantum mechanics (*60*). Which is more important to chemists, the quantum-mechanical theories of the universe or the laws of chemical kinetics that account for the real behavior of chemically reacting systems?

Why has CH_4 a tetrahedral structure? Why does our solar system contain about nine planets? These are theological questions, thus extrascientific. In the middle ages in Europe, learned philosophers (theologians) are alleged to have debated how many angels could dance on the head of a pin; at a conference I have heard famous chemists disputing whether a certain structural effect in a transition-metal compound was due more to "pi donation" or to "back donation into d orbitals". In 1723 Jonathan Swift chronicled a fabulous voyage of one Lemuel Gulliver to Balnibarbi where he observed speculative research in many varieties; in the past 60 years innumerable chemists have attributed all kinds of chemical and physical phenomena to (nonexistent) orbitals. Is the progress of science an illusion?

Chemistry is not only a science of molecules but also a science of materials. Chemistry is the only basic science to constitute the foundation of a major secondary industry. Chemistry owes its importance in the modern community to its materials, not to its molecules. All the space devoted to orbitals, aufbau principle, hybridization, electronegativity, resonance, sigma and pi bonds, hyperconjugation, HOMO, LUMO, inductive and mesomeric effects, and other excess baggage of that ilk that burdens the textbooks of general, inorganic, organic, and (even) physical chemistry, and the corresponding proportion of the curriculum and time in lecture and tutorial classes, detracts from more instructive and accurate content about chemical reactions, chemical substances, and mixtures as materials. The conspiracy interpretation[7] of quantum mechanics to which Condon (*7b*) referred has its analogue currently in the infatuation of many academic chemists with orbitals. Clearly the authors of textbooks perpetrate myths such as that the structure of methane is tetrahedral because of sp^3 hybridization, and similar fallacies, not because they understand quantum mechanics but because they lack this understanding. The readers of these textbooks, be they professors or students, duly perpetuate and augment the same fictions because they apparently constitute the current paradigm in chemistry. Like the legendary emperor who displayed his newest suit of a material so fine as to be invisible, the authors and professors (teachers) who naively parrot these old untruths succeed only in exposing their ignorance. What I have tried to do in this essay is to present a reason for the change of our thinking about the teaching of chemistry away from atoms and orbitals. In this endeavor, I share similar concerns with Bent (*61*, *62*) and others who have recently expressed their dissatisfaction with the current approach, but I have further attempted to demonstrate the fallacious foundations of this approach. "Quantum chemistry" or the quantitative and mathematical quantum-mechanical theory applied to molecular structure and properties is unnecessary and irrelevant in the general undergraduate curriculum in chemistry, at least in the compulsory component. The qualitative ("hand-waving") explanations of molecular structure and reactions based on orbitals and such ilk are not science (i.e., are nonsense) and should consequently be completely discarded. Instead the effort of chemical educators should be expended to demonstrate the myriad chemical substances and properties of real matter that make chemistry, the science of materials as well as molecules, the central science in our present world.

Coda

Poor Wilhelmy! The reader may recall that in 1850 Ludwig Ferdinand Wilhelmy conducted perhaps the first experiment in quantitative chemical kinetics (*63*). His experiment, which many chemists have since repeated in the practical laboratory for undergraduate physical chemistry, consisted of measurement with time of the change of the angle of optical rotation of linearly polarized light passed through an acidic aqueous solution of sucrose as it "inverted" to glucose and fructose. Many authors of textbooks of physical chemistry now decree that the study of quantum mechanics must precede chemical kinetics, presumably so that chemical dynamics, the time evolution of quantum states related to simple atomic and molecular processes applicable in the gaseous phase at very small pressures, can form a basis for the study of the kinetics of chemical change under more common or macroscopic conditions. So, following this absurd regimen, Wilhelmy would have to wait 75 years for the discovery of pioneer quantum mechanics before he could perform his experiment. But alas, poor Wilhelmy! Pioneer quantum mechanics provides no explanation of optical activity—for that quantum electrodynamics (*64*) is required, although omitted from those textbooks. So Wilhelmy would still be waiting.

Appendix: Interpretation of Photoelectron Spectra

We have already noted that free (i.e., as in a dilute gas) but confined stable molecules may exist in states of discrete energy, consisting principally of translational, rotational, vibrational, and electronic contributions. We may suppose that for a stable, neutral molecule there exists in general some manifold of electronic states. Some excited states of this molecule, having energies greater than the minimum energy to ionize the molecule, may correspond to states of the molecular cation.[8] In typical experiments of photoelectron spectroscopy, transitions occur between some electronic state of the neutral molecule, commonly only the ground electronic state, and various electronic states of the molecular cation. Ionization is effected by means of absorption of a photon of energy greater than the molecular ionization energy. One applies the law of conservation of energy to account for the photonic energy as the sum of several terms: the measured kinetic energy of the ejected electron, the minimum energy to effect molecular ionization, the vibrational and electronic energy of the cation, relative to the ground (rotational, vibrational, and electronic) state of the neutral molecule, and the rotational and translational energy of the cation, which are commonly negligible. So far this mode is quite general and yields no insight into the electronic structure of the neutral molecule.

To proceed further, we consider that, although all electrons in a molecule are identical and indistinguishable, there exist bands of energies having negative values (with respect to the molecular cation of minimum internal energy infinitely separated from an electron, both particles being at rest). Such bands are well established in the interpretation of conducting and semiconducting crystalline phases, but for a free molecule a band consists of energies within only a narrow range. Then the photoelectron spectrum can indicate the number of these energy bands by the number of distinct processes (separate transitions or systems) leading to a singly ionized molecule. In the spectrum of H_2, one observes only a single system, consisting of a progression with successive vibrational excitation of the cation H_2^+ (and in this case also showing (*21*) resolvable rotational excitation), thus denoting the existence of only one significantly stable electronic state of H_2^+; the adiabatic ionization energy, correspond-

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[7] "Perhaps the mood was best summed up by Bergen Davis (1869–1958). . . who commented on quantum mechanics in the spring of 1928 that, 'I don't think you young [physicists] understand it any better than I do, but you all stick together and say the same thing.' This has been called the conspiracy interpretation of quantum mechanics." (*7b*).

[8] In recent years many experiments, for instance by microwave and infrared spectroscopy, have been made directly on such cationic molecules, like CO^+, OH^+ and HCO^+, permitting one to characterize these species and to determine accurately the parameters that describe their geometric structure. In fact the ions HCO^+, H_3O^+, OH^- among others exist to a significant extent in hydrocarbon flames on the common Bunsen burner, for instance.

ing to the transition from the vibrational ground state $v'' = 0$ in H_2 to its counterpart $v' = 0$ in H_2^+, is slightly greater than the ionization energy of the H atom. In this case, we associate both electrons of the H_2 molecule with the same energy band. However, one should note that the association of energy bands, in molecules containing more electrons than two, with particular electrons would be as great a fallacy as association of electrons with particular orbitals (mathematical functions). Instead one can simply use the number of distinct transitions as a measure of the number of energy bands. One can, however, compare the energy of a given band of the molecule with the corresponding ionization energies of the separate constituent atoms; appreciable changes of these energies upon molecule formation indicate significant alteration of the electron distribution in the region of the corresponding nucleus. By this means we can interpret those photoelectron spectra that are reasonably free of complications related to secondary processes following photoionization.

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Literature Cited

1. Pauling, L. C. *J. Am. Chem. Soc.* **1931,** *53*, 1367–1400.
2. Pauling, L. C. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960.
3. Pauling, L. C. *Proc. Nat. Acad. Sci. U.S.A.* **1928,** *14*, 359–362.
4. McQuarrie, D. A. *Quantum Chemistry;* Oxford University: Oxford, 1983; p 360.
5. Duff, D. G. *Chem. Brit.* **1987,** *23*, 350–354.
6. Primas, H. *Chemistry, Quantum Mechanics and Reductionism*, 2nd ed.; Springer: Berlin, 1983.
7. Condon, E. U.; Odabasi, H. *Atomic Structure;* Cambridge University: Cambridge, 1980; (a) p 64; (b) p 68.
8. Heisenberg, W. *Z. Phys.* **1925,** *33*, 879–893.
9. Dirac, P. A. M. *Proc. Roy. Soc. London* **1925,** *A109*, 642–653.
10. Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics*, 3rd ed.; Pergamon: London, 1977.
11. Dirac, P. A. M. *Principles of Quantum Mechanics*, 4th ed.; Oxford University: Oxford, 1958; (a) p 94; (b) p 283; (c) p 253; (d) p 136.
12. Bloch, F. *Phys. Today* **1976,** *29* (12), 23–27.
13. Chang, C.; Pelissier, M.; Durand, P. *Phys. Scripta* **1986,** *34*, 394–404.
14. Jordan, T. F. *Quantum Mechanics in Simple Matrix Form;* Wiley: New York, 1986. The elegant exposition of the ideas in this book should dispel the inaccurate notion that matrix mechanics is of limited applicability or excessively complicated.
15. Born, M.; Oppenheimer, J. R. *Ann. Phys. Leigzig* **1927,** *84*, 457–484.
16. Mulliken, R. S. *Science* **1967,** *157*, 13–24.
17. Adams, W. H.; Clayton, M. M. *Int. J. Quantum Chem. Symp.* **1986,** *S19*, 333–348.
18. Millikan, R. C. *J. Chem. Educ.* **1982,** *59*, 757.
19. Goldman, S. P.; Dalgarno, A. *Phys. Rev. Lett.* **1986,** *57*, 408–411.
20. Pauling, L. C. *J. Chem. Phys.* **1983,** *78*, 3346.
21. Asbrink, L. *Chem. Phys. Lett.* **1970,** *7*, 549–552.
22. Potts, A. W.; Price, W. C. *Proc. Roy. Soc. London* **1973,** *A326*, 165–179.
23. Gelius, U.; Svensson, S.; Siegbahn, H.; Basilier, E. *Chem. Phys. Lett.* **1974,** *28*, 1–7.
24. Wright, J. S.; Buenker, R. J. *J. Chem. Phys.* **1985,** *83*, 4059–4068.
25. Coxon, J. A.; Ogilvie, J. F. *J. Chem. Soc. Faraday Trans. II* **1982,** *78*, 1345–1362.
26. Murrell, J. N.; Kettle, S. F. A.; Tedder, J. M. *The Chemical Bond;* Wiley: New York, 1978; pp 138–140.
27. McWeeny, R. *Coulson's Valence;* Oxford University: Oxford, 1979; (a) p 150; (b) p 213; (c) p 144.
28. Atkins, P. W. *Physical Chemistry*, 2nd and 3rd eds.; Oxford University: Oxford, 1982 and 1986.
29. Gillespie, R. J. *Chem. Can.* **1976,** *28* (11), 23–28.
30. Cooke, D. B. *J. Mol. Struct.* **1988,** *169*, 79–93.
31. Boys, S. F. *Proc. Roy. Soc. London* **1950,** *A200*, 542–554.
32. Yang, W. *Phys. Rev. Lett.* **1987,** *59*, 1569–1572; *Phys. Rev.* **1988,** *A38*, 5494–5503.
33. Eland, J. H. D. *Photoelectron Spectroscopy*, 2nd ed.; Butterworths: London, 1984.
34. Daudel, R.; Stephens, M. E.; Burke, L. A.; Leroy, G. E. *Chem. Phys. Lett.* **1977,** *52*, 426–430.
35. Bader, R. W. F.; Stephens, M. E. *J. Am. Chem. Soc.* **1975,** *97*, 7391–7399.
36. Mezey, P. G.; Daudel, R.; Czismadia, I. G. *Int. J. Quantum Chem.* **1979,** *16*, 1009–1019.
37. Daudel, R. In *Localization and Delocalization in Quantum Chemistry;* Chalvet, O.; Daudel, R.; Diner, S., Eds.; Reidel: Dordrecht, Holland, 1976; Vol. 2, pp 3–14.
38. Dunitz, J. D.; Seiler, P. *J. Am. Chem. Soc.* **1983,** *105*, 7056–7058.
39. Messmer, R. P.; Schultz, P. A. *Phys. Rev. Lett.* **1986,** *57*, 2653–2656.
40. Schultz, P. A.; Messmer, R. P. *Phys. Rev. Lett.* **1987,** *58*, 2416–2419.
41. Messmer, R. P.; Schultz, P. A.; Tatar, R. C.; Freund, H. J. *Chem. Phys. Lett.* **1986,** *126*, 176–180.
42. Hinze, J.; Whitehead, M. A.; Jaffe, H. H. *J. Am. Chem. Soc.* **1963;** *85*, 148–157.
43. Townes, C. H.; Dousmanis, G. C.; White, R. L.; Schwarz, R. F. *Discussion Faraday Soc.* **1954,** *19*, 56–64.
44. Ogilvie, J. F.; Rodwell, W. R.; Tipping, R. H. *J. Chem. Phys.* **1980,** *73*, 5221–5229.
45. Kirschner, S. M.; Le Roy, R. J.; Tipping, R. H.; Ogilvie, J. F. *J. Mol. Spectrosc.* **1977,** *65*, 306–312.
46. Woolley, R. G. *Chem. Phys. Lett.* **1986,** *125*, 200–205, and references therein.
47. Ogilvie, J. F. *Int. Rev. Phys. Chem.* **1986,** *5*, 197–201; Tipping, R. H.; Ogilvie, J. F. *Chin. J. Phys.*, in press.
48. Thomas, I. L. *Phys. Rev.* **1969,** *185*, 90–94.
49. Ogilvie, J. F. *Chem. Phys. Lett.* **1987,** *140*, 506–511, and references therein.
50. Woolley, R. G. *Adv. Phys.* **1976,** *25*, 27–52.
51. Woolley, R. G. *J. Chem. Educ.* **1985,** *62*, 1082–1084.
52. Ogilvie, J. F. *J. Mol. Spectrosc.* **1988,** *128*, 216–220.
53. Roeggen, I. *J. Chem. Phys.* **1986,** *85*, 969–975.
54. Bader, R. F. W.; Nguyen–Dang, T. T. *Adv. Quantum Chem.* **1981,** *14*, 63–124.
55. Bell, J. S. *Speakable and Unspeakable in Quantum Mechanics;* Cambridge University: Cambridge, 1987.
56. Ebsworth, E. A. V. *Acc. Chem. Res.* **1987,** *20*, 295–301.
57. Pippard, A. B. *Contemp. Phys.* **1988,** *29*, 393–405.
58. Norman, E. B.; Gazes, S. B.; Crane, S. G.; Bennett, D. A. *Phys. Rev. Lett.* **1988,** *60*, 2246–2249.
59. Rutherford, E. *Sber. Akad. Wiss. Wien. Abt. 2A* **1911,** *120*, 300.
60. Greenland, P. T. *Nature*, **1988,** *335*, 298.
61. Bent, H. A. *J. Chem. Educ.* **1984,** *61*, 421–423.
62. Bent, H. A. *J. Chem. Educ.* **1986,** *63*, 878–879.
63. Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper and Row: New York, 1987.
64. Craig, D. P.; Thirunamachandran, T. *Molecular Quantum Electrodynamics—An Introduction to Radiation—Molecule Interactions;* Academic: London, 1984.

California Association of Chemistry Teachers
1990 Summer Conference

The theme of the 1990 Summer Conference sponsored by the California Association of Chemistry Teachers will be geochemistry for chemistry and earth science teachers. The conference will be held August 13–17 on the campus the College of Notre Dame in Belmont, California, on the San Francisco Bay peninsula. Richard Hazlett, Assistant Professor of Geology at Pomona College, will be the instructor of the short course, which will provide teachers with an introduction to the role of chemistry in describing and explaining volcanic activity, the formation of caverns and ore deposits (diamonds, oil, and other "earthly" treasures), and the origin of earth's air and seas. Teachers will participate in coordinated labs in the afternoons and take home their own home-grown "gems". In addition, the traditional textbook exhibit, general lectures, group discussions, idea exchange sessions, and social events will be part of the program. The Conference fee is $75 without credit or $125 with credit. Further information may be obtained from Mr. Leigh A. Wilson, Lynbrook High School, 1280 Johnson Ave., San Jose, CA 95129; (408) 366-7721.