THE NATURE OF THE CHEMICAL BOND 1993
There are no such *things* as orbitals!

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1 Introduction

Almost two decades ago a fairly senior biochemist consulted me about the interpretation of optical spectra of simple compounds in the ultraviolet region. After being educated in classical biochemistry in Britain he taught in a relatively isolated institution; he had evidently never become acquainted with the fundaments of quantum chemistry, even to the extent of solving by his own hand the most common such problem, the *particle in a one-dimensional box*. With the best of intentions he sought however to write a textbook on spectroscopy for students of biochemistry on the grounds that no adequate text existed; without hesitation (or comprehension) he was fully prepared to invoke 'orbitals' to explain these spectra and--who knows how many--other phenomena. Although I had previously entertained vague doubts about the conventional description of diverse chemical effects in terms of this panacea, that incident convinced me that the general understanding of quantum chemistry and its relation to macroscopic measurements on chemical, physical and biological systems left much to be desired. During the succeeding fifteen years I collected information from the chemical literature that I cumulatively presented in various lectures around the world; an essay appeared [1] eventually in the Journal of Chemical Education with essentially the same title as that above (apart from the date). That article generated much debate both private and public, according to further papers and letters to the editor of that journal and elsewhere. After a further few years without much improvement of the chronically unsatisfactory general understanding of quantum chemistry and its relationship to various phenomena especially as reflected in the teaching of chemistry, it appears worth while to renew the discussion by means of another explicit attack on ignorance and muddled thinking that the present unsatisfactory conditions in chemical education proclaim still to exist. Perhaps the title is misleading, as I claim no great success in solving the insoluble problem of the nature of the chemical bond--whatever that might be. Readers should understand at the outset that the subtitle is ostensibly a more accurate indication of the theme of my discussion than the title, although the two aspects are closely linked. Subject to that reservation, the following text before the epilogue is essentially a slightly revised restatement of the discussion previously published [1], to which I have added further illustrations pertinent to the theme arising from recent experience.

E. S. Kryachko and J. L. Calais (eds.), Conceptual Trends in Quantum Chemistry, 171–198.

In 1931 Pauling published a theory [2] that has during succeeding years had eat influence on the thinking of chemists. That paper, actually the first of seven der the general title *The Nature of the Chemical Bond*, was followed by a monograph] based on lectures at Cornell University, but the paper [2] refers to an earlier blication [4] under the title *The Shared-electron Chemical Bond* that was stated to ntain several original ideas greatly amplified and extended both in papers in the ries and within the monograph. The remainder of the title of the initial paper [2] of e series is *Application of Results Obtained from the Quantum Mechanics and from a heory of Paramagnetic Susceptibility to the Structure of Molecules*. During the veral decades since the appearance of the root paper [4], great advances in the nderstanding of properties of chemical substances have naturally resulted from all ree activities of chemists--experimental, theoretical and computational. Because mong the experiments spectral measurements of simple compounds under conditions f negligible intermolecular interactions have been especially important, we illuminate ur discussion with the interpretation of selected spectra. As a consequence of the arious developments, one can now critically appraise the ideas that were generated in e early days of the quantum era; during that period the hopes and wishes for a uantitative understanding of the fundamental bases of chemical structure and reactions xceeded the then current ability to test their correctness or objectivity.

In this essay we are concerned with three particular aspects of quantum echanics in modern chemistry, namely the fundamental structure of quantum echanics as a basis of chemical applications, the relationship of quantum mechanics to tomic and molecular structure and the consequent implications for chemical education. n so proceeding we adopt generally an historical perspective for the context of our resent state of development. We incorporate several original ideas and unfamiliar nterpretations as well as naturally to recall pertinent recent results from the research iterature. After we distinguish between quantum laws and quantum theories, we iscuss the most fundamental principles of quantum mechanics. Because chemists have een traditionally exposed to only one approach to quantum theory, they have become eluded about the generality of certain concepts, such as orbitals and electronegativity; he objective of the discussion of quantum theories is to distinguish what is fundamental rom what is artifact. The structure of the molecule methane occupies a central osition in the teaching of much chemistry; we contrast the qualitative and obsolescent deas with the more quantitative information now available from spectral easurements. Because photoelectron spectra have been asserted [5] to prove the *xistence* of molecular orbitals, we devote particular attention to an alternative nterpretation that we apply specifically to CH_4. As diatomic molecules are relatively imple systems, a fully quantitative analytic (algebraic) treatment of their spectral roperties is practicable; we cite evidence that structural information can be derived ust as well by approaches based on classical mechanics as by various quantal pproaches. With this basis we finally advocate a more intellectually honest approach to both the thinking of chemists and the teaching of chemistry that recognises chemistry to be not only a science of molecules but also a science of materials. A principal objective of all this discussion is a critical assessment of some qualitative concepts of quantum chemistry, such as atomic and molecular orbitals and electronegativity, that have evolved since Pauling's paper [4] to become engrained in the fabric of modern chemical education. Here we examine a few ideas in the context of their historical generation, naturally placing most emphasis upon both the most fundamental ideas and recent pertinent contributions.

2 Quantum Laws and Quantum Theories

A half century after Dalton's atomic hypothesis about 1807, Couper proposed [6] the first enduring notions about molecular structure, reinforced by Kekule, van't Hoff and Lebel within the next two decades. Thus was formed 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 diverse but based on a simple framework of a few chemical bonds about each atomic centre. During the nineteenth 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 between atomic centres was thus widely accepted by the end of the nineteenth century, the quantitative experimental proof had to await the twentieth century.

The dawn of this century coincided with the birth of the quantum era, initiated by Planck's explanation of the spectral distribution of radiant energy from a black body. The basic hypothesis was that light could be radiated not continuously but with energy only in integer multiples of $h\nu$. One can derive [7] Planck's law of radiation from classical statistical mechanics with no quantum assumption whatsoever; for this reason, even though quantum theories flourish, their historical foundation has been largely superseded [7]. We proceed to outline the quantum laws most significant for chemical purposes.

We summarise in the table some fundamental physical properties of molecules and photons. Free molecules may exist in states of quantised total energy but radiant energy exists in quanta called photons. A photon as the discrete unit of monochromatic radiation characterised by frequency ν, wavenumber $\tilde{\nu}$ and wavelength λ, related by $\nu = c\tilde{\nu} = c/\lambda$ in vacuo, has neither net electrical charge nor rest mass; its energy E follows from Planck's relation $E = h\nu$, h being Planck's constant and c being the speed of light in vacuo. The photon has both a definite linear momentum $|\mathbf{p}| = h/\lambda$ and a definite angular momentum $|\mathbf{J}| = h/2\pi = \hbar$, the latter quantity independent of λ or ν. In contrast, a free molecule may be electrically neutral or may carry a net electric charge in units of the protonic charge. Although no quantum theory so far known to chemists seems to require that molecular mass be quantised[*], that the mass of any known stable (enduring) molecule (of a specified isotopic composition) is almost an integer multiple of the mass of the hydrogen atom remains empirically without exception. Likewise the magnitude of the protonic charge lacks theoretical justification, but if a magnetic monopole exists then electric charge should be quantised [8]. The total energy of a molecule that can move freely within some confining but large space is the sum of

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[*] Although the equivalence of mass and energy recognised by Einstein has eliminated mass as a separately conserved quantity, for operations in the chemical laboratory the conservation of mass remains an exceedingly useful rule. The conservation of mass and energy collectively is formally preferable to that of either property separately.

Physical Properties of Molecules and Photons

property	molecule	photon
charge	$0, \pm 1\,e, \pm 2\,e, \ldots$	0
mass (at rest)	$M > 0$	0
total energy	$E \approx E_{tr} + E_{el} + E_{vi} + E_{rot}$	$E = h\nu$
linear momentum	$\lvert\mathbf{p}\rvert > 0$	$\lvert\mathbf{p}\rvert = h/\lambda$
angular momentum	$\lvert\mathbf{J}\rvert = [J(J+1)]^{\frac{1}{2}}$	$\lvert\mathbf{J}\rvert = \hbar$

discrete (but not rigorously separable) contributions arising from the translational motion of the centre of mass relative to a system of coordinates fixed in space, the nuclear motions vibrational and rotational about the centre of molecular mass, and the electronic motions about the nuclei; the quantum number pertaining to total angular momentum (apart from nuclear spin) has the symbol J. In the absence of strong electromagnetic fields molecules may exist in states having angular momenta equal to half an integer multiple of the reduced Planck constant $\hbar$ (h divided by 2π). Within a finite enclosure a free molecule exists in states of discrete linear momentum. Thus the quantities energy, linear and angular momentum, mass and charge that were the subjects of laws of conservation during the nineteenth century are recognised to be ultimately discrete or quantised at the microscopic level. We thus consider the experimental proof of the discreteness of these five quantities under appropriate conditions to constitute the quantum *laws* of nature.

The chemist Bjerrum in 1912 made the first attempt to construct a quantum *theory* of atoms or molecules in relation to the vibrational and rotational motions of diatomic molecules; to explain the then known infrared spectra this theory was unsuccessful. Based on Rutherford's model of the nuclear atom, Bohr's theory of the one-electron 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 centre of mass of the system of the two bodies) to integer values of Planck's constant led to the energy of the atom taking only values proportional to the inverse of the square of the same integer; the radius of the orbit was directly proportional to the square of this integer, the proportionality factor being (approximately) the Bohr radius a_o. We know now that the energy of the one-electron atom has practically no direct dependence on the state of angular momentum of the atom; hence the energy of such an atom having a particular value of the quantum number n for energy remains essentially degenerate for varied values of the quantum number l $(l < n)$ for orbital angular momentum. This apparent success of Bohr's theory thus depends on the fortuitous cancellation of two errors, namely circular orbits and the dependence of energy on the quantum number for angular momentum; one could scarcely wonder that the theory fails entirely to explain quantitatively the spectra or properties of atoms containing two or more electrons, or even the molecule H_2^+ having only one electron.

Enduring quantum theories began with the pioneer quantum mechanics [7] of Heisenberg and Schrodinger; created between 1922 and 1927, and digested between 1927 and 1933 during which period these procedures were applied to atoms and molecules by Heitler, London and Hellmann (among many others), these are generally the only quantum theories that chemists have encountered. After Born recognised [9a] the necessity for a mechanical theory, i.e. one that treats the positions and momenta of elementary particles, Heisenberg [10] discovered the property that these quantities can fail to commute; Dirac [11] immediately understood this condition to constitute 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, the subscript j or k denoting one of the axes x, y or z in a cartesian system for instance, then we write this fundamental principle of commutation in the compact form

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

here i means the square root of -1, and the Kronecker delta function δ_{jk} takes the value 1 if $j=k$ or 0 otherwise. Although it is well known (cf Landau and Lifshitz [12] for instance) that one can derive from this equation Heisenberg's principle of indeterminacy, that one can also derive the de Broglie relation $\lambda = h/p$ is less widely appreciated.* Although de Broglie postulated this relation in 1923, it was widely known only later. Learning of this relation in 1926, Debye commended [13] to Schrodinger the search for a wave equation to take account of the effects of a wave associated with a moving particle.

What kinds of quantities are subject to this failure to commute? Mere numbers are obviously exempt from such a restriction. Quantities of two kinds qualify, and each kind is the basis of pioneer quantum mechanics in one form. In general matrix multiplication is not commutative: Heisenberg, Born and Jordan developed matrix mechanics. An algebraic quantity x also fails to commute with the differential operator with respect to the same quantity, thus d/dx: on this basis Schrodinger developed wave mechanics. As we can choose to have a representation based on either the coordinate with the quantity q and the corresponding operator for momentum $-i\hbar d/dq$ or the momentum with the quantity p and the corresponding operator for position $i\hbar d/dp$, two approaches to wave mechanics are possible; typically the former is preferred because potential energy is generally expressed more readily in terms of position (coordinates) than in terms of momenta. The operands of the operators d/dp and d/dq must obviously be distinct functions and hence have dissimilar graphical representation. Despite the then known requirements of the theory of relativity, Schrodinger's equation dependent on time embodies derivatives that are of second order with respect to space coordinates but first order with respect to 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. Dirac [14b] concluded that Heisenberg's approach is more fundamental in the theory of quantised fields. Dirac [14c] described a third approach to quantum mechanics in terms of a relativistically correct wave equation containing matrices as coefficients of first derivatives with respect to both time and space coordinates; for the one-electron atom

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*The proof is implicit in Dirac's book [14a], to which we refer the reader for details of notation. We take as starting point the transformation function $<q|p>$ connecting the momentum and coordinate representations, in which $|p>$ are the basis kets of the momentum representation. In summary this transformation function must be the solution of the differential equation resulting from the replacement of p by the corresponding differential operator $-i\hbar d/dq$; hence $<q|p> \sim e^{2\pi ipq/h}$. 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.

this approach leads naturally to a fourth quantum number pertaining to 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 that contain two or more electrons the hamiltonian in Dirac's equation yields no true solutions for bound states [15]. Dirac also developed a further approach [14] in terms of operators for the processes of creation and destruction; these ladder operators apply not to mechanical variables but to energy states between which transitions may occur.

What we have endeavoured 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 pioneer quantum mechanics [7]; these, the matrix mechanics of Heisenberg, Born and Jordan and the wave mechanics of Schrodinger, are absolutely equivalent procedures for the solutions of certain problems and have therefore correspondingly equivalent limitations of applicability. By these means one can calculate approximate values of certain observable properties of, for instance, molecular systems. The unavoidable conclusion of the recognition that these two distinct methods are equivalent 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.

3 Application of quantum mechanics to atomic and molecular structure

Although in his first paper in the specified series [2] Pauling alluded to matrix mechanics, thereafter he, in common with almost all other chemists, ignored its existence, despite the fact [16] 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 the physicists Heitler and London 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 [17] that introduces into--indeed imposes upon--quantum mechanics the classical idea of molecular structure. Strongly influenced by the apparent success of that calculation on H_2 (the accuracy of the results was actually poor 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 ideas of resonance, and of hybridisation--the formation of linear combinations of atomic wavefunctions 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 distinct atomic centres. Mulliken invented the term orbital, defined in his review *Spectroscopy, Molecular Orbitals and Chemical Bonding* [18] with characteristic obfuscation as "something as much like an orbit as is possible in quantum mechanics". An orbital is precisely a mathematical function, specifically a solution of Schrodinger's equation for a system containing one electron, thus an atomic orbital for the atom H and a molecular orbital for H_2^+. Although the atomic wavefunctions are comparatively easy to use in calculations, the solutions for H_2^+ have in general a more complicated form; hence a linear combination of atomic functions on distinct centres serves as an approximation to a molecular orbital.

Before proceeding to consider molecules, we devote attention to the structure of atoms. First of all, we must understand clearly that no atom exists within a molecule [19], 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 independent of the utility of the approximation of atomic functions to construct molecular wavefunctions 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 centre. The periodic chart serves as a basis of classification of various chemical and physical properties of elementary chemical substances. Following many less successful attempts to classify chemical elements, Mendeleyev based his periodic chart on experimental evidence; chemical and physical properties are periodic as the atomic number is increased from unity, although there were of course recognised to exist more or less gradual trends or variations of properties within a given family or column of the chart. Based in part on the existence of these periodic properties of the chemical elements and in part on atomic spectra, Pauli had already in 1925 demonstrated the necessity for a quantum number for electronic spin beyond the three quantum numbers previously deduced from the analysis of atomic spectra [9]. A common approach in teaching the electronic configuration of atoms is based on the solutions of Schrodinger's equation for the one-electron atom. Even this conventional specification of such a configuration of an atom in terms of orbitals implies a representation based on artifacts within one calculational method--wave mechanics. In practising the *aufbau* procedure, we include this fourth quantum number in a way entirely *ad hoc* because Schrodinger was unable to render any account of this parameter in the solution of his wave equations, dependent or independent of time. If we associate chemical inertness and resistance to liquefaction with an electronic configuration known as a *closed shell*, we predict that an atom of the first three noble gases would contain 2, 10 or 28 electrons, hence corresponding to the elements helium, neon or nickel. Although the first two results are correct, clearly the prediction fails when the atomic number Z exceeds 10. The reason for this failure is the lack of account of interelectronic repulsion because the simple orbital picture of an atom (or molecule) is based on nonrepelling electrons, 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 typical discussions of the chemical bond. One may of course introduce rules *ad hoc* to correct for this drastic simplification, such as the $(n+l)$ or diagonal rule, but such rules have limited utility. In this regard Millikan [20] has described his generation of two computer programmes to reproduce the electronic configurations of the first 106 elements: one incorporates all the rules and exceptions, and the other is simply a list of the 'correct configurations' to fit available experimental evidence. Which programme was shorter (i.e. having the smaller number of statements (in BASIC)? The latter! Clearly recognised by Millikan [20], 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 according to any simple physical theory.

In contrast there have been developed methods to calculate atomic energies and the frequencies of spectral transitions. The procedure originated by 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 in turn each electron and calculating the average field of the remaining electrons; the wavefunction 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 resultant wavefunctions, and consequently the total (approximate) eigenfunction that is their product, are negligibly altered in consecutive iterations.* Under these conditions of the *self-consistent field*, the energy of the atomic system converges to a finite value. With the disregard of even relativistic effects, this value is inaccurate; 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 configurational interaction or the perturbational theory of many bodies. The important conclusion from this brief outline of a computational procedure is that, although one may start the calculation with a basis set of orbitals, the simple solutions of Schrodinger's equation for the one-electron atom, by the time that one attains the Hartree-Fock limit, or beyond, the nature of the initially chosen one-electron functions is irrelevant. Thus only at the beginning of the calculation, and even then only in a mathematical sense (within the context of a particular computational method), do the orbitals have any meaning.

A novel approach to the equations of Dirac, Hartree and Fock with the use of a finite basis set was claimed [21] 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 applications to systems with many electrons; this development would permit in principle the calculation of atomic and molecular properties that suffer from no neglect of relativistic effects (the variation of mass with velocity). Thereby chemists might have been enabled to escape from the (self-imposed) tyranny of Schrodinger's equation, but during the several years since this claim was announced little or no further progress has been reported. Thus the *philosopher's stone* for calculations of atomic and molecular structure is, so far, as elusive as its literal precursor to make gold from base metal.

Proceeding to consider molecular structure, we first define that this term signifies at least a fairly rigid arrangement of atomic nuclei (surrounded by their associated electrons) in space in three dimensions. There are of course several further aspects of molecular structure. Topology is concerned with the order of connection of the atomic centres. Conformation relates to the shape of the structure and to the relationship of one portion of the structure to other segments with intermediate atomic centres in a line of connectivity ('chemical bond'); the existence of structural and

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*Contrary to the impressions given in nearly all accounts of the procedure due to Hartree and Fock, all the electrons are fit simultaneously, not iteratively from one to the next. Moreover, for a system of N electrons and M basis functions (orbitals) one could solve Schrodinger's equation in one step by solving the problem of a matrix of size N^M; such a solution would automatically include configurational interaction. As for any molecule but the simplest the quantity $N^M \approx N^{2N}$ implies a large matrix, the approximation due to Hartree and Fock provides a more tractable starting point for the full computation.

rotational isomers is associated with conformational features. Configuration pertains in part to the spatial arrangement at chiral centres in molecules of compounds exhibiting optical activity (the ability of substances or their solutions to rotate the plane of linearly polarised light); the existence of enantiomers and diastereomers is associated with configurational features. To a chemist, the most meaningful geometric attributes of molecules are the distances between any pairs of nuclei, or equivalently the lengths of bonds (distances between nuclei or atomic centres considered to be connected by a chemical bond) and the angles between pairs of bonds sharing a common atomic centre. Further structural aspects include any quantity that may be represented as a function of distance with respect to nuclear coordinates; instances include the function for the potential energy, according to which the geometric structure represents values of the nuclear coordinates in a set for which the energy has somewhere 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 that for the electric dipolar moment, spin-orbital interaction etc.) that may be either determined directly according to theoretical calculation or evaluated indirectly from experimental data.

Because the study of diatomic molecules (those containing two atomic nuclei but obviously not two atoms) reveals less information about certain qualitative aspects of molecular and electronic structure than polyatomic molecules that appear to have some shape, we consider first methane (in its electronic ground state). In its equilibrium conformation, the molecule CH_4 has the shape of a regular tetrahedron; we mean that four planes, each defined by three hydrogen nuclei (at their equilibrium positions relative to the carbon nucleus) in a set, define a tetrahedron in three-dimensional space; the carbon nucleus is located at the geometric centre of the regular tetrahedron. That this structure implies sp^3 hybridisation is a common but fallacious assumption. (At this point let us state explicitly that such a description is valid only within the valence-bond model, in turn within the approximation of non-repelling electrons treated according to Schrodinger's equation, thus only within wave mechanics, and specifically the latter within the coordinate representation.) This notion of sp^3 hybridisation persists despite Pauling's acceptance [3,22] that such a description is inaccurate even within the narrow confines of the model just specified. Chemists have been long accustomed to believe that a molecule of methane contains four equivalent C-H bonds; according to a tradition also of long standing with each bond is associated one pair of electrons to which the connected atomic centres each contribute generally one electron. Is there experimental evidence pertinent to the latter attribute? Before one attempts to seek to answer this question, one must understand that a molecule of methane contains ten electrons that are fundamentally 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 to interpret data from such an experiment, illustrated by reference to the spectrum of H_2.

In examining the photoelectron spectrum of CH_4 in its entire range, we find three distinct systems [23, 24], corresponding to adiabatic (first) ionisation energies $/10^{-18}$ J about 2.0, 3.6 and 47.6. From the presence in the first region of three overlapping features, one deduces that CH_4^+ in its electronic ground state is subject to a

Jahn-Teller distortion which removes the degeneracy that would otherwise exist if the regular tetrahedral equilibrium conformation of the electronic ground state of the neutral molecule CH_4 were retained. The diffuse vibrational structure excitation of the overlapping components extends through the region $(2.0\text{-}2.6)\times10^{-18}$ J. The ionisation energy in this range is comparable with the first ionisation energies of both C and H atoms. The energy of the transition indicated by the second system, in the region $(3.6\text{-}3.9)\times10^{-18}$ J, is similar to the energy of the first excited state of the atomic ion C^+ (relative to the ground state of C). The third region is characteristic of carbon, varying only slightly in various compounds. We deduce from these experimental data that the electrons of CH_4 have energies in three distinct bands, not merely two that might be supposed on the basis of eight 'valence' and two 'core' electrons; hence this deduction *would* be entirely consistent with association of only effectively six electrons with the first band of energies, and then two further electrons with each further band, *if* we could distinguish electrons in this way. As electrons are absolutely indistinguishable, all we can deduce therefrom is that the primitive model of eight equivalent 'valence' electrons in CH_4 is inconsistent with this experimental evidence. Alternatively we seek to apply the two relations mentioned in relation to Bohr's theory of the H atom. Although these equations are not rigorous in their original form, they are found to be approximately correct according to accurate quantum-mechanical theory; the average or most probable distance between the proton and the electron replaces the exact radius of the circular orbit in the second relation. Taking these two relations together, we conclude that the greater the ionisation energy of a particular system or the energy of electrons associated with a particular band, the larger the average distance from some nucleus of the remaining electrons. Because the second and third ionisation energies of CH_4 much exceed the ionisation energy of atomic H but are comparable with ionisation energies of atomic C to known states of C^+, the nucleus in CH_4 with respect to which one must consider the average distances must be that of C. The implication is that of the ten electrons in the CH_4 molecule only six are on the average about as near 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 [22] acceptance that the atomic configuration s^2p^2 of C is important, although this denotation of an electronic configuration marks merely a possible initial stage of a calculation according to a particular procedure.

We proceed to consider a calculation of the structure and energy of CH_4 in its electronic ground state according to the approach of wave mechanics. The calculation is immodestly described as *ab initio*--from the beginning or from first principles, although the magnitudes of the charges of the nuclei and electrons and of the mass of the electron are in fact assigned experimental values. The process of the calculation then begins with the choice of basis set, such as two 1*s* and four sp^3 hybridised orbitals for the electrons contributed by the carbon atom and one 1*s* orbital for the electron contributed by each hydrogen atom. The next stage is the calculation of the self-consistent field for each electron in turn 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 (maintained fixed during the calculation according to the scheme of Born and Oppenheimer), the internuclear distances in the set 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 leads 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 length of the bond C-H is approximately correct, but certainly not accurate (according to the criterion of the experimental uncertainty). Computations according to quantum mechanics are at present a valid and useful method to predict not only molecular energies but also, by means of the procedure of Born and Oppenheimer, other molecular properties among which the parameters of the geometric structure are important. In those cases for which experimental data of high quality are available, the latter data are generally much more accurate than the calculated prediction. For instance, even for the diatomic molecule HCl the best theoretical value [25] 1.277×10^{-10} m of the equilibrium internuclear separation differs from the experimental value $(1.27460388 \pm 0.00000108) \times 10^{-10}$ m derived from an analysis of spectral data [26] by about 2500 times the experimental standard error (including that in the fundamental physical constants).

The important conclusion about such a calculation *ab initio* of 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 *p* orbital, or two digonal *sp* hybrids plus two further *p* orbitals, or merely one *2s* and three *2p* (unhybridised) atomic orbitals, precisely the same value of the energy and the same values of the geometric parameters define the equilibrium structure [27]. This conclusion is true if one uses only a small basis set limited to the atomic orbitals that pertain to the description of the constituent atoms in their ground state; this conclusion is true *a fortiori* 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. Hence hybridisation is at least irrelevant; moreover the use of hybridised 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 [27]. To quote from *Coulson's Valence* [28a], "hybridisation is not a physical effect but merely a feature of [a] theoretical description"--hybridisation 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 hybridisation, there neither exists now nor has ever existed any quantitative theoretical or experimental justification of such a statement. For instance, in a recent edition of a popular textbook of physical chemistry [29], we read 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 a later edition [29], the question "Why is CH_4 tetrahedral?" once again evokes an answer by reference to orbitals and hybridisation, although the causal relationship is less succinctly stated. Gillespie [30] quoted an instance of a textbook of general chemistry in which the author wrote that the structure of methane is tetrahedral because of sp^3 hybridisation, and a few pages later that the hybridisation is known to be sp^3 because the structure is tetrahedral--a completely and explicitly circular argument! Is the argument of Atkins [29] less circular because it is implicit? We quote again from *Coulson's Valence* [28b]: "It would be quite wrong to say that, for example, CH_4 was tetrahedral because the carbon atom was sp^3 hybridised. The equilibrium geometry of a molecule depends on energy and energy only ...". In a collection of papers to mark the anniversary of Pauling's paper [4], Cook [31] agreed that "hybridisation cannot explain the shapes of molecules"; he also argued that "hybridisation is not arbitrary" but is "something which happens". The former attribute is logically meaningful only within the valence-bond approach to the solution of Schrodinger's equation within the coordinate representation--obviously a parochial context, and the mysterious temporal connotation in the latter description is an evident mistake.

How then do we know that methane has a tetrahedral structure? van't Hoff and Lebel inferred that shape in 1874 from chemical information. The structure deduced from experiments with diffraction of electrons is entirely consistent with that conclusion. We may perform calculations of the kind so called *ab initio* 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 can even be done in principle without invoking orbitals[*] as a starting point [32], although severe problems in evaluation of integrals have so far precluded the production of an actual algorithm for such a purpose [33]. Orbitals, we emphasise continually, *lack physical existence*; they are merely mathematical functions in one particular approach (i. e. wave mechanics, within its coordinate representation) to the mathematical solution, by analytic or numerical means, of a particular differential equation. In other words, there are no such *things* as orbitals, not things tangible, material objects, as chemists generally consider nuclei and electrons. Again in quotation from *Coulson's Valence* [28c], "... orbitals do not exist! They are artifacts of a particular theory, based on a model of independent particles ...", i.e. based on non-repelling electrons. For this reason also we refrain from interpreting photoelectron spectra as involving the ionisation of electrons from (or even associated with) particular molecular orbitals, despite the widespread practice of this fallacy [for instance 5, 34].

The classification of electrons as bonding, nonbonding or antibonding is similarly erroneous because electrons are fundamentally indistinguishable. Careful analyses of the electronic densities in molecules have been made; the objective was to determining whether electrons may be considered to be 'localised'. The essential idea is that one might specify within a molecule a certain region of space, called a loge [35], in which to find one and 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 about half the length of a bond from a nucleus but in a direction away from other nuclei, then it could be considered a nonbonding pair, classified as core or lone pair respectively. Although the criteria of localisation produced somewhat distinct regions of bonding and nonbonding pairs in BH [36] and BH_4^- [37], in CH_4, NH_3, H_2O and HF the electrons were found to be increasingly delocalised [37]. Such details of the electron density were found [38] to be much more sensitive to the quality of the basis set than the total energy (and therefore to any structural parameters deduced from the energy gradients); specifically, increased quality of the basis set in general produced decreased localisation. 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 band in the system) and adiabatic (corresponding to the onset of the system) ionisation energies has been commonly supposed to indicate the ionisation of a bonding (or antibonding) electron, even the large ionisation energies measured by means of xrays to effect photoionisation have accompanying vibrational

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[*] In fact for many years 'molecular-orbital' calculations have been made formally without the use of atomic orbitals as basis functions, but the one-electron functions of the gaussian type [39] that have been used--for convenience of evaluation of integrals--have been chosen in sets essentially to mimic atomic orbitals.

structure [25]; such a supposition leads unnecessarily to even 'core' electrons being bonding (or possibly antibonding). Furthermore, because the formation of a molecular cation from a neutral molecule enhances delocalisation of the remaining electrons [40], one must draw only with great care any deductions from a photoelectron spectrum that involves a transition from typically a neutral molecule to a cation. We conclude that the either experimental or computational evidence for localised electrons within a molecule is in general weak, in particular for CH_4.

An enduring notion about the chemical bond is that it is characterised by the accumulation of electronic charge in the region between the nuclei. Accurate measurements [41] of electronic density by means of xray crystallography indicate that such an accumulation may not in every case accompany formation of a bond. Whether such a conclusion is also required by the results of calculations in which multiple 'bent bonds' between the atomic centres of carbon in FCCF [42] and C_6H_6 [43] and between the atomic centres C and O in CO_2 [44] are found to be favoured over the conventional description 'sigma' and 'pi' remains to be seen.

Although Pauling introduced [3] electronegativity to signify the power of an atom to attract electrons, we might reasonably expect that the difference, if not too small, of electronegativities of two atoms might reliably indicate the relative electric polarity relative to the molecular axes of a diatomic molecule containing these same atomic centres. As electronegativity is not a directly measurable quantity, such as ionisation energy or electron affinity, various definitions [28] yield distinct scales. Some scales are based directly on a combination of measurable properties, but the scale due to Hinze *et al.* [45] depends on hybridisation--one imaginary quantity based unshakably on another! The agreement between the various series is generally good, except for those due to Pauling based on thermodynamic data [46]. Of the several scales of electronegativity that exist [28], all concur that the difference between the electronegativities of the atoms C and O is moderately large, about one third the difference of electronegativities of Li and F, with O being more electronegative than C. We might therefore be misled to expect the polarity of CO to be $^+CO^-$, but the experimental evidence [47] for the electronic ground state indicates unequivocally $^-CO^+$; similar discrepancies exist for other molecules. The magnitude of the electric dipolar moment of CO at its equilibrium internuclear separation is relatively small, only about -3×10^{-31} C m. The variation of the dipolar moment with internuclear distance is somewhat complicated. Unlike the hydrogen halides for which the electric dipolar moment has a single extremum near the equilibrium distance R_e [48], CO displays two extrema in its function [49] displayed in the accompanying figure. At internuclear distances R larger than R_e the polarity is $^+CO^-$, whereas for R less than R_e the polarity is $^-CO^+$, with the dipolar moment approaching nil toward both limits of the united atom (Si) and separate atoms (C and O). How can any naive concept as embodied in a scale of electronegativity lead in general to the reliable and quantitative prediction of such varied behaviour within a particular electronic state or for separate electronic states of a given molecule?

Excluding from our consideration molecules that are electronically excited [50], there exist in their electronic ground states [51] stable molecules that lack the rigidity taken to characterise molecular structure, apart from less stable molecules (complexes) such as H_2Ar within which the moiety H_2 seems to rotate almost freely. Instances of stable molecules are NH_3, classified according to the Born-Oppenheimer scheme as

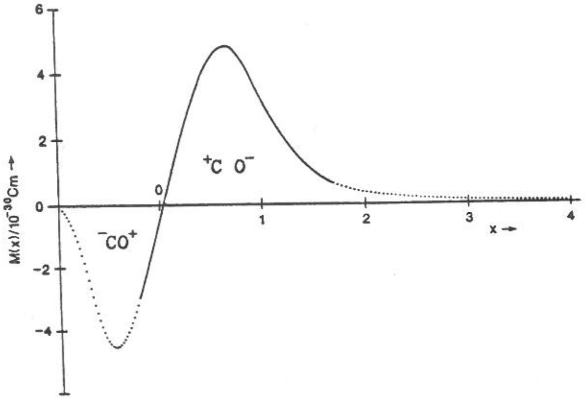

Figure. The function for the electric dipolar moment of CO in the electronic ground state; the full curve represents the function defined from experimental data; the dotted curve represents the theoretically inferred approach to known limits at $R=0$ and $R \to \infty$;
$x \equiv (R - R_e)/R_e$

being pyramidal even though (classically) it passes through the (average) planar conformation between opposite pyramids 10^9 times per second, PF_5 and $Fe(CO)_5$ that contain nominally distinct equatorial and axial bonds to the central atomic centre but in which these bonds interchange fairly rapidly (pseudo-rotation), XeF_6 that seems to have a structure describable only as a distorted octahedron, and bullvalene $C_{10}H_{10}$ that at 373 K shows by nuclear magnetic resonance spectra (of both ^1H and ^{13}C) that all H atomic centres are structurally equivalent to each other and that all C atomic centres 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, according to the Born-Oppenheimer treatment, of these structures and the associated molecular properties may produce misleading results. An attempt [52] to surpass the limitations of the Born-Oppenheimer approximation in a calculation of the structure of NH_3 using 'orbitals' for both protons and electrons led to the interesting (and prospectively physically meaningful) result that the structure was planar, but with a large amplitude of vibration of the protons perpendicular to the plane; the computational procedure was apparently defective, but a revised calculation seems not to have been made. Certainly we are aware of circumstances in which the Born-Oppenheimer approximation is most valid, namely for ground or other electronic states of diatomic molecules separated by relatively large energies from adjacent states; in these cases the adiabatic and nonadiabatic corrections to the Born-Oppenheimer potential energy may be relatively small [53]. Conversely, for electronically excited states of polyatomic molecules not well isolated, for transition structures that are not true eigenstates at all, for stable electronic ground states near the dissociation limit (and therefore necessarily near other electronic states), for states having both potentially high symmetry and degeneracy as a result of net orbital angular momentum (giving rise to various Jahn-Teller effects), and for exotic molecules containing particles of mass smaller than that of the proton, the approximation is of questionable validity.

According to rigorous quantum mechanics, a molecule lacks extension in space or time; if a description of a given experiment uses molecular eigenstates, then no structural interpretation is possible [7, 50, 54, 55]. When in the course of a complete 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 [7] of classical properties, such as molecular structure or shape, is in direct contradiction to the superposition principle of pioneer quantum mechanics. Being a a classical concept, molecular structure is thus extraneous to pioneer quantum mechanics [7]. To seek a quantum-mechanical explanation of molecular structure is therefore logically inconsistent. Which is more important to the chemist, quantum mechanics or the concept of molecular structure? 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 approximate quantum-mechanical calculation, we must take care to distinguish, in the nuclear case just as in the electronic case, between such a probability distribution and the molecular structure according to the classical idea [50].

Because molecular structure is a classical concept, the structures of molecules and crystals may be experimentally determined by purely classical means. In the experiments of electron diffraction of gases at small densities, or of xray diffraction of crystals, or of neutron diffraction of crystals (in the absence of anomalous magnetic properties), no information about the quantum numbers pertaining to the diffracting objects is obtained whatsoever. In fact the electron density probed by xrays and the field of the electric potential sensed by diffracted electrons is characteristic of a continuous distribution of matter with local maxima and minima. Molecular spectroscopy, well known to be a powerful experimental method to determine 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 [54].

Let us examine briefly diatomic molecules in which the nature of the structural deductions is most clear. A comprehensive and quantitative analytic theory to take into account all the effects within a particular electronic state has been developed [56]. Three separate approaches to the derivation of the algebraic expressions in this theory have been developed: classical mechanics [57] using Fourier series, of course assuming the quantum *laws* of states of discrete energy etc.; quasiclassical mechanics using the action integrals of Bohr's quantum theory [58], as extended by Wilson and Sommerfeld, in the formalism due to Jeffries, Brillouin, Kramers and Wentzel;* a formal quantum-mechanical approach, specifically through Rayleigh-Schrodinger perturbation theory [59], of course assuming the Born-Oppenheimer separation of electronic and nuclear motions. The notable feature of these distinct methods is that they each yield identical results [51] in analytic form.◆ Hence in order to provide a quantitative treatment of vibration-rotational energies from which are derived the structural information desired by chemists, quantum mechanics is superfluous. One

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*For this reason, the old quantum theory due to Bohr is worthy of inclusion in courses on quantum mechanics in chemistry and physics [58] but not in general chemstry in relation to the H atom or its spectrum.

◆Agreement is exact for at least the leading terms. Some differences in terms of higher order are found between the classical method and the other two; the latter results agree completely with one another to all orders. The classical formulation has not been refined sufficiently to allow a decision whether these differences need to exist [57].

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 centre of molecular mass vary temporally, seem inconsistent with molecules existing in eigenstates having properties independent of time. Further development of an analytic treatment [60] of the adiabatic effects (arising because the internuclear potential energy of a diatomic molecule depends not only on the distance between the nuclei but also slightly on their relative momenta, hence on their mass) and nonadiabatic effects (as the electrons fail to follow perfectly the nuclei in both their rotational and vibrational motions) has allowed the accurate determination of equilibrium internuclear separations R_e entirely independent of nuclear mass [26] within the (small) limits of the uncertainty of the frequencies of vibration-rotational transitions; consistent with the reservation stipulated above, such an internuclear distance pertains not to a particular eigenstate but to the hypothetical inaccessible minimum of the potential-energy function. 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 practised.

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 'Valence-Shell Electron-Pair Repulsion' theory, owes its development [28] to Sidgwick, Powell, Gillespie and Nyholm. However not only are its predictions prone to error, such as the many exceptions for any groups attached to a central atomic centre other than hydrogen atoms [61], but also--and more importantly--its basic premises of more or less equivalent localised 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 [62] concluded that "the VSEPR model can no longer be considered a valid framework for the discussion of molecular equilibrium geometries". In what might be regarded as an attempted defence [63] against this criticism (although citation of Roeggen's paper was absent), a property of the electronic charge distribution was used to demonstrate the correlation between the localised electron pairs of this model and the presence of local concentrations of charge in the 'valence shell' of a central atomic centre in a molecule, but the interaction between the electron pairs and the core of the central atom may not have been adequately taken into account. As the distribution of electronic charge in a molecule is a continuously varying function, numerous schemes of its partition into 'atoms', 'bonding pairs', loges etc. are practicable [64], but so far no proposal is entirely convincing. To find a more acceptable classical theory of molecular structure remains a challenge to the ingenuity of chemists.

4 Implications for Chemical Education

In the preceding paragraphs we have discussed the fundamental principles of quantum mechanics, the quantum laws and quantum theories, and the relationship of quantum-mechanical methods to atomic and molecular structure. These concepts have relevance to the ways that all chemists think about their discipline, 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 distinct logical types, as do analogously molecules and mathematical functions such as orbitals; as Primas has argued [7], a category fallacy results when categories of distinct logical types are treated as equivalent.

A molecule consists formally of only electrons and nuclei, certainly not orbitals nor even atoms [19]. The properties of charge densities calculated by means of the molecular-orbital approach have been used [65] to define an 'atom'. 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. It would be clearly preferable to devise a name other than atom for such moieties of molecules so as not to distort the significance 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 (relatively dense gases, liquids or solids), by definition free molecules no longer exist, but, if the intermolecular interactions are relatively weak, then some properties, such as spectral, of these phases may resemble to some extent those either measured for the ensenbles of free molecules in dilute gases or calculated by methods so called *ab initio*. When we make measurements of certain types, such as spectral, on gases at sufficiently small densities, then to a good approximation we may take those measurements to pertain directly to molecular properties; for measurements of other types or for less dilute conditions, then the measured property pertains to the medium, the totality of all the interacting nuclei and their electrons, rather than to individual molecules. Moreover, as we undertake such spectral measurements on substances as an increasing function of density, the alterations of properties may seem to be continuous in the range from the dilute gaseous phase to the bulk liquid phase, for instance; this behaviour should not be taken to imply logically that the material consists simply of the molecules on which we might practise 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 according to the methods of quantum mechanics or statistical mechanics. Thus just as there exist no atoms within molecules [19], there exist in a certain sense 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 stoichiometry; in these cases the alteration of most physical or chemical properties from the dilute gaseous phase to the bulk solid phase is not gradual. There are further cases such as amorphous mixtures, polymeric materials and solutions or suspensions in dipolar solvents for which the molecular notion is entirely inapplicable. Even though we might develop some approximate procedure (because of simplifications, much more approximate in principle than the methods for small molecules so called *ab initio*) 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 1993? We know what it is not: it is not a stick between two balls that the organic chemists of the nineteenth 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 electronic 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 cloud chambers, nor, more generally, for the definiteness, the particularity, of the world of experience, compared with the indefiniteness, the waviness, of the wavefunction" [66]. 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 [67] that "planarity at N in di- and trisilylamines has been correlated with $(p \rightarrow d)$ pi-bonding from N to Si", especially because the primary evidence for such $(p \rightarrow d)$ pi-bonding is the selfsame planarity--another circular argument? From the evidence of both photoelectron spectra and the results of quantum-chemical 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 electrically 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 He_2 ($^3He_2$ lacks even a single bound vibrational state in its ground electronic state [68], although $^4He_2$ appears to have precisely one bound state minutely below its dissociation limit [69]) 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 beginning words, *The Nature of the Chemical Bond*, in the title of Pauling's paper [2] but the end of the title, *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 approximately such structure that like the experimental methods suffer 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 assert 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 fairly accurate for such a simple system, also concur in that structure, providing that experiment has directly or indirectly furnished that evidence. In a thoughtful essay titled *The Invincible Ignorance of Science* [70], Pippard discussed 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 [7] as "We can calculate everything", that the Schrodinger equation, leading to orbitals, the misleading *aufbau* principle etc. is the fundamental basis of chemistry?

The prototypical reaction traditionally employed to illustrate chemical kinetics of first order is, paradoxically, not primarily a chemical reaction at all but rather the radioactive decay of some unstable nucleus. This decay has been tested experimentally [71] over half-lives having a broad range, namely 0.01-45. Throughout this range no deviation was found from the exponential decay characterised by Rutherford [72]. Such exponential behaviour is formally incompatible with quantum mechanics [73]. Which is more important to chemists, the quantum-mechanical theories of the universe or the laws of chemical kinetics that account for the real behaviour 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 (or 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 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 voyage of one Lemuel Gulliver to Balnibarbi in which he observed speculative research on diverse topics; in the past sixty years, innumerable chemists have attributed chemical and physical phenomena of all kinds to [nonexistent] orbitals. Is the progress of man's thinking an illusion?

Chemistry is not only a science of molecules, but also a science of materials. Chemistry remains the only basic science to constitute the foundation of a major industry. Chemistry owes its importance in the modern community to its materials, not to its molecules. All the space devoted to orbitals, the *aufbau* principle, hybridisation, resonance, sigma and pi bonds, electronegativity, hyperconjugation, HOMO, LUMO, inductive and mesomeric effects and the like excess baggage that burdens the textbooks of general, inorganic, organic and (even, if to a lesser extent) physical chemistry, and the corresponding proportion of the curriculum and duration of lecture and tutorial classes, detracts from more instructive and accurate content about chemical reactions, chemical substances, and mixtures as materials. The conspiracy interpretation* of quantum mechanics to which Condon [9b] referred has its analogue currently in the infatuation of many academic chemists with orbitals. The authors of textbooks clearly perpetrate myths such as that the structure of methane is tetrahedral because of sp^3 hybridisation, 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 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 mistruths succeed only in exposing their ignorance. What I have tried to undertake in this essay is to present a reason for the alteration of our thinking about the teaching of chemistry away from atoms and orbitals. In this endeavour, I share similar concerns with Bent [74, 75] and others who have expressed their dissatisfaction with the traditional approach, but I have 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 explanations ('hand waving') of molecular structure and reactions based on orbitals and such ilk are not science (i. e. are nonsense) and should consequently be entirely discarded. The effort of chemists should instead be expended to demonstrate the

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*"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." [9b]

myriad chemical substances and properties of real matter that makes chemistry, the science of materials as well as molecules, the central science of 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 [76]. His experiment, which many chemists have since repeated in the practical laboratory for undergraduate physical chemistry, consisted of temporal measurement of the variation of the angle of optical rotation of linearly polarised light passed through an acidic aqueous solution of sucrose as it 'inverted' to glucose and fructose. Many writers of textbooks of physical chemistry decree that the study of quantum mechanics must precede that of chemical kinetics, presumably so that chemical dynamics, the temporal evolution of quantum states related to simple atomic and molecular processes applicable in the gaseous phase at minute pressures, can form a basis for the study of chemical alteration under more common or macroscopic conditions. So following this absurd regimen, Wilhelmy would have to wait seventy-five 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 in terms of stationary quantum states; quantum electrodynamics [77] is required, although omitted from those textbooks. So Wilhelmy would still be waiting.

Epilogue

The first published reaction to the preceding essay was a paper titled *There Are No Such Things as Orbitals--Act Two!* [78] that appeared in the Journal of Chemical Education after an interval of only ten months, much smaller than the typical publication period of that journal. The neglect of the existence of matrix mechanics, which was almost complete in Pauling's paper [2], is here complete. Simons appeared content to ignore the fact that orbitals are an artifact of one particular approach, wave mechanics, apart from any further mixing and confounding of valence-bond and molecular-orbital terms that, for instance, organic chemists might employ *ad libitum* in 'explanations' of structure or reactivity. In contrast, a potential-energy function--its curve for a diatomic molecule in two dimensions or its hypersurface for a polyatomic molecule in many dimensions--is a construct common to most, if not all, procedures based on the Born-Oppenheimer separation of electronic and nuclear motions, although it is redundant to the purely quantum-mechanical method of the generator coordinate approach [79]. This paper [78] that cited only my paper [1] constitutes essentially 'old wine in old bottles'; although most content is unexceptionable, it is merely unilluminating, consistent with the shallow depth of its scholarship. Perhaps the author might have been encouraged to reflux his murky ideas for a greater period, so that he could have distilled them into a clearer and more concentrated product.

Edmiston provided instances in support of my thesis of the fallability of current qualitative explanations of chemical phenomena [80]; if perhaps he had time to examine the monographs by Primas [7] and by Craig and Thirunamachandran [77] he might possess less confidence in the integrity of the current paradigm. Quantum electrodynamics, the necessity of which Hirschfelder, Wilson and Feynman recognised to treat chemical phenomena, provides at present the most precise description of the interaction of radiant energy and matter, whereas the more conventional approach, to treat the molecules quantum-mechanically and the radiation classically, fails to render an account of various phenomena [81]. Edmiston's deduction that I appear to favour the "Heisenberg matrix approach" is mistaken; my argument is simply that because that approach exists, which he at least recognises and appreciates, there is hence nothing fundamental about the wavefunctions and orbitals that are artifacts of an alternative approach. Scott's commentary [82] might have been more pertinent some decades ago (contemporary with the works that he cites), before the advances in both experiment and computational power that profoundly affect not only the conduct of current chemical science but also the teaching of it; nevertheless there is much of value in the writing of Polanyi and other authors that can benefit our current philosophical appreciation of the state of chemical science provided that we bear in mind the historical context. Scerri's concern [83], and that of Nelson [84] that led to a calculational 'proof', with the relative ordering of orbitals 3d and 4s for atoms of certain metallic elements is obviously misplaced; not only is "in strictly quantum-mechanical terms the electronic configuration of a many-electron atom meaningless", but in matrix mechanics the very orbitals of which the order is questioned are redundant and meaningless. Although an appropriate matrix (in general of infinite order) fulfills the same purpose within a calculation according to matrix mechanics as an orbital (of some kind--hydrogenic, canonical, linear combination etc.) within a calculation according to wave mechanics, a matrix is clearly no wavefunction; each is an artifact of a particular calculational approach, not a fundamental atomic property, and has no meaning independent of that calculational approach.

A correspondent has stated that he "prefers a universe [in which] science can attempt to answer the big question 'WHY'"? For many chemists the answer to the question "why does some phenomenon occur?" is "because of orbitals", which is equivalent to "because of Schrodinger's equation". According to this approach the further question "Why Schrodinger's equation?", although logical, is ignored because this problem lies clearly outside the province of chemical competence. If Schrodinger had devoted all his energies to his other pursuits, then *the* Schrodinger's equation might never have appeared. Would chemistry or physics have been the poorer? We should still have matrix mechanics that preceded the discovery of wave mechanics; because in principle the two calculational methods are entirely equivalent, algorithms to implement calculations of electronic structure would presumably have been developed in terms of matrices, in which case they might have been readily adaptable for efficient execution on current computers with vector processors. One might imagine the content of textbooks of general chemistry under these hypothetical circumstances. Whether an alternative explanation [85] of the chemical bond in terms of entropy of the electrons is useful or valid remains to be proved.

Another correspondent pointed out that the principle of equivalence of mass and energy signifies that mass and energy are merely distinct manifestations of the same property of matter. Whether molecular mass is necessarily quantised because its total energy is (under certain conditions) quantised requires further consideration.

In a review *A Quantum Theory of Molecular Structure and its Applications* [86], we find the (conventional) statement "It is a postulate of quantum mechanics that everything that can be known about a system is contained in the state function Ψ"; in further exposition the same state function appears as the operand of a laplacian operator. The author obviously equated quantum mechanics with wave mechanics to the exclusion of matrix mechanics. More fundamentally, one can question the first statement. Because the postulated state function can be determined only by the solution of a mathematical problem involving a hamiltonian (or equivalent construct), and because the state function after its calculation can reflect only those terms in that same hamiltonian that were employed to generate the state function, then it would appear to follow logically that the hamiltonian is more fundamental than the state function. Furthermore one can specify a hamiltonian (with only slight variation in its form) for application in matrix mechanics, in wave mechanics, for use in Dirac's relativistic wave equation etc. whereas application of a particular state function (wavefunction) is clearly restricted to one particular calculational method.

Experiments on scattering of energetic electrons by molecules have been taken as the pretext for astounding claims. In a review [87] titled *Wavefunction Mapping in Collision Experiments* the approximation of independent particles is invoked to interpret experiments in which ionisation of a molecule is effected by means of a collision with an incident electron. Even within such a questionable framework of interpretation there is no explicit pretense to measure the phase of the wavefunction, as only the square of the purported wavefunction is involved. Moreover these wavefunctions differ from those conventionally invoked as they belong to the momentum representation, not in terms of coordinates. By means of a similar experiment the authors [88] claimed to achieve *Orbital Imaging of the Lone Pair Electrons in* NH_3 and other compounds. In this case accompanying molecular-orbital calculations were done with wavefunctions with a minimum basis set of quality STO-3G. According to the abstract, the "electron density in each of the outermost molecular orbitals of $N(CH_3)_3$ and NF_3 was found to exhibit a very much higher degree of *s* character than the corresponding orbital in NH_3. This behaviour is clearly predicted by molecular-orbital calculations which indicate appreciable delocalisation of electron density away from the nitrogen in $N(CH_3)_3$ and NF_3. The observed results for $N(CH_3)_3$ are contrary to predictions based on commonly used intuitive arguments involving lone pairs, molecular geometry and hybridised orbitals." In later work by these authors both the quality of the experimental results and of the computations was stated to be improved, but the ability to make measurements on orbitals associated with electrons of a particular kind (i.e. 'lone pair') was not impaired. The incredible ability of these experiments to distinguish the indistinguishable and to measure the immeasurable recalls to mind past instances of pathological science [89].

Electron spectroscopy, with either photons or electrons incident on molecules, is not uniquely endowed with fallacies related to orbitals. For rotational spectroscopy orbitals have been commonly invoked in the discussion of the structure determined from the rotational and other parameters; as a not recent instance, " ... to indicate back bonding from Cl to the *d* orbitals of Si; we conclude that such back bonding is negligible in sulfur dichloride" [90]. Some decades ago in the interpretation of vibrational spectra, varying hybridisation was invoked to be the result of orbital following by electrons of the nuclei during angular deformation, but during the present mature phase of infrared (and Raman) spectrometry interpretation of the measurements is more generally made in terms of functions for potential energy for frequency data and for dipolar moment (for instance, see the figure) for intensity measurements. Although such functions are not observable properties, they are common to classical, quasiclassical and quantal (within the Born-Oppenheimer separation of electronic and nuclear motions) treatments, and are thus not artifacts of a particular calculational approach; in the generator coordinate approach [79] which is fully quantum-mechanical such functions are redundant. In contrast the common description of electronic spectra (in the visible and ultraviolet regions) is replete with such gibberish; for instance transitions n-π^* and π-π^* by organic chemists are invoked to distinguish relatively weak and continuous absorption in the near ultraviolet from intense and possibly diffusely structured absorption farther in the ultraviolet. The statement "It is an experimental fact, reproduced by high-quality *ab initio* calculations, that the singlet $\sigma\rightarrow\sigma^*$ excitation energy is much lower for the Si-Si bond than for the C-C bond" [91] defies credulity, despite its recent appearance in a reputable chemical journal accompanied by a diagram purportedly representing "the dissociation of bonds between two C sp^3 orbitals (left) and between two Si sp^3 orbitals (right) in their S_0, T_1 and S_1 states"; I make here no attempt to disillusion the deluded author, who can doubtless seek relief according to clues to a more rigorous interpretation in the preceding discussion if he wishes. Following the publication of our preceding version [1], perhaps readers will discern decreased frequency of publication of papers with titles such as *Electronegativity Equalisation and the Deformation of Atomic Orbitals in Molecular Wavefunctions* [92] and *Trigonally Quantised Ligand Field Potentials, d-Orbitals and d-Orbital Energies* [93] that result from misdirected zeal for research. To counterbalance such nonsense we find reasoned arguments of Woolley [50], Sutcliffe [94] and Amann [95]; the latter article is prefaced with a quotation of Coulson: "Here is a strange situation. The tangible, the real, the solid, is explained by the intangible, the unreal, the purely mental. Yet that is what we chemists are always doing, wave-mechanically or otherwise." Is such explanation a productive activity for either the chemist or the chemical educator?

We conclude as we began, with discussion of an article [96] by Pauling, in this case written in his old age. Obviously without consulting the readily accessible paper [97] specified in the monograph by Primas [7] that I cited, Pauling denounced the statement "that it is possible to derive Planck's radiation law ... without quantum assumptions ..." as "clearly false". Pauling perceived no need of revision of his book [3] after the third edition; as criticism that molecular theory was ignored therein has amply appeared elsewhere [for instance 98], I need not belabour that point. If Pauling could enlighten me how to calculate the specific (optical) rotation of HCFClBr, or alanine, in the L form by means of purely valence-bond theory, I should be grateful. Pauling confers on me the honour of agreeing [96] that molecular-orbital theory should be omitted from beginning courses in chemistry; according to my experience valence-bond and resonance theories alienate just as effectively the more capable students, who resent being asked to comprehend the incomprehensible. Kasha commented on the defects of the valence-bond method for actual numerical calculations on polyatomic molecules [99], although careful calculations according to this method for molecules containing less than ten electrons may be useful [100]. Between the quantitative nature of the valence-bond theory, as practised by McWeeny [100] for instance, and the qualitative nature of resonance and electronegativity as preached by Pauling, there is only a tenuous link. "Pauling was always careful to distinguish sharply between the nature of the formal valence-bond theory and his own resonance structure theory, abstracted from it qualitatively and intuitively." [99] All these ideas took root in the chemical community after 1930 when "Pauling was the most flamboyant, dashing, dramatic chemical theorist at large in the world of chemistry. ... Blond wavy hair flying, blue eyes sparkling, arms waving in demonstration, Pauling hypnotised more than a generation of chemists" [99] who were infected by his enthusiasm too strongly for their weak mathematical antibodies to resist. Mulliken described Pauling as "a master salesman and showman" [98]; since antiquity such traits have been associated with the promotion of goods of questionable value. Pauling opened the Pandora's box from which sprang the monsters resonance, hybridisation, electronegativity etc., propelled from his lips and from his pen, enveloping in their wake even more vacuous but virulent, qualitative 'quantum chemistry' from other, confused sources, to pollute the minds of students of chemistry during the past sixty years. Pauling made many positive contributions to the development of structural chemistry; let us hope that aspects of his work less worthy of enduring fade rapidly from view so as not to detract from his truly admirable achievements.

Appendix -- Interpretation of Photoelectron Spectra

We have already noted that a free (i.e. as in a dilute gas) but confined stable molecule may exist in states of discrete energy, consisting principally of translational, rotational, vibrational and electronic contributions. We may suppose that for a neutral molecule there exists in general some manifold of electronic states. Some excited states of this neutral molecule, having energies greater than the minimum energy to ionise the molecule, correspond to states of the molecular cation.* In experiments of photoelectron spectroscopy, transitions occur between an electronic state of the neutral molecule, commonly only the electronic ground state, and various electronic states of the cationic molecule. Ionisation is effected by means of absorption of a photon of energy greater than the molecular ionisation energy. To apply the law of conservation of energy, we account for the photonic energy by the sum of several terms--the energy to effect molecular ionisation, the kinetic energy of the ejected electron (which is generally measured directly), the relative kinetic energy of the cation (practically negligible, as a result of conservation of linear momentum after the cation and electron are formed from the photon and the neutral precursor of the cation), and the vibrational and electronic energy of the cation, relative to the ground (rotational, vibrational and electronic) state of the neutral molecule, and the rotational energy of the cation that is commonly negligible. So far this model is general and yields no insight into the electronic structure of the neutral molecule.

To proceed further, we consider that, although all the electrons of the molecule are equivalent 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 of energy 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 ionised molecule. In the case 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 showing [101] resolvable rotational excitation), thus denoting the existence of only one

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*Many experiments, such as by microwave and infrared spectroscopy, are made directly on cationic molecules, such as CO^+, OH^+ and HCO^+, allowing one to characterise these species and to determine accurately the parameters that define their geometric structure. In fact the ions HCO^+, H_3O^+ and OH^- among others exist to a significant extent in flames of hydrocarbons, even on the common Bunsen burner.

significantly stable electronic state of H_2^+; the adiabatic ionisation energy, corresponding to the transition from v" =0 in H_2 to v'=0 in H_2^+, is slightly greater than the ionisation energy of the H atom. In this case, we associate both electrons of the molecule H_2 with the same energy band. For molecules containing more electrons than two, the association of energy bands 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 rough measure of the number of bands of energy. One can compare the energy of a given band of the molecule with the corresponding ionisation energies of the separate constituent atoms; appreciable variations of these energies upon molecular 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 overlapping energy bands and other complications related to secondary processes following photoionisation. An alternative approach to the interpretation of photoelectron spectra is to consider the distribution of intensity in the spectrum to reflect formally the density of electronic states in the cation, and indirectly in the molecule; this approach is perhaps more useful for relatively large molecules or for samples in condensed phases.

In an explanation [102] of photoelectron spectra that maintains the common infection with the artifacts orbitals, Simons has demonstrated the application of symmetry: equivalent properties of a molecule, such as the four bonds--one between carbon and each hydrogen atomic centre in CH_4--are not independent of one another. I was ignorant of neither these symmetry properties nor their importance in the analysis of molecular spectra but omitted this aspect under pressure of brevity. Although the methods of group theory, of which molecular symmetry is a particular application, are powerful in a qualitative manner, for quantitative predictions of differences of energy between observable spectral features that arise from nominally equivalent properties mere symmetry is inadequate. In any terms (absolute or fractional), the difference between the first two energies of ionisation measurable in the photoelectron spectrum of CH_4 much exceeds that between the second and third systems in the photoelectron spectrum of H_2O. The qualitative deduction of distinct average distances of electrons from the C nucleus in CH_4, discussed in the text above, is based much more on the large magnitude of this 'splitting' rather than merely that a splitting exists. The principal objective of my generating an explanation of this observable phenomenon, namely the photoelectron spectrum, was to avoid the use of mathematical artifacts, orbitals, for this purpose; apart from his use of inverted and circular arguments and the category fallacy, Simons has without hesitation plunged into this slough of quicksand on which I dared not tread. For orbitals to be used in a quantum-chemical computation of the spectrum would be unobjectionable provided that the nature of the results was not erroneously attributed to purported physical significance of details of the basis set: matrix mechanics or even electron densities in wave mechanics might in principle be used alternatively to effect the calculation without these particular artifacts.

Acknowledgment

I thank all those persons who kindly provided comments and criticism throughout the periods of my lectures and papers on this subject.

References

[1] Ogilvie, J. F. (1990) J. Chem. Ed. **67**, 280-289.
[2] Pauling, L. C. (1931) J. Am. Chem. Soc. **53**, 1367-1400.
[3] Pauling, L. C. (1960) "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, U.S.A., 1960.
[4] Pauling, L. C. (1928) Proc. Nat. Acad. Sci. U.S.A. **14**, 359-362.
[5] MacQuarrie, D. A. (1983) "Quantum Chemistry", Oxford University Press, Oxford, U. K., p. 360.
[6] Duff, D. G. (1987) Chem. Brit. **23**, 350-354.
[7] Primas, H. (1983) "Chemistry, Quantum Mechanics and Reductionism", 2nd ed., Springer-Verlag, Berlin, Germany.
[8] Dirac, P. A. M. (1931) Proc. Roy Soc. London, **A133**, 60-77.
[9] Condon, E. U. and Odabasi, H. (1980) "Atomic Structure", Cambridge University Press, Cambridge, U.K., (a) p. 64; (b) p. 68.
[10] Heisenberg, W. (1925) Z. Phys. **33**, 879-893.
[11] Dirac, P. A. M. (1925) Proc. Roy. Soc. London, **A109**, 642-653.
[12] Landau, L. D. and Lifshitz, E. M. (1977) "Quantum Mechanics", 3rd ed., Pergamon, London, U. K.
[13] Bloch, F. (1976) Phys. Today, **29** (12), 23-27.
[14] Dirac, P. A. M. (1958) "Principles of Quantum Mechanics", 4th ed., Oxford University Press, Oxford, U.K., (a) p. 94; (b) p. 126; (c) p. 136.
[15] Chang, C., Pelissier, M. and Durand, P. (1986) Phys. Scripta, **34**, 394-404.
[16] Jordan, T. F. (1986) "Quantum Mechanics in Simple Matrix Form", Wiley, New York, U. S. A.
[17] Born, M. and Oppenheimer, J. R. (1927) Ann. Phys. Leigzig, **84**, 457-484.
[18] Mulliken, R. S. (1967) Science, **157**, 13-24.
[19] Adams, W. H. and Clayton, M. M. (1986) Int. J. Quantum Chem. Symp. **S19**, 333-348.
[20] Millikan, R. C. (1982) J. Chem. Ed. **59**, 757.
[21] Goldman, S. P. and Dalgarno, A. (1986) Phys. Rev. Lett. **57**, 408-411.
[22] Pauling, L. C. (1983) J. Chem. Phys. **78**, 3346.
[23] Potts, A. W. and Price, W. C. (1973) Proc. Roy. Soc. London, **A326**, 165-179.
[24] Gelius, U., Svensson, S., Siegbahn, H. and Basilier, E. (1974) Chem. Phys. Lett. **28**, 1-7.
[25] Wright, J. S. and Buenker, R. J. (1985) J. Chem. Phys. **83**, 4059-4068.
[26] Ogilvie, J. F. (1993) International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, U.S.A., paper WE05, and to be published.
[27] Murrell, J. N., Kettle, S. F. A. and Tedder, J. M. (1978) "The Chemical Bond" Wiley, New York, U.S.A.
[28] McWeeny, R. (1979) "Coulson's Valence", Oxford University Press: Oxford, U. K., (a) p. 150; (b) p. 213; (c) p. 144.
[29] Atkins, P. W. (1982 and 1986) "Physical Chemistry", 2nd and 3rd ed., Oxford University Press: Oxford, U. K.
[30] Gillespie, R. J. (1976) Chem. Can. **28** (11), 23-28.
[31] Cook, D. B. (1988) J. Mol. Struct. **169**, 79-93.
[32] Yang, W. (1987) Phys. Rev. Lett. **59**, 1569-1572.
[33] Yang, W. (1990) Adv. Quantum Chem. **21** 293-302.

[34] Eland, J. H. D. (1984) "Photoelectron Spectroscopy", 2nd ed., Butterworths, London, U.K.

[35] Daudel, R. (1992) J. Mol. Struct. **261**, 113-114.

[36] Daudel, R., Stephens, M. E., Burke, L. A. and Leroy, G. E. (1977) Chem. Phys. Lett. **52**, 426-430.

[37] Bader, R. W. F. and Stephens, M. E. (1975) J. Am. Chem. Soc. **97**, 7391-7399.

[38] Mezey, P. G., Daudel, R. and Czismadia, I. G. (1979) Int. J. Quantum Chem. **16**, 1009-1019.

[39] Boys, S. F. (1950) Proc. Roy. Soc. London, **A200**, 542-554.

[40] Daudel, R. (1976) in "Localization and Delocalization in Quantum Chemistry" (ed. Chalvet, O., Daudel, R. and Diner, S.) **2**, 3-14, Reidel, Dordrecht, Holland.

[41] Dunitz, J. D. and Seiler, P. (1983) J. Am. Chem. Soc. **105**, 7056-7058.

[42] Messmer, R. P. and Schultz, P. A. (1986) Phys. Rev. Lett. **57**, 2653-2656.

[43] Schultz, P. A. and Messmer, R. P. (1987) Phys. Rev. Lett. **58**, 2416-2419.

[44] Messmer, R. P., Schultz, P. A., Tatar, R. C. and Freund, H. J. (1986) Chem. Phys. Lett. **126**, 176-180.

[45] Hinze, J., Whitehead, M. A. and Jaffe, H. H. (1963) J. Am. Chem. Soc. **85**, 148-157.

[46] Sacher, E. and Currie, J. F. (1988) J. Elect. Spectrosc. Relat. Phen. **46**, 173-177.

[47] Townes, C. H., Dousmanis, G. C., White, R. L. and Schwarz, R. F. (1954) Discussion Faraday Soc. **19**, 56-64.

[48] Ogilvie, J. F., Rodwell, W. R. and Tipping, R. H. (1980) J. Chem. Phys. **73**, 5221-5229.

[49] Kirschner, S. M., Le Roy, R. J., Tipping, R. H. and Ogilvie, J. F. (1977) J. Mol. Spectrosc. **65**, 306-312.

[50] Woolley, R. G. (1986) Chem. Phys. Lett. **125**, 200-205 and references therein.

[51] Ogilvie, J. F. (1986) Int. Rev. Phys. Chem. **5**, 197-201.

[52] Thomas, I. L. (1969) Phys. Rev. **185**, 90-94.

[53] Ogilvie, J. F. (1987) Chem. Phys. Lett. **140**, 506-511.

[54] Woolley, R. G. (1976) Adv. Phys. **25**, 27-52.

[55] Woolley, R. G. (1985) J. Chem. Ed. **62**, 1082-1084.

[56] Ogilvie, J. F. (1988) J. Mol. Spectrosc. **128**, 216-220.

[57] Tipping, R. H. and Ogilvie, J. F. (1990) Chin. J. Phys. **28**, 237-251.

[58] Miller, W. H. (1986) Science, **233**, 171-177.

[59] Fernandez, F. M. and Ogilvie, J. F. (1990) Phys. Rev. **A42**, 4001-4007.

[60] Fernandez, F. M. and Ogilvie, J. F. (1992) Chin. J. Phys. **30**, 177-193 and 499.

[61] Myers, R. T. (1992) Monats. Chem. **123**, 363-368.

[62] Roeggen, I. (1986) J. Chem. Phys. **85**, 969-975.

[63] Bader, R. F. W., Gillespie, R. J. and MacDougall, P. J. (1988) J. Am. Chem. Soc. **110**, 7329-7336.

[64] Roeggen, I. (1991) Int. J. Quantum Chem. **40**, 149-177.

[65] Bader, R. F. W. and Nguyen-Dang, T. T. (1981) Adv. Quantum Chem. **14**, 63-124.

[66] Bell, J. S. (1987) "Speakable and Unspeakable in Quantum Mechanics", Cambridge University Press, Cambridge, U. K.

[67] Ebsworth, E. A. V. (1987) Acc. Chem. Res. **20**, 295-301.

[68] Ogilvie, J. F. and Wang, F. Y. H. (1991) J. Chin. Chem. Soc. **38**, 425-427.

[69] Luo, F., McBane, G. C., Kim, G., Giese, C. F. and Gentry, W. R. (1993) J. Chem. Phys. **98**, 3564-3567.

[70] Pippard, A. B. (1988) Contemp. Phys. **128**, 216-220.
[71] Norman, E. B., Gazes, S. B., Crane, S. G. and Bennett, D. A. (1988) Phys. Rev. Lett. **60**, 2246-2249.
[72] Rutherford, E. (1911) Sber. Akad. Wiss. Wien. Abt. 2A, **120**, 300.
[73] Greenland, P. T. (1988) Nature, **335**, 298.
[74] Bent, H. A. (1984) J. Chem. Ed. **61**, 421-423.
[75] Bent, H. A. (1986) J. Chem. Ed. **63**, 878-879.
[76] Laidler, K. J. (1987) "Chemical Kinetics", 3rd ed., Harper and Row, New York.
[77] Craig, D. P. and Thirunamachandran, T. (1984) "Molecular Quantum Electrodynamics--an Introduction to Radiation-Molecule Interactions", Academic, London.
[78] Simons, J. (1991) J. Chem. Ed. **68**, 131-132.
[79] Lathouwers, L and van Leuven, P. (1982) Adv. Chem. Phys. **49**, 115-189.
[80] Edmiston, C. (1992) J. Chem. Ed. **69**, 600.
[81] Andrews, D. L., Craig, D. P. and Thirunamachandran, T. (1989) Int. Rev. Phys. Chem. **8**, 339-383.
[82] Scott, J. M. W. (1992) J. Chem. Ed. **69**, 600-602.
[83] Scerri, E. R. (1992) J. Chem. Ed. **69**, 602.
[84] Nelson, P. G. (1992) Ed. Chem. **29**, 84-85.
[85] Gankin, V. V. and Gankin, Y. V. (1991) "The New Theory of Chemical Bonding and Chemical Kinetics", ASTA, St. Petersburg, Russia.
[86] Bader, R. F. W. (1991) Chem. Rev. **91**, 893-928.
[87] McCarthy, I. E. and Weigold, E. (1988) Rep. Prog. Phys. **51**, 299-392.
[88] Bawagan, A. O. and Brion, C. E. (1987) Chem. Phys. Lett. **137**, 573-577.
[89] Rousseau, D. L. (1992) Amer. Sci. **80**, 54-63.
[90] Davis, R. W. and Gerry, M. C. L. (1977) J. Mol. Spectrosc. **65**, 455-473.
[91] Michl, J. (1990) Acc. Chem. Res. **27**, 127-128.
[92] Magnusson, E. (1988) Aust. J. Chem. **41**, 827-837.
[93] Perumareddi, J. R. (1988) Polyhedron, **7**, 1705-1718.
[94] Sutcliffe, B. T. (1992) J. Mol. Struct. **259**, 29-58.
[95] Amann, A. (1992) S. Afr. J. Chem. **45**, 29-38.
[96] Pauling, L. C. (1992) J. Chem. Ed. **69**, 519-521.
[97] Boyer, T. H. (1969) Phys. Rev. **186**, 1304-1318.
[98] Rigden, J. S. (1990) Phys. Today, **43** (5), 81-82.
[99] Kasha, M. (1990) Pure Appl. Chem. **62**, 1615-1630.
[100] McWeeny, R. (1989) Pure Appl. Chem. **61**, 2087-2101.
[101] Asbrink, L. (1970) Chem. Phys. Lett. **7**, 549-552.
[102] Simons, J. (1992) J. Chem. Ed. **69**, 522-528.