

THE HYDROGEN ATOM ACCORDING TO WAVE MECHANICS – V IMPLICATIONS OF MULTIPLE COORDINATE SYSTEMS

J. F. Ogilvie

Centre for Experimental and Constructive Mathematics, Department of Mathematics, Simon Fraser University, Burnaby, British Columbia V5A 1S6 Canada
Escuela de Química, Universidad de Costa Rica, Ciudad Universitaria Rodrigo Facio, San Pedro de Montes de Oca, San José, 11501-2060 Costa Rica

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Abstract

Because Schroedinger's temporally dependent or independent partial-differential wave equation for the hydrogen atom is solvable in spatial coordinates in four distinct systems, the properties of those solutions, and even the quantum numbers in sets that characterize those wave or amplitude functions, are parochial to each such system. The relations among the wave functions of the hydrogen atom, wave mechanics and molecular structure are discussed. Quantum mechanics is argued to be largely irrelevant in chemical education.

Resumen

La ecuación de onda parcial-diferencial temporalmente dependiente o independiente de Schroedinger para el átomo de hidrógeno se puede solucionar en coordenadas espaciales en cuatro sistemas distintos. Sin embargo, las propiedades de dichas soluciones e incluso los números cuánticos en conjunto que caracterizan esas funciones de onda o amplitud son muy propias a cada sistema. Por lo anterior, se discuten las relaciones entre las funciones de onda del átomo de hidrógeno, la mecánica ondulatoria y la estructura molecular. Por otro lado, se argumenta que la mecánica cuántica es en gran medida irrelevante en la educación química.

Key words: hydrogen atom, wave mechanics, orbitals, atomic spectra

Palabras clave: átomo de hidrógeno, mecánica de onda, orbitales, espectro atómico

I. INTRODUCTION

In London in 1815, an English chemist and physician named William Prout published an hypothesis, based on inaccurate measurements of molar masses of the known chemical elements, that the hydrogen atom was the only truly fundamental object and that atoms of other chemical elements comprised aggregates of hydrogen atoms of varied number [1]. In Manchester in 1915, Ernest Lord Rutherford, a physicist who anyhow became Nobel laureate in chemistry for his discovery of the transmutation of chemical elements, concluded from experiments in which he bombarded nitrogen atoms with α particles that perhaps the nuclei of all elements were made of

* Corresponding author: ogilvie@cecm.sfu.ca

hydrogen nuclei; in Cambridge in 1920, he named the atomic nucleus of hydrogen a proton. In Cambridge also in 1920, following his production of the first mass spectrograph in 1919, Francis Aston formulated the *whole-number rule* whereby the masses of atomic isotopes are practically integer multiples of the mass of the hydrogen atom. In Cambridge in 1932, Sir James Chadwick's discovery of the neutron completed a simple interpretation of an atomic nucleus of mass number A as comprising Z protons and $A - Z$ neutrons, supplanting Prout's hypothesis. The spectre of Prout's hypothesis, however, lingers in chemistry in that many calculations, and more numerous qualitative explanations, of atomic and molecular properties are based on an assumption that all electrons in any atom behave according to the central field of the model of atomic hydrogen.

In preceding articles in this sequence on the hydrogen atom according to Schroedinger's wave mechanics, we solved the pertinent partial-differential equation in coordinates of four systems -- spherical polar [2], paraboloidal [3], ellipsoidal [4] and spheroconical [5] -- to yield explicit algebraic formulae [6] for amplitude functions that generate the distribution of density of negative charge associated with one electron in the vicinity of an atomic nucleus of charge $+Z e$; atomic number $Z = 1$ for H itself. We distinguish between amplitude functions, which arise from the solution of the temporally independent Schroedinger equation in terms of only three spatial variables, in various systems, and wave functions, resulting from solution of the temporally dependent equation involving three spatial variables and time [7]. In this essay we compare the results for those four coordinate systems for the hydrogen atom and discuss the validity of a contemporary form of Prout's hypothesis.

A treatment of the hydrogen atom in coordinates in any system within quantum mechanics must reproduce the energies of the discrete states as being approximately inversely proportional to the square of a positive integer, generally denoted n ; n thus becomes an *energy quantum number*. The latter result is a conclusion purely from experiment, specifically the numerological deduction made initially by Balmer in 1885 and elaborated on a more physical basis by Rydberg in 1888 from wave lengths λ/m of spectral lines in the visible region attributed to atomic hydrogen. Balmer's formula is equivalent to

$$\lambda = B n^2 / (n^2 - 2^2)$$

in which fitted parameter $B = 3.6456 \times 10^{-7}$ m became known subsequently as the Balmer constant; integer n assumes values 3, 4, 5, 6 for only four lines $\alpha, \beta, \gamma, \delta$ in the so-called Balmer series, respectively. Rydberg deduced a more general formula for these spectral lines, measurable as circular frequency ν or wave length λ in the optical spectrum, equivalent to

$$\Delta E = E_2 - E_1 = R h c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = h \nu = h c / \lambda$$

containing, with Planck constant h and speed of light c , rydberg constant R in wavenumber unit that is the most accurately known fundamental physical constant (as R_∞); that experimentally observable quantity thus corresponds to an energy difference between states characterised with positive integers n_1 and n_2 , with $n_1 < n_2$. These lines are associated with transitions between states of the hydrogen atom, according to the interpretation originally proffered by Nicholson and Ritz. The energies of these discrete states of the hydrogen atom are hence implied to be expressible as

$$E = - R h c / n^2 + C,$$

in which C is a constant that includes all other energy of the atomic system, such as mass energy, that is not significantly involved in a transition between the states that yield an observed spectral line, and that can hence be ignored for our present purpose. Without C , the energies are negative because work must be done to remove an electron from a region near a positively charged nucleus. We accordingly view n as *an integer quantity that is purely experimentally derived*, bereft of any intrinsic theoretical significance, but which any acceptable theoretical treatment must reproduce. This formula might be the first result of an analysis in quantum physics, and has no inherent connexion, except precursor, to quantum mechanics that it preceded by a few decades. We must, however, expect that any succeeding wave-mechanical derivation of a solution of Schroedinger's equations in coordinates of various systems for discrete states yield parameters, parochial to each treatment, of which an appropriate combination becomes equivalent to that positive integer, n .

II.SOLUTION OF SCHROEDINGER'S EQUATIONS IN FOUR SYSTEMS OF COORDINATES

We summarise in table 1 the results for the four coordinate systems [2 - 5] that enable solutions of Schroedinger's temporally independent equation, specifying the coordinates and the respective quantum numbers, with the formula of the combination to express those quantum numbers to correlate with the energy quantum number. Note that the use of ξ and η in both ellipsoidal and spheroconical systems must not be taken to imply a relation of these coordinates between these systems.

TABLE 1. System of coordinates and associated quantities

system	coordinates	quantum numbers	formula for n
spherical polar coordinates	r, θ, ϕ	k, l, m	$k + l + 1$
paraboloidal coordinates	u, v, ϕ	n_1, n_2, m	$n_1 + n_2 + m + 1$
ellipsoidal coordinates	ξ, η, ϕ	n_ξ, n_η, m	$n_\xi + n_\eta + m + 1$
spheroconical coordinates	ξ, r, η	k, l, κ	$k + l + 1$

Some coordinates are common to two or three systems, such as equatorial angle ϕ for the former three systems and radial distance r for the first and fourth systems; equatorial or magnetic quantum number m and radial k and azimuthal l quantum numbers are correspondingly common to those particular systems. Energy quantum number n , which has an indisputable experimental basis as explained above, is likewise expressed as a varied combination of other quantum numbers depending on the system, as indicated in the table above. The shapes and nodal properties of surfaces, but not greatly their sizes for a given value of energy and hence energy quantum number n , of amplitude function ψ at a set constant value appropriately chosen analogously vary appreciably with the system of coordinates, although common trends of nodal surfaces are perceptible between the systems, as demonstrated in the figures of the preceding four parts of this series [2 - 5].

Of amplitude functions in the four systems of coordinates, which should one choose? As wave mechanics is one method within a collection of such algorithms for calculations on an atomic scale, the choice must depend on the purpose of a calculation on the hydrogen atom, or other atom with only one electron, in which the amplitude functions serve as working formulae. The overwhelmingly best known system comprises, of course, spherical polar coordinates, which are described in Schroedinger's paper simply as polar coordinates [7]; as the properties of the Laguerre

and Legendre polynomials, also discussed in the third paper of Schroedinger [7], involved therein are highly developed, calculations are generally rapid. This system is applicable to a hydrogen atom, or to any other atom with only one electron, that is isolated -- no other matter in the vicinity, no applied electric field apart from an electromagnetic wave in the form of light that might interact classically with the atom in absorption, emission or scattering. Practically all textbooks of chemistry allude to these amplitude functions, generally in mistaken contexts; some such textbooks, particularly in physical and inorganic chemistry, describe their properties with accurate formulae but more or less inaccurate figures depicting poorly defined surfaces and shapes. The authors of textbooks on quantum mechanics in physics typically content themselves with the mathematical details of this solution of the temporally independent Schroedinger equation in spherical polar coordinates, and present some exemplary formulae. Following Schroedinger's own solution of his equation in paraboloidal coordinates [7], some textbooks of quantum mechanics in physics treat also this system, but no known textbook of chemistry even mentions that this system exists for the hydrogen atom. Common to spherical polar, paraboloidal and spheroconical amplitude functions, Laguerre polynomials, applied for paraboloidal spatial variables both u and v , are just as easy to manipulate, and calculations are generally rapid. Schroedinger applied [7] this paraboloidal system of coordinates to treat, with perturbation theory that he concurrently developed, the hydrogen atom in an homogeneous electric field; the purpose was to calculate the Stark effect, explicitly the shifting and splitting of spectral lines as a result of hydrogen atoms being subjected to a uniform electric field [3]. Other contexts of calculations in which these paraboloidal coordinates are particularly useful include the photoelectric effect, the Compton effect and a collision of an electron with a H atom; in each case, a particular direction in space is distinguished according to some external force [8]. In ellipsoidal coordinates, one focus of an ellipsoid is located at or near the atomic nucleus; the other focus, at distance d , is merely a dummy location; as the latter can become the location of a second atomic nucleus, the associated amplitude functions become formally applicable to a diatomic molecule, which has been the reason for the attention given to these coordinates [9]. These amplitude functions, derived directly, contain confluent Heun functions [4], which pose difficulties of calculation because they lack a simple polynomial expression. Some indirect derivations of amplitude functions in the literature [9], through solutions of the differential equations in series, have hence been expressed in terms of polynomials; the shapes of these functions at a particular value of $\psi(\xi, \eta, \phi)$ depend appreciably on that distance d [4]. For all three preceding coordinate systems, equatorial angle ϕ is one variable; its presence in a resulting derived amplitude function has invariably this form,

$$\Phi(\phi) = \frac{e^{(i m \phi)}}{\sqrt{2 \pi}} = \frac{\cos(m \phi) + i \sin(m \phi)}{\sqrt{2 \pi}}$$

in which the presence of $i = \sqrt{-1}$ with equatorial quantum number m dictates generally complex total amplitude functions; their intrinsic real, cosine, and imaginary, sine, parts hence preclude depiction of total surfaces in real space of three dimensions unless $m = 0$. As a further complication, confluent Heun functions in ellipsoidal coordinates ξ and η have also an intrinsically complex nature [4]. In contrast, each and every amplitude function in spheroconical coordinates as directly derived is prospectively entirely real [5, 6] -- thus no imaginary part, enabling a direct plot of each such surface. Calculations with the general Heun functions in two spheroconical coordinates are easier than with confluent Heun functions; the third coordinate is just the separation r between electron and nucleus, the same as in spherical polar coordinates [2]. These spheroconical

coordinates have thus much to recommend them for a general discussion of the intrinsic wave-mechanical properties of the hydrogen atom, and should effectively supplant the spherical polar coordinates for this purpose.

The incontestable fact that the shape of a surface of an amplitude function in coordinates of the four specified systems depends on that system has profound implications for chemical or physical interpretations. The most momentous implication is that not only is any such shape merely an artifact of one particular coordinate system, but even the quantum numbers, as presented in table 1, associated with any such amplitude function are equally artifacts of that system [6]. Such shapes are, of course, not entirely independent: an appropriate linear combination of amplitude functions in one system has an algebraic form that is subject to a transformation of coordinates to generate a particular amplitude function in another system corresponding to the same value of energy, and hence quantum number n . A shape of a surface of such a combination, at a selected value of ψ , is hence identical with a shape of a particular amplitude function directly derived in another system when plotted in common cartesian coordinates. Which particular shape or system one might choose must thus be arbitrary; any conclusion in relation to specific properties of the hydrogen atom based arbitrarily on any such particular shape or the pertinent parochial quantum numbers is unwarranted and fallacious. The only constant quantity is the energy quantum number, n , which is independent of any system, consequent of its experimental origin as explained above.

About three quarters of all mass in the known universe is composed of hydrogen, in mostly atomic and plasma forms. Being a system comprising two bodies, that atomic form, supposing point masses, is amenable to an exact mathematical treatment in classical or quantum mechanics, such as that in each of the four preceding parts [2 – 5] of essays in this series according to a particular system of coordinates. The present importance of hydrogen in chemistry is related, however, not to its separate atomic nature, nor even to its incorporation in innumerable chemical compounds of diverse nature; to the contrary, the presumed importance lies in a gratuitous assumption and expectation that the calculated properties of atomic hydrogen, with $Z = 1$, might somehow be directly pertinent to both atoms of other elements, with $Z > 1$, and molecules or materials containing those elements -- virtually Prout's hypothesis. Employing such an assumption amounts to extrapolation from a point, a practice that anybody must agree in isolation to be indefensibly illogical, even insane [10].

At this point we recall the distinctions among quantum physics, quantum chemistry and quantum mechanics. Quantum physics implies experiments or observations on an atomic scale and the principles that arise therefrom; a prototypical instance is the generation of a formula for the energies of the hydrogen atom in states of discrete energy, according to the work of Balmer and Rydberg, as explained above. The first observation of quantum physics was the discovery by William Wollaston in Cambridge of black lines in the solar spectrum; of these lines, subsequently classified by Fraunhofer, those designated C, F, G', h correspond to lines α , β , γ , δ of the Balmer series, respectively. Quantum mechanics is recognised [11, 12] to imply a collection of methods of calculation, or algorithms, applicable to a system on an atomic scale; among at least twelve such methods [13, 14] including relativistic wave mechanics of Dirac, non-relativistic wave mechanics [6] has been applied to generate the amplitude functions of the hydrogen atom in the four systems of coordinates presented in preceding parts of this series [2 - 5]. Quantum chemistry is generally understood to imply a programmed calculation of electronic structure of molecules or materials with atomic nuclei in more or less fixed relative positions; such calculations made with standard computer programs have been developed to an astonishing degree of sophistication, and have become an established accessory to the exercise of research in practical organic and inorganic

chemistry, apart from innumerable separate calculations of atomic and molecular structure and properties of varied scientific worth. Although some practitioners might fancy a description of their work as being *ab initio* -- from first principles, apart from the typically calibrated basis sets, their restriction to electronic motion and electrostatic interactions defines an incontestably *semi-empirical* constituent, a reversion to classical mechanics in which the motion of the atomic nuclei is treated classically, if at all; such a restriction is unnecessary, but its avoidance imposes a cost that a traditional molecular structure is generally precluded as a result [15]. A separate treatment of electronic and nuclear motions is nearly invariably based on an approximation resulting from an analysis originally undertaken by Born and Oppenheimer [16], and has since been discussed continually and expansively in increasing sophistication. One aspect of that analysis of which a casual user of quantum-chemical programs might be unaware is that the concept of a curve or hypersurface of potential energy, supposed to govern the relative locations and motions of atomic nuclei, is valid only in the immediate vicinity of a point of a local minimum energy, corresponding to a particular molecular structure or conformation; any extrapolation of calculations away from that immediate vicinity must again be deprecated, with such results possibly at great variance with experimental data [17].

A crucial component of most computer programs for quantum chemistry is a set of functions, called basis functions, each likely centred on an atomic nucleus at a fixed relative location. In the early years of such calculations, functions of Slater type were used to diminish the effort of manual calculations: these Slater functions resembled amplitude functions of the hydrogen atom in spherical polar coordinates, but had no radial node; they conform to a correct cusp condition at the local origin corresponding to the location of the respective atomic nucleus. When computational resources expanded, the basis functions of form exactly those of the explicit hydrogen functions in spherical polar coordinates became tractable, but major computational efficiency was achieved on replacing each such hydrogen-like function with functions of gaussian type in a small set [18], even though the cusp condition at the atomic nucleus was forsaken. Amplitude functions for a molecule treated in such a calculation are prepared as linear combinations of these basis functions, each set on a separate atomic centre. The extent and success of these calculations are phenomenal: the derived molecular structures, with slightly adjusted relative nuclear locations to generate a local minimum of energy, have accuracies generally comparable with determinations from experiments of essentially classical nature -- electron or xray diffraction, for instance; molecular properties, such as electric-dipolar moments and polarizabilities are also generally reproduced in a reasonably satisfactory manner, but the best basis sets to generate a structure might not be the best for particular properties associated with that structure. An alternative approach, still involving protracted numerical calculation based on Schroedinger's equation, relies on the intermediacy of density functionals instead of basis functions that mimic amplitude functions of the hydrogen atom; in this case the spatially dependent densities of electronic charge replace those amplitude functions as quantities to be varied to obtain the best energy of the system. Although in some cases the density functionals are based on amplitude functions of form that of hydrogen, in other cases, for instance [19], no such amplitude function is involved. The results from such calculations with density functionals might be less accurate, with reference to experimental quantities, than those directly based on amplitude functions or their gaussian mimics, but, as a compromise with substantially decreased duration and hence cost of those calculations, their accuracy suffices for various purposes, especially with large molecules or aggregates of atomic centres. In contrast, the application of software to implement *molecular mechanics* [20] is nearly as effective to calculate a molecular structure and

selected properties, at greatly decreased computational cost, and with no pretence of wave-mechanical provenance.

What is critically necessary that one understand about these calculations on systems containing multiple (i.e. more than one) electrons, either separate atoms or their aggregates in molecules or materials, is the distinction between the explicit amplitude functions of the hydrogen, or other one-electron, atom and the selected basis sets that might or might not rely on those functions. The amplitude functions of the hydrogen atom have become traditionally called *orbitals*, a term that Mulliken with characteristic obfuscation invented to signify a mathematical function as near a physical trajectory or orbit, in the context of a Bohr atom, as is possible in wave mechanics [21]. Apart from such an atomic orbital, there is a possibility of a molecular orbital, which corresponds to an exact solution of Schroedinger's equation for a system of one electron in the vicinity of two or more atomic nuclei that are accorded fixed relative locations. The shape of a surface of such a molecular orbital at a particular value depends definitively on a conformation or the relative spatial locations of those atomic nuclei; for instance, a surface of a molecular orbital for H_2^+ in its state of least energy must have a shape disparate from that of a surface of a respective molecular orbital for H_3^{2+} in its state of least energy. These direct molecular orbitals have little practical interest; for this reason we neglect them. The typical method to generate a molecular orbital for use in systems of multiple electrons and multiple nuclei is to form a linear combination of atomic basis functions, as mentioned above; such a molecular orbital is really a molecular basis function. The crucial point is that one must not confound an *orbital*, which is an amplitude function derived as a *result* of a calculation with Schroedinger's equation for an atom with one electron, i.e., the *output* from such a calculation, with a *basis function* that is an assumed component to enable, and is *within*, a calculation for a system of multiple electrons, i.e. the *input* for the latter calculation; that basis function has no intrinsic meaning apart from that calculation. For these systems of multiple electrons, quantum numbers are no longer uniquely defined, which condition is characteristic of a classical system. For only an atomic system of one electron is the energy defined with a single quantum number, i.e. n .

The *aufbauprinzip* -- building-up principle -- that has been, since Bohr in 1921, applied to formulate a supposed electronic configuration of atoms with multiple electrons is another casualty of a recognition that, among the four sets that we have derived for separate systems of coordinates, a choice of quantum numbers for the hydrogen atom is arbitrary, apart from the fact that an atom with multiple electrons in any case suffers the loss of identifiable quantum numbers. As Millikan recognised [22] even before the present context arose of multiple sets of quantum numbers to describe the hydrogen atom depending on the coordinate system, the *aufbauprinzip* is an illusion: the periodic chart of the chemical elements is not a theoretical result, but rather the product of experiment not derivable according to any physical or chemical theory, notwithstanding the fact that sufficiently extensive quantum-chemical calculations can, through brute force, reproduce satisfactorily the properties of atoms that might be measurable or supposed to be predictable. Although the diagonal rule of Madelung, about 1926, makes a slight concession to the loss of central symmetry in the presence of multiple electrons in the vicinity of a single atomic nucleus, hence eliminating the degeneracy attributed to quantum number l , the principle is still essentially based on an extrapolation from the hydrogen atom. Bohr formulated this rule of thumb, another manifestation of Prout's hypothesis, before the development of quantum mechanics. Nearly a century afterward, there continues naïve and superficial debate about the ordering of some elements in columns of the periodic chart to avoid long rows. The state of an atom, or molecule, is defined purely by its energy and its angular momentum; only changes of energy, with possible associated changes of angular momentum, are observable in transitions between states of an atom,

but, unlike the formula of Rydberg presented above for transitions of the hydrogen atom, absolute quantum numbers associated with energy, but not angular momentum, are inevitably undefined.

Electrons are fundamentally indistinguishable: there is no *s* electron, no *p* electron ... in an atom, no σ electron, no π electron, no bonding electron, no lone pair ... in a molecule; there are only electrons [10]. The culprit for the original flagrant violation of this undeniable physical principle was G. N. Lewis, then in Harvard University USA, apparently beginning shortly after the discovery of electrons as individual physical particles by J. J. Thomson in 1897, following a concept by R. Laming published in 1838 and the naming by G. J. Stoney in 1891, all in England. The subsequent promulgations of electron pairs by Kossel and by Lewis and the octet rule and various elaborations by I. Langmuir inspired L. C. Pauling, on the basis of an inadequate understanding of the then new quantum mechanics -- despite his study of mathematical physics during his doctoral research, to develop his ideas about the nature of the chemical bond [23]. As Pauling was a highly effective orator [24], his evangelistic fervour motivated many other authors whose understanding of the physical principles and of the mathematics of the wave-mechanical method was much less than his own; these were gullible scientists or teachers whom Valiunas described as "that sad benighted chemistry professoriate" [25]. Pauling's approach to the application of quantum-mechanical concepts in chemistry was deeply intuitive and qualitative, in contradistinction with the fundamentally mathematical nature of quantum mechanics; for practical purposes, his resonance and valence-bond theories are largely ignored at present, although organic chemists continue blindly to insert various related terms into their qualitative explanations of molecular structure and reactions. With regard to the hydrogen atom, although Pauling and Wilson [26] cited Schroedinger's third article in the series *Quantisation as a Problem of Proper Values* [7] in which the latter author solved the hydrogen atom in paraboloidal coordinates with the respective quantum numbers, Pauling failed to recognise the significance of the fact that a second coordinate system already existed in the fact of this solution, which implies an arbitrary choice between them of both amplitude functions and quantum numbers to describe that hydrogen atom. Likewise, although Pauling and Wilson mentioned matrix mechanics [26] in a book that appeared a few years after Teller confirmed the applicability of ellipsoidal coordinates [27] that Pauling likewise ignored, he failed to recognise that any amplitude function as a solution of Schroedinger's equation is an artifact of one particular method -- wave mechanics -- of many methods within quantum mechanics, not a physically observable quantity. Although Thomson generated a stream of electrons in an evacuated chamber, and with sufficiently sensitive methods might have identified the arrival of an individual, single electron at his detector, in chemical matter there is only a total density of negative electronic charge, variably distributed in the vicinity of positively charged atomic nuclei, not capable of being partitioned into single particles in particular regions or volumes of relative space. Any such attempted partition, according to some capriciously chosen criterion, is inevitably arbitrary. That density can be effectively calculated with quantum-chemical programs, or even measured -- although accuracy is a challenge -- in experiments involving diffraction of electrons and xrays.

III. SIGNIFICANCE FOR CHEMICAL EDUCATION

In year 1990 there appeared an essay of title *The Nature of the Chemical Bond 1990* [28], which deliberately recalled the same words as in the title of Pauling's highly influential book; the latter first edition appeared a half century before [29], in turn based on articles in a series published during the preceding decade. The subtitle of that essay, *There are no such things as orbitals*, provides a more cogent indication of its tone; in that subtitle, *thing* is supposed to imply a tangible object

rather than an abstract entity. According to Bohr, a wave function is an abstract object – simply an element of a theory used to make predictions about observations, with which interpretation one can fully concur. Although that essay attracted the positive attention of theoretical chemists and physicists, which led to its republication in a monograph [10] in an expanded form in the company of other theoretically or computationally oriented essays, it was effectively ignored by most chemists, or seemed to be treated as lacking relevance for the way that practising chemists and poorly qualified instructors -- "that sad benighted chemistry professoriate" [25] indoctrinated with uncomprehended and fallacious ideas for two or three generations -- proceed to discuss their experimental and computational results and to teach further generations the same nonsense.

That essay [28, 10], which contained information and ideas about the explanation of molecular structure and chemical binding collected during two decades, was essentially a qualitative critique of contemporary abuse of various terms mistakenly derived from not only quantum mechanics but also its preceding *old quantum theory* of Bohr, W. Wilson, Sommerfeld and others; a fatal deficiency of this old quantum theory was a failure to find methods to calculate the intensity of a spectral line, which Schroedinger achieved *at a stroke* in his third paper introducing wave mechanics [7]. This melange of ideas about definite orbits and a primitive understanding of the hydrogen atom calculated in only spherical polar coordinates originated during a period when a quantitative understanding of the fundamental bases of chemical structure and reactions exceeded the then current ability to test their correctness or objectivity. Despite the enormous advances in experimental, theoretical and computational capabilities and activities in chemistry that might be deployed at present to combat the obscurity and inaccuracy of those ill formed ideas, the latter linger, to the detriment of chemical education and an improved understanding of the structure of chemical matter and its reactions. Within those computational activities, one must recognise and emphasize the importance of advanced mathematical software, such as *Maple*, that enables the direct algebraic solution of Schroedinger's equations in multiple systems of coordinates, as presented in preceding parts of this series [2 - 5]. Equally compelling is the power of contemporary computers applied to purely numerical quantum-chemical calculations, generally described as *quantum chemistry*, of the properties of both molecules, small and large, and materials -- crystalline phases, atomic layers and intermediate matter on a nanometre scale that engenders novel properties and capabilities for applications in diverse areas of science and technology. We reiterate that orbitals, as amplitude functions for the hydrogen atom, arise as a result of the former algebraic calculations but are superfluous as basis functions to facilitate the latter numerical calculations.

We mention above the fallacy perpetrated by G. N. Lewis in attempting to locate individual electrons at particular points in relative space, contrary to the fundamental indistinguishability of electrons and the indeterminacy of such individual location. One might recognise the next major fallacy as being due to N. Bohr; his *aufbauprinzip* essentially amounts to extrapolation from a point, regardless whether Madelung's modification is taken into account. The grossest harm to chemical education arose, however, from Pauling's failure to recognise, among other aspects, that amplitude functions in spherical polar coordinates represent an arbitrary choice of the two coordinate systems that Schroedinger himself applied in the solution of his equations [7]. Pauling's attention was directed to the structure of chemical matter on an atomic scale: the full title of his book [29] was *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*. Before that book or its preceding papers of the same title appeared, Teller [27] had recognised the importance of ellipsoidal amplitude functions of the hydrogen atom that are applicable to a chemical bond, unlike both spherical polar and paraboloidal amplitude functions. Within Pauling's book [29] in its three editions appear innumerable descriptions of such structure in terms of orbitals, which are

merely amplitude functions -- mathematical formulae -- appropriate in spherical polar, paraboloidal and spheroconical coordinates to only an atom with only one electron and that is isolated from other atoms. As such, these formulae and their nearly universal depictions in spherical polar coordinates constitute an arbitrary choice; the alternative, ellipsoidal functions, would have been a superior choice for Pauling but he ignored them. All these amplitude functions must be perceived as purely mathematical formulae and abstract quantities lacking finite spatial extent, parochial to wave mechanics and foreign to other methods of quantum mechanics, as Bohr recognised: according to wave mechanics, a single hydrogen atom in its ground state might formally occupy the entire universe, but without exclusion of other atomic centres. Even though most amplitude of any such function for small values of the pertinent quantum numbers occurs at distances comparable with internuclear separations in molecules or crystals, as our figures in preceding parts directly demonstrate in coordinates in any of the four systems [2 - 5], the point is that these figures pertain expressly to a hydrogen, or other one-electron, atom: their extrapolated application to atoms with multiple electrons is unwarranted and unjustifiable.

A half century elapsed after the origination of wave mechanics before Woolley proclaimed a truth [30] that should have been obvious much earlier, namely that a calculation according to wave mechanics in which the electrons and atomic nuclei of a selected system are treated on a par practically forfeits the possibility of an interpretation of the results in terms of a somewhat rigid frame of atomic nuclei in a particular relative geometric arrangement surrounded by the associated electronic density: the latter is the essence of molecular structure. As atomic nuclei are distinguishable from electrons, and even from one another if the atomic and mass numbers differ, a structure of a diatomic molecule, expressed as an internuclear distance, is formally and practically definable, but, ironically, such a diatomic molecule lacks other than a trivial shape or structure. If one simply writes, for a particular assembly of N nuclei and n electrons in a polyatomic molecule, a full hamiltonian operator that includes only terms for the kinetic energy of both electrons and nuclei with the electrostatic potential energy of all their interactions -- which corresponds to the standard hamiltonian in the practice of quantum chemistry apart from an inclusion here of nuclear kinetic energy, one finds clearly that the result of the solution of the Schroedinger equation, necessarily by purely numerical means, yields only an energy, or rather prospectively a manifold of energies of all states discrete and continuous. For a particular collection of nuclei and electrons, those energies would encompass all possible conformational isomers, such as ethanol and dimethyl ether for C_2H_6O [11], or cyclopropene, allene and propyne for C_3H_4 [31]. As such a classical molecular structure is incompatible with quantum mechanics, to justify or to rationalise such a structure with arbitrarily selected amplitude functions based on wave mechanics for a hydrogen atom is profoundly illogical, despite the fact that semi-empirical calculations, based roughly on Schroedinger's equation used selectively without nuclear kinetic energy, can reproduce or even predict such structure in favourable cases. In the most accurate such calculations including perturbation theory to large order to take extensive account of electron correlation, any relation between the details of the basis set and the eventual structure is lost in the quest for an ever more negative minimum energy of the system. In typical contemporary discussions of molecular structure in chemical education, an invocation of orbitals of one kind or another divorced from such calculations is the mechanism of a circular argument, whether implicit or explicit: a known molecular structure is considered to imply chosen orbitals or their combinations as hybrids on particular atoms, and then that orbital configuration is applied to explain the structure. The process is blatantly fraudulent [32], and incomprehensible to students unless and until they themselves become indoctrinated, so as to repeat, in the manner of a parrot, or to echo -- replete with distortions, such explanations. To abandon such arguments incorporating

orbitals and to teach, honestly and frankly, molecular structure as a consequence of experimental measurements of a classical nature is unquestionably a more effective heuristic strategy.

Although some introduction to *quantum mechanics*, generally only wave mechanics, has become universally an integral component of the teaching of physical chemistry, somewhat displacing chemical kinetics that constitutes the treatment of transformations of chemical matter that are the *raison d'être* of chemical science, within an undergraduate curriculum there might be insufficient time to transmit an intimate knowledge of the theoretical basis and construction of quantum-chemical programs and their effective use that must precede their competent application in other than a superficial manner. In any case, such applications are of largely marginal interest in the general practice of chemistry. One contemporary pretext for the teaching of quantum mechanics is as a basis of molecular structure, but such molecular structure is incompatible with rigorous quantum mechanics [30]! Clearly not only orbitals but also quantum mechanics, as a collection of mathematical methods [13], can be opportunely discarded from general chemical education until the post-graduate level; if topics of quantum physics, such as the details of atomic spectra and the photoelectric effect of molecules or solid materials, be deemed germane for significant objectives, there is no objection to their discussion, free from the baggage of orbitals. For the purposes of analytical chemistry, electronic transitions of atoms play an important role in practical quantitative analysis, but the traditional treatment of atomic spectra in analytical or physical chemistry is inadequate for other than a superficial description of the underlying phenomena. Photoelectron spectra in typical practice must be recognised to be concerned with transitions of a molecule from a, generally neutral, ground electronic state to various electronic states of a molecular cation, not to a loss of an electron from a fictitious atomic or molecular orbital.

Despite the astonishing progress of both experimental techniques to characterise the structure of molecules and other chemical matter and of computational schemes to reproduce that structure and its associated properties, the chemical bond [33, 34], whatever that might be, remains just as much an enigma as when the first chemists and physicists sensed the presence of geometrical order at an atomic level during the mid-nineteenth century. What is a chemical bond? One might respond with the same answer attributed to Thomas Aquinas who was asked to define time: "I knew before you asked me". There are strong bonds and weak bonds, short bonds and long bonds; bonds might form or break, oscillate or rotate. A chemical bond might exist in the minds of chemists who perceive a qualitative description of diverse chemical matter, but neither experiment nor theory nor calculation unequivocally elucidates its palpable existence. What we can measure and calculate are the mean distances between centres of electronic charge associated with atomic nuclei and the density of electronic charge in the vicinity of those atomic nuclei; any attribution of a chemical bond between two such nuclei is, from a quantitative point of view, inevitably a figment of one's chemical imagination.

Atomic and molecular spectra are integral and invaluable tools of the practice of chemistry; their introduction and treatment are essential components of chemical education, but their discussion can rely on classical description and explanation, in combination with quantum laws or the laws of discreteness [28]; in practice, that classical description occurs anyhow, despite the pretence to embellish with terms of ostensibly quantum-mechanical aggrandizement. Many textbooks of physical chemistry introduce quantum-mechanical -- nearly invariably merely wave-mechanical -- concepts before discussing the spectra of simple molecules. Other textbooks of physical or inorganic chemistry, increasingly generated, usurp the primary role of macroscopic chemical thermodynamics by beginning with microscopic quantum mechanics. Although the latter practice might seem logical, apart from the schism between quantum mechanics and molecular structure, its systematic development to encompass, for instance, liquid crystals, or even

van't Hoff's equation for osmotic pressure that has likewise practical applications, would take forever. With regard to quantum mechanics and spectra, the historical order was the reverse of the relative placement in current textbooks. The first observation in quantum physics was likely the discovery of dark lines within the emitted continuum of the solar spectrum, by Wollaston in Cambridge in 1802; these lines were subsequently classified by Fraunhofer, as mentioned above. The regularities in atomic spectra, deduced by Balmer, and in molecular spectra, by Deslandres nearly concurrently, then became the first quantitative analyses in quantum physics. The recording of structure in the bands of infrared spectra of gaseous diatomic molecules after a few years created a further impetus for the understanding of the *quantum laws of matter and radiation* [10,28]. As Bjerrum's first quantum theory of molecules, related to these infrared spectra, that appeared in 1912, so preceding Bohr's quantum theory of the hydrogen atom, also preceded Rutherford's recognition of the nuclear atom, it was bound to be unsuccessful [35]. By 1920 the distinction among rotational, vibrational and electronic motions in simple molecules in relation to their spectra was appreciated. Such rotational and vibrational motions are incontestably a classical interpretation -- nobody has ever directly observed a molecule undergoing a vibrational motion, on a time scale $\sim 10^{-13}$ s, or even a rotational motion, on a time scale $\sim 10^{-10}$ s. What one can observe through x-ray diffraction is that the electronic density around an atomic nucleus in a crystalline sample might become more compact as the temperature of the crystal is decreased toward 0 K. The electronic motions associated with spectral transitions at photon frequencies $\sim 10^{15}$ Hz are more difficult to picture in classical terms than the vibrational -- internal -- motion of a molecule, or rotational -- external -- motion about an axis within the molecule; a simplistic description as involving a density of electronic charge near some particular nuclei that is altered between the states involved in an electronic transition, whether or not accompanied with altered internuclear distances in the case of molecules, might serve for that purpose. According to quantum mechanics, there are no such rotational and vibrational motions, just as there is no molecular structure, and for the same reason; as mentioned above, there are only energies of states of which some energy differences between discrete states might be associated, classically, with rotational or vibrational transitions. The relative order of rotational, vibrational and electronic transitions with generally increasing frequency or energy of photons is no guide to the nature of such a transition; for instance, a transition between two electronic states of nitrogen oxide, NO, distinguished by their angular momenta expressed in their term symbols, ${}^2\Pi_{3/2} \leftarrow {}^2\Pi_{1/2}$, occurs in the midst of transitions associated with rotational motion of H₂O. An appeal to quantum mechanics to explain rotational or vibrational motions is clearly yet another logical fallacy. In particular, a canonical linear harmonic oscillator, possessing a quadratic dependence on displacement, is a farcical basis for a model of a diatomic molecule; apart from its evenly spaced and uncountable discrete energies with thus no finite dissociation energy, and apart also from transitions only between states of adjacent energies, its rotational parameters increase systematically with vibrational energy, contrary to the general systematic decrease of these parameters for any real diatomic molecular species. That canonical oscillator serves as a useful exercise in physics to introduce the diversity of quantum-mechanical methods [11], but has little relevance to chemistry. Even its invocation to explain the continuous spectral distribution from a *black body* is superseded [36]; according to its continuous nature, that distribution is, in any case, inconsistent with a necessity of an interpretation involving discrete quantities. Associations of roughly evenly spaced lines in the far infrared region with rotational motions and (more) roughly evenly spaced bands in the mid- and near-infrared regions with vibrational motions are readily argued on the basis of the isotopic effects, between ${}^1\text{H}^{35}\text{Cl}$ and ${}^2\text{H}^{35}\text{Cl}$ for instance, and, by analogy, for spectral features of other molecules in those regions [37]. On the same basis, the lack of appreciable effect of nuclear mass on spectral lines at the onset of a

spectral system in the visible and ultraviolet regions warrants an association with a transition between electronic states, which might be accompanied with vibrational and rotational energies altered from those of the ground state. With a separation of nuclear and electronic motions, quantum-mechanical methods are, however, useful to generate the relative energies of states of an asymmetric rotor, for instance.

For atomic or molecular spectra based directly on properties described formally as intrinsic angular momenta of electrons and nuclei, such as nuclear magnetic resonance or electron paramagnetic resonance, wave mechanics is essentially useless, because Schroedinger's equations involve spatial coordinates that are inapplicable to these *spin* phenomena. For instance, in discussing these molecular spectra on the basis of chemical shifts and coupling parameters, some textbooks of physical chemistry present a matrix, with its component matrix elements to be made diagonal to yield the energies of states, or a determinant of that matrix, without admitting the relation to the original matrix mechanics. The eventual description of magnetic-resonance spectra in those books proceeds to become qualitative and pragmatic; this approach is typical in organic chemistry, which suffices for the effective use of NMR spectra that play an enormous role in the conduct of organic and inorganic chemistry. As there is no classical basis of these magnetic-resonance spectra, unlike spectra associated with rotational and vibrational motions, a pragmatic approach is unavoidable. Incidentally, Dirac considered matrix mechanics to be more fundamental than wave mechanics [38], in part because Schroedinger's approach applied in quantum electrodynamics led to intractable infinities whereas Heisenberg's approach was practicable. Ironically, particular textbooks on quantum mechanics and theoretical chemistry such as that by Eyring, Walter and Kimball [39], and more recently those by J. Simons [40, 41], for instance, make no concession to the fact that matrix mechanics was ever developed -- even though it was the instigation for wave mechanics. This myopic view of quantum mechanics for chemical purposes is deprecable.

IV. CONCLUSION

In summary, on the basis of the preceding arguments, one can cogently argue to abandon not only the use of orbitals of a hydrogen, or other one-electron atom, except within that specific context -- to eliminate a vestige of Prout's hypothesis, but also the teaching of quantum mechanics in chemistry, before the post-graduate level in chemistry for perceived specialist purposes. Without that extrapolation from a point, even the teaching of the solution of the hydrogen atom, as presented in the four preceding parts [2 - 5], seems to be worthless other than as a mathematical exercise in physics, unessential for chemistry. A reader might assess the authority of this author who makes such an apparently radical proposal: the author has demonstrated and lectured in chemistry in several branches, and in mathematics and physics, for several decades; our qualifications include books on molecular spectrometry [37], models for structural chemistry [42] and mathematics for chemistry [43]. A knowledge and practice of wave mechanics are demonstrated in the preceding parts of this series [2 - 6], and a broader practical application of quantum mechanics in three methods elsewhere [11], although our knowledge is far from complete [12]. Quantum mechanics, we reiterate, constitutes undeniably a collection of mathematical methods or algorithms [13, 14], applicable to calculations pertaining to phenomena on an atomic scale. If students are not expected to make significant use of these methods, apart from esoteric exercises in their development, what is the heuristic value of consuming valuable time and resources in their presentation, to the detriment of other and genuinely chemical topics?

That Planck's flawed derivation of a formula for radiation from a black body, which is a continuous spectral distribution, initiated the era of quantum mechanics is a fallacy as mentioned above [35]. Einstein's derivation of the photoelectric effect depended critically on the quantum laws of matter and radiation [10]; his treatment appears simple, but its value at the time of its generation was that it was seminal in establishing such discrete or *quantum* properties, which are an essential basis for the understanding of molecular spectra and molecular structure. Heisenberg's principle of indeterminacy that limits the precision with which complementary variables, such as the position and momentum of a particle on an atomic scale, can be measured simultaneously is applicable to an experimental description of measurements on that scale; for instance, although one can generate flashes of light of duration on an attosecond scale, i.e. $\sim 10^{-17}$ s, the consequent uncertainty or spread of energy precludes the observation of purported atomic vibrations. Aware of these conditions, an instructor of physical chemistry can astutely design courses that genuinely prepare a student to appreciate the structures, properties and transformations of molecules and chemical matter, without the distracting and resisted mathematical digressions that reflect a lack of comprehension of the global scope of chemistry. Authors of textbooks for chemistry in all its branches should revise their content accordingly. The pernicious cycle of instructors, or educational administrators, selecting textbooks to prescribe for their students on the basis of their own superficial understanding, or even ignorance, and then authors pandering to the crudity of those selectors, must be severed.

Writing before the emergence of the present revelations about the wave mechanics of the hydrogen atom, Pritchard advocated a revision of the theory of chemical binding, or "the teaching of valence theory" [44]. Such a proposal might presuppose that a description based on electrons being distinguishable or their distribution depending on amplitude functions in an arbitrarily selected system of coordinates is a legitimate objective, whereas the preceding discussion tends to demolish such a description. Because the structure of molecules and chemical materials is a quintessential concern of chemistry, as a basis of a description of chemical reactions, and as that structure is classical in nature, seeking a quantum-mechanical explanation of that incompatible structure is illogical and bound to fail. One might hope for, and work toward, an innovative development of a theory or models to yield an interpretation of the structure of molecules and materials that lacks obvious artifacts, whilst recognizing and applying the practical value of mathematical tools and the software of quantum chemistry, and molecular mechanics, in the praxis of chemistry. Through analytical chemistry that defends the quality of life, and organic chemistry that enables great advances in medicine, and inorganic chemistry with material science that creates an ever improved and expanding range of materials, not to mention the associated chemical industry, chemistry remains the central science. Let us obliterate the pseudo-science based on orbitals and irrelevant quantum mechanics so that chemistry and chemists can legitimately contribute to the solutions of global problems.

V. REFERENCES

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