Wave-mechanical Model for Chemistry (Reprint: To be published in Foundations of Chemistry)

Jan C. A. Boeyens

Centre for the Advancement of Scholarship, University of Pretoria

February 13, 2015

Abstract

The strength and defects of wave mechanics as a theory of chemistry are critically examined. Without the secondary assumption of wave-particle duality, the seminal equation describes matter waves and leaves the concept of point particles undefined. To bring the formalism into line with the theory of special relativity, it is shown to require reformulation in hypercomplex algebra that imparts a new meaning to electron spin as a holistic spinor, eliminating serious current misconceptions in the process. Reformulation in the curved space-time of general relativity requires the recognition of nonlinear effects that invalidate the practice of linear combination of atomic orbitals, ubiquitous in quantum chemistry, and redefines the electron as a nondispersive wave packet, or soliton.

Keywords: wave mechanics, quaternion, nonlinearity, soliton, electron

1 Introduction

Solution of Schrödinger's wave equation was greeted with the expectation of providing a mathematical tool for the easy simulation of chemical processes. For a variety of reasons it turned out not to be the expected panacea and the situation was further complicated by the incorporation of some dubious assumptions that misled the chemical community for more than half a century.

This communication reviews some successes of wave mechanics applied to chemical problems, but went largely unnoticed, due to persistent use by theorertical chemists of flawed algorithms such as orbital hybridization and linear combination of atomic orbitals. Recent developments, inspired by taking cognisance of space-time topology and leading to a proper understanding of electron structure and spin, matter waves, and nonlinear effects, are briefly outlined.

2   The Model

The nuclear model of the atom requires that interatomic interaction be visualized in terms of extranuclear valence electrons, wave-mechanically associated with atomic cores. The wave equation has been solved only for the hydrogen electron and this solution must perforce serve as a model for all other atoms. The physical meaning of the wave function is not beyond dispute and Madelung's hydrodynamic interpretation [1], which comes closest to the intuitive chemical model of an atomic nucleus, spherically surrounded by a diffuse charge cloud, is assumed.

A spherically symmetric central field is therefore assumed for all free atoms. Any interaction distorts the spherical symmetry and the wave function of the electron in interaction will be modified accordingly. In three dimensions the allowed modes of distortion are described by Laplace's equation, which is a linear differential equation.

Irrespective of the physical nature of an electron or the interpretation of the wave function, standard procedures apply in solving the equation. The basic assumption is that a three-dimensional hydrodynamic potential is adequately approximated by the product of three one-dimensional functions:

$$V = V_1(x_1) \cdot V_2(x_2) \cdot V_3(x_3)$$

Most commonly the independent variables are defined as either cartesian or spherical polar coordinates.
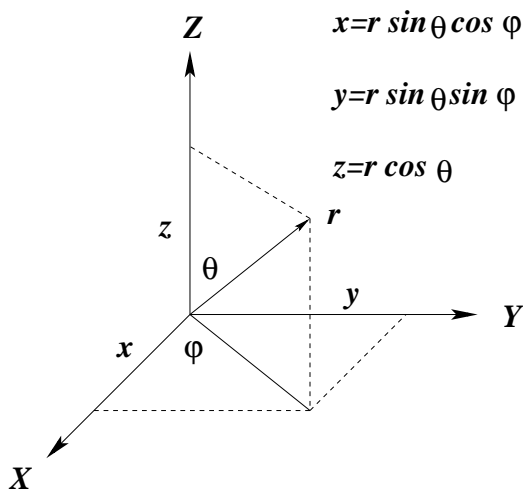
Separation of the variables is achieved by substituting the product function into Laplace's equation, which in cartesian form reads

$$\nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \,.$$

After differentiation and division by V it reduces to

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = 0 \,.$$

Each term is a function of one variable only and therefore independently equal to some constant, *e.g.*

$$\frac{d^2X}{dx^2} = KX \,.$$

By defining the constant as a squared quantity the resulting *Helmholtz* equation is solved by an exponential function. For $K = k_1^2$, $X(x) = c\exp(\pm k_1 x)$. Noting that $e^a \cdot e^b = e^{(a+b)}$, the overall solution follows as

$$V(x, y, z) = e^{k_1 x + k_2 y + k_3 z} \,,$$

such that $k_1^2 + k_2^2 + k_3^2 = 0$.

The simplest solution has $k_1^2 = k_2^2 = k_3^2 = 0$. This amounts to three orthogonal linear distortions, which is at variance with the distortion expected from a directed chemical interaction, which would be better described by assuming $k_1 = ik_2$, $k_3 = 0$, to give

$$X = c_1 e^{\pm kx} \quad , \quad Y = c_2 e^{\pm iky} \quad , \quad Z = c_3 e^{\pm k_3 z}$$

i.e.

$$V_k = c_1 e^{k(x \pm iy)}$$
$$V_z = \pm c_2 z$$

Given that a complex exponential is mathematically equivalent to a rotation, the complex pair, V_k, is interpreted as circular distortions, in opposite sense, perpendicular to the polar Z direction. The polar coordinate that identifies the direction of interaction, is labeled arbitrarily.

To analyze the problem in spherical polar coordinates the mathematics is more complicated, but the result is the same. In this case solution is effected by separation into a radial equation, solved by spherical Bessel functions, and an angular equation solved by spherical surface harmonics. The set of surface harmonics, equivalent to the cartesian functions considered before, are of the form:

$$Y_0 = \sqrt{\frac{3}{4\pi}}\cos\theta \propto \frac{z}{r}$$
$$Y_{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi} \propto \frac{x \pm iy}{r}$$

The cartesian result follows from Euler's formula

$$e^{i\varphi} = \cos\varphi + i\sin\varphi$$

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and the cartesian–polar–transformation.

In chemical texts frequent use is made of the property of linear differential equations that any linear combination of solutions constitutes another solution. One such exercise is to make linear combinations of two complex harmonics:

$$Y_+ + Y_- = \frac{x + iy}{r} + \frac{x - iy}{r} \to \frac{x}{r}$$

$$Y_+ - Y_- = \frac{x + iy}{r} - \frac{x - iy}{r} \to \frac{iy}{r}$$

Noting that $Y_0 = z/r$, the outcome is

$$Y_0' \propto \frac{x}{r}$$

$$Y_{\pm 1}' \propto \frac{z \pm iy}{r} \,,$$

effectively amounting to a $\pi/2$ rotation of the polar axis from Z to X. It is readily demonstrated [2] that any rotation of axes corresponds to some linear superposition, and *vice versa*.

3   Wave Mechanics

Wave-mechanical analysis of diatomic interaction develops along similar lines. The formalism is based on Schrödinger's simulation of the electronic behaviour on an isolated hydrogen atom. Without specifying the physical nature of the electron it is assumed to interact with the central electrostatic field of a stationary proton. The general three-dimensional wave equation

$$\nabla^2 \Psi = \frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2}$$

is modified in terms of de Broglie's postulate that relates wavelength, λ, to mechanical momentum, p, through Planck's action constant, $h = p\lambda$, for matter waves [4]. After separating space and time coordinates the amplitude equation

$$\nabla^2 \psi = \frac{2m}{\hbar^2} (E - V) \psi \,,$$

which is used to analyze chemical problems, is an eigenvalue equation for kinetic energy, closely related to Laplace's equation.

In polar coordinates the equation separates into radial and angular parts, the latter identical to spherical surface harmonics. The radial function specifies the electronic energy in the central field, with potential energy of $V = e^2/(4\pi\epsilon_0 r)$ at a point distant r from the proton.

3.1 Hydrogenic Wave Functions

The eigenfunction solutions of the amplitude equation are more commonly simply known as *wave functions*. A wave function in polar coordinates is a product function of the type:

$$\psi = R(r) \cdot \Theta(\theta) \cdot \Phi(\varphi) \,.$$

The eigenvalues of each type are characterized by a set of quantum numbers:

$$
\begin{aligned}
R(r) &: & n &= 1, 2, 3 \ldots & &\text{(Principal quantum number)} \\
\Theta(\theta) &: & l &= 0, 1, 2, \ldots, (n-1) & &\text{(Orbital quantum number)} \\
\Phi(\varphi) &: & m_l &= -l, \ldots, +l & &\text{(Magnetic quantum number)}
\end{aligned}
$$

The total energy of the electron is specified by the principal quantum number, $E \propto -1/n^2$. As mentioned before, the angle-dependant $Y(\theta, \varphi)$ are the Laplacian surface harmonics. In wave-mechanical practice they are interpreted as angular-momentum eigenfunctions. This interpretation had clearly been carried forward from Bohr's planetary model, which treated the electron as an orbiting particle. In the wave-mechanical model this interpretation leads to an awkward dilemma in the case where $l = 1$ and $m_l = 0$. The orbital quantum number would specify non-zero angular momentum with a contradictory zero component ($m_l = 0$) in an applied magnetic field.

The standard interpretation is clearly inadequate and casts some doubt on the assumed particle nature of the electron. However, a more convincing interpretation will have to await a more detailed analysis.

The particle model causes another interpretational problem. Chemical intuition, in line with all experimental evidence, pictures the hydrogen atom as a non-polar spherical object. Like the two-dimensional planetary model, such an atom cannot be rationalized in terms of an electronic particle that orbits the nucleus at high speed, without radiating away its energy.

The alternative, according to the Copenhagen interpretation of quantum mechanics, considers the wave function as describing a *probability wave* that controls the electronic particle. Although the nature of the wave remains unspecified, its effect on the electron is that it may appear, at any time, at any point, with equal probability. Given a probability sphere that limits the extent of the atom, the electron is potentially present, at any given instant, at all points within the sphere. It can be localized at any point, chosen by an external observer, using a suitable probe. This is the picture, which, with little variation, is presented by virtually all textbooks as the quantum-mechanical description of the hydrogen atom.

This interpretation has some serious philosophical implications. It is immediately obvious to be at variance with an objective reality. Without a measurement there is no electron. This concept had been refined to the point where it is seriously asserted [5] that 'the moon is demonstrably not

there when nobody looks'. Another complication is that the electron occurs with equal probability at all points until it is located somewhere by a measurement, which is said to "collapse the wave function". The electron instantaneously ceases to exist at all other points. The only way in which information of the measurement can be broadcast over all space, is by "spooky interaction at a distance", in direct conflict with the special theory of relativity.

This weird behaviour emerges only with the assumption of an electronic particle, despite the overwhelming evidence that a beam of electrons undergoes diffraction in the same way as electromagnetic waves of X-ray wavelength.

By giving up the identification of Schrödinger wave functions with probability waves, an obvious alternative is identification with real physical matter waves, as was consistently insisted on by the author of the wave equation.

3.2 Non-hydrogen Atoms

In the same way that a classical many-body problem defies mathematical analysis, Schrödinger's equation for non-hydrogen atoms cannot be solved in closed form. Approximate simulations are all based on the hydrogen results, augmented by spectroscopic evidence, and the unrealistic assumption that all electrons behave according to the central-field harmonics of the hydrogen model. Available electronic levels on any atom are assumed to precisely follow the calculated hydrogen spectrum, without any guidance on the way that electrons are distributed over the available levels in the ground state.

A useful assumption, designed to visualize wave mechanics, proposed that each electron should be confined to the wave-mechanical analogue of a Bohr orbit, dubbed an *orbital*, with a unique set of quantum numbers, n, l, m_l. However, in order to correlate with atomic spectra and the periodic table of the chemical elements it was further necessary that each orbital should accommodate two electrons.

The way in which a beam of silver atoms splits into two distinct components in an inhomogeneous Stern-Gerlach magnetic field was interpreted as arising from two possible orientations of the magnetic moment of an electron in a singly-occupied atomic orbital. It was eventually agreed that the observed magnetic moment was associated with intrinsic angular momentum, called spin, carried by the electron.

The concept of spin is an entirely non-classical notion, but ironically it does not appear in wave-mechanical analysis either. It entered into physical science as an empirical concept, assumed to be described by an additional quantun number, s. Based on the observation that the degeneracy of an l sub-level amounts to $2l+1$, the two-fold variability associated with spin was interpreted to imply $2s + 1 = 2$, *i.e.* $s = 1/2$, $m_s = \pm 1/2$. It has become standard terminology that each atomic orbital can accommodate only two

electrons of opposite spin, without precise definition of an orbital. A more meaningful proposition is that each electron in an atom is characterized by a unique set of four quantum numbers, n, l, m_l, m_s, known as the *exclusion principle*.

Over the years the orbital concept has acquired a completely different meaning in chemical bonding theory. In the context of real atomic orbitals it occurs in contradiction of the exclusion principle. In particular, the rotation of cartesian axes on linear combination of complex wave functions, as discussed before, was misinterpreted as creating a three-fold degenerate set of real orbitals, with common $m_l = 0$, in conflict with the exclusion principle. To avoid further confusion it is recommended that the term orbital should finally be abandoned and eliminated from chemical terminology.

Wave-mechanical simulation of the electronic structure of non-hydrogen atoms is done by the method of a self-consistent field, also known as Hartree-Fock simulation. Additional electrons are added to the hydrogen system with suitably increased nuclear charge. A radial distribution function for each electron is variationally optimized in turn, within the central field of the nucleus and all other electrons, assuming the (n, l) multiplet structure as in hydrogen to apply, until self-consistency is reached. The major complication arises from the need to incorporate inter-electron repulsions. The angle-dependence for each electron is assumed to be correctly described by the corresponding hydrogen harmonic functions. The latter are strictly defined in a central field, which is approximately valid only for the outermost electron in the system.

3.2.1 Compressed Atoms

Normalization integrals in HF analysis are calculated over all space and the final result therefore refers explicitly to isolated atoms. To allow for the effect of the environment, as in a chemically crowded system, the normalization should be terminated at a suitable finite value of the radial distance. This is equivalent to isotropic compression of the free atom.

The effect of isotropic compression is to displace all electronic energy levels to higher values. Compression is achieved [6] by repeating HF simulation under boundary conditions that restrict the electron density to a sphere of radius r_0 through a multiplication factor of

$$S = \exp\left[-\left(\frac{r}{r_0}\right)^p\right] \text{, for } p >> 1$$

before normalization. The process is continued with decreasing r_0 until at a critical compression radius the most energetic electron in the system reaches the ionization limit. The electron is decoupled from the field of the atomic core and finds itself in an impenetrable hollow sphere at constant potential, with ground-state energy, $E = h^2/(8mr_0)^2$.

When compressed to its ionization radius the decoupled (valence) electron is spread over a sphere of uniform density, with an effective wave function given by the step function,

$$\psi(r) = \sqrt{3c/4\pi n}\left(\frac{1}{r_0}\right)S$$

where c is a constant and n the principal quantum number according to the HF shell structure.

Physically the activated valence electron is pictured as a standing spherical wave that encloses the atomic core, the size of which is allowed for by the constant c. It is argued that in this state the electron is free to interact with another similarly activated electron wave, resulting in a single wave that envelops both atomic cores as a diatomic molecule. The radii of spherically confined waves, as defined here, can be calculated directly from the maxima of SCF wave functions [7, 8] normalized over spheres of constant density, as $r_a = \sqrt[3]{3u^2(r)/\pi}$. This entire calculation can be duplicated by the analysis of atomic wave structures, using elementary number theory [9].

The two sets of radii are remarkably alike and promising as a basis for the simulation of generalized interatomic covalent interactions using the effective wave function.

3.2.2 Generalized Heitler-London Method

Simulation of covalent interaction was first performed by Heitler and London for H_2, by variation of a linear combination of $1s$ atomic wave functions. To model the more general case of homonuclear diatomic molecules the interacting atoms in their valence states are described by monopositive atomic cores and two valence electrons with constant wave functions. Assuming the cores to be clamped in fixed positions the electronic motion is described by the Schrödinger equation

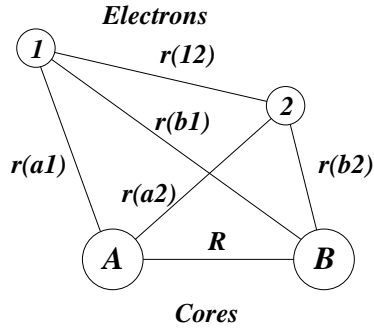$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi$$

In atomic units[1] length is measured in units of a_0, energy in rydberg units (27.2 eV), and the Hamiltonian operator is formulated as:

$$H = -(\nabla_1^2 + \nabla_2^2)/2 - (1/r_{a1} + 1/r_{a2} + 1/r_{b1} + 1/r_{b2}) + 1/r_{12} + 1/R$$

with all variables as in the diagram:

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[1]$m = \hbar = e = 4\pi\epsilon_0 = 1$

The molecular wave function is defined by the combination of atomic wave functions:

$$\psi = \psi_a(1) \cdot \psi_b(2) + \psi_a(2) \cdot \psi_b(1)$$

which ensures equal sharing of exchanged electrons. At given internuclear distance the ground-state energy-eigenvalue solution is obtained by integration of the differential equation over all space:

$$E = \frac{\int \psi H \psi d\tau}{\int \psi \psi d\tau}$$

The mathematical procedure consists of well-documented textbook material [10].

If the valence-state wave functions are written in their simplest, hard-sphere form,

$$\psi(r) = \sqrt{3c/4\pi n}/r_0 \ , \ 0 < r < r_0, \ c = 0.46$$

The Heitler-London integrals can be evaluated directly by summation over the atomic ionization spheres.

The Heitler-London calculation, without further modification, applies only to homonuclear first-order interaction. However, it could be modified [11] by a few simple assumptions to deal with general heteronuclear interactions of all orders numerically. The published results are in excellent agreement with experiment.

Remark: The results obtained for H_2 by the method of James and Coolidge [12], with wave functions constructed numerically by linear combination of hundred or more terms, are indisdinguishable from the most accurate spectroscopically measured values. Such extensive superposition must inevitably result in uniform density as in the valence state proposed here for generalized Heitler-London simulations. The success of this scheme is then no longer surprising.

3.3   The Quantum Potential

Madelung's hydrodynamic interpretation [1] of Schrödinger's equation was based on assuming a wave function in polar form with real amplitude R and

phase S, $\Psi = R \exp(iS/\hbar)$. Substituted into the time-dependent equation,

$$i\hbar \frac{\partial \Psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V \right) \Psi \,,$$

followed by the separation of real and imaginary parts, it results in a *continuity equation*,

$$\frac{\partial}{\partial t}(R^2) + \frac{\partial}{\partial x}\left(\frac{R^2}{m}\frac{\partial S}{\partial t} \right) = 0$$

and an analogue of the classical Hamilton-Jacobi equation:

$$\frac{\partial S}{\partial t} + \frac{(\nabla S)^2}{2m} - \frac{\hbar^2}{2mR}\nabla^2 R + V = 0 \,.$$

It differs from the classical equation only in the appearance of the term

$$V_q = -\frac{\hbar^2 \nabla^2 R}{2mR}$$

now generally known as the quantum potential.

Madelung interpreted $R^2 = \rho(\boldsymbol{r})$ as the density of a continuous fluid with stream potential $\boldsymbol{v} = \nabla S/m$ to define hydrodynamic continuity. In this case the 'quantum potential' arises in the effects of an internal stress in the fluid.

This promising model could not be reconciled with the conviction of an electron as a particle, which persisted despite the conspicuous mathematical evidence of a wave structure. Subsequent efforts by de Broglie, Bohm, Takabayasi, Holland and others, to develop the hydrodynamic model into an alternative ontological theory, all stumbled on the notion of particle-and-wave. The first meaningful alternative of an electron as a spherical standing wave is perhaps due to Milo Wolff [13], but the impact of his work has been minimal. However, it is in satisfying accord with Madelung's model, assuming all extranuclear electrons to coalesce into a spherical composite standing wave with a nodal structure, defined by Schrödinger's equation, that marks the boundaries of the quantum shells.

3.3.1 Electronegativity

The quantum-potential concept explains the paradoxical conclusion that a spherically confined valence electron has neither kinetic nor potential energy. The answer is that the non-zero ground-state energy must be quantum potential energy. By recognizing this as the chemical potential of the valence state [14] it directly defines the elusive concept of electronegativity.

3.3.2 Non-local interaction

As the expression for quantum potential contains the variable R in both numerator and denominator it may be argued not to fall off with distance

and hence could mediate non-local interaction. However, this is pure conjecture and its effects are more likely confined to local holistic systems, such as molecules [2].

4 Space-Time Effects

A constant source of unease that plagued the probabilistic interpretation of wave mechanics since its inception, has been the conflict with the theory of relativity. The way in which a collapsing wave function transmits information defines a *non-local* effect, in contrast to the basic premise of relativity theory that the finite speed of light can never be exceeded.

This discrepancy amounts to more than a problematic interpretation and may be traced back to the mathematical formulation of the the two theories. Whereas wave mechanics is defined in three-dimensional space, relativity is a four-dimensional theory in space-time, which implies mathematical equivalence of space and time coordinates. A comparison of the transformation between relatively moving frames of reference, as defined in classical Galilean relativity and by the relativistic Lorentz transformation, highlights the difference. For relative motion along the x-coordinate one has:

Galilean   Lorentzian

$x' = x - vt$ $x' = (x - vt)/\beta$, $\beta = \sqrt{1 - v^2/c^2}$

$t' = t$ $t' = (t - vx/c^2)/\beta = \beta t$

Although the expressions become identical in the limit where $v \ll c$, the Lorentz transformation demands that the electromagnetic field only exists in four-dimensional (Minkowski) space-time of special relativity. The invariant separation between points in Euclidean space and Minkowski space-time compares like:

$$d^2 = x^2 + y^2 + z^2 \quad vs \quad d^2 = x_0^2 + x_1^2 + x_2^2 + x_3^2 \, , \, x_0 = ict$$

Whereas the d'Alembertian expression,

$$\Box^2 V = \nabla^2 V - \frac{1}{c^2}\frac{\partial^2 V}{\partial t^2} \equiv \frac{\partial^2 V}{\partial x_0^2} + \frac{\partial^2 V}{\partial x_1^2} + \frac{\partial^2 V}{\partial x_2^2} + \frac{\partial^2 V}{\partial x_3^2} = 0$$

allows separation of space and time variables in Euclidean space it is forbidden in Minkowski space-time. In this sense Schrödinger wave mechanics is incomplete, as claimed [15], but never convincingly demonstrated by Einstein. Solution of d'Alembert's (4D Laplacian) equation, without separation of the variables, requires the use of hypercomplex algebra.

4.1 Electron Spin

On writing the Lorentz transformation in the form of a 4×4 matrix it is recognized as a four-dimensional complex rotation, which on closer scrutiny

reveals the same characteristics as the electron spin function. The simplest formulation of the Lorentz rotation is in terms of quaternions, the elements of four-dimensional hypercomplex algebra. It is the same algebra first use by Maxwell to define the electromagnetic field.

In the same way that two real numbers may be combined to create a complex number a quaternion results from the combination of two complex numbers, $u = a + ib$ and $v = c + id$:

$$q = a + ib + jc + kd \; ; \; q = a_0 + \sum_{i=1}^{3} a_i e_i$$

$$q* = a - ib - jc - kd$$

where the e_i are generalizations of $\sqrt{-1}$, in matrix notation:

$$1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \; e_1 = \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix} , \; e_2 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} , \; e_3 = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$$

with the rule of composition: $i^2 = j^2 = k^2 = ijk = -1$. The d'Alembert equation has hypercomplex quaternion solutions, also known as *spinors*.

The quaternion equivalent of Euler's equation for a complex number, $z = re^{i\theta}$ follows as

$$e^{\theta(i\alpha + j\beta + k\gamma)} = \cos\theta + \sin\theta(i\alpha + j\beta + k\gamma) ,$$

an exponential of unit length. The general quaternion in the form

$$Q \exp \theta(i\alpha + j\beta + k\gamma)$$

represents a four-vector of length Q. Unlike complex algebra, quaternion multiplication is not commutative. By analogy with complex exponentials, the product of two quaternions describes complex rotations in the same way that complex numbers correspond to rotations of real vectors[2]. It is for this reason that quaternions feature in the Lorentz transformation of special relativity and define spin as four-dimensional action.

Consistent with the definition of spin in units of $\hbar/2 = h/4\pi$, it defines a rotation of period 4π, unlike rotation about an axis that repeats the original arrangement after 2π. In three dimensions this is known as *spherical* rotation [16] or rotation about a point, visualized by rolling a coin around a second stationary coin.

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[2]As the operation $i^2 = -1$ represents a $180°$ rotation on the real line the imaginary number i represents a rotation of $90°$. Likewise the i, j, k in a quaternion represent three orthogonal $90°$ rotations.
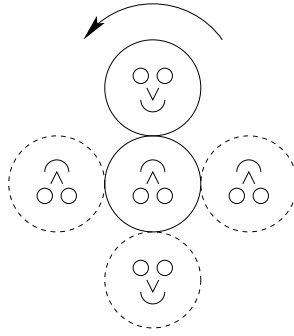
The original arrangement is repeated only after rotation of 4π. It represents an element of four-dimensional symmetry, which does not appear in three dimensions.

Two perennial mysteries of quantum theory are immediately resolved by this observation: the inability to derive electron spin analytically in three-dimensional wave mechanics and the unexpected commutation properties of quantum-mechanical pairs of conjugate variables. Quaternion variables do not commute. The obvious answer is to find quaternionic solutions of d'Alembert's 'matter-wave equation', also known as the Klein-Gordon equation, to replace traditional quantum theory. The theoretical justification of this proposal is that only the theory of relativity can account for the nature of the electromagnetic field and only in Minkowski space-time. All known quantum phenomena are intimately related to this same field and hence cannot be characterized correctly in three dimensions. It explains why spin variables must be added empirically to 3D quantum models, such as Dirac's equation.

To solve Dirac's equation it is necessary to separate space and time variables, which destroys the quaternionic spin function, to be re-inserted by hand [17]. The common textbook statement that spin is a relativistic effect results from a misreading of Dirac theory. The more correct statement is that spin is a four-dimensional phenomenon. It is measured in units of action, the same as angular momentum, which is two-dimensional ($h/2\pi$) and one-dimensional vibration (h).

Mechanical models to demonstrate the operation of spherical rotation [16, 18] elucidate the mechanism whereby an isolated spinning region of space moves through the medium without developing shear in a surrounding surface of discontinuity. The entanglement that develops on cylindrical rotation of 2π relaxes, almost miraculously, after 4π rotation perpendicular to an initial half turn. The composite motion is more like a continuous wobble than a rotation and the three dimensions of space participate symmetrically in the motion. The initial arrangement is restored after each rotation of 4π and only a half-frequency cyclical wave of strain is generated in the medium.

There is no transfer of energy and the spinning core may be likened to a

dispersion-free wave packet (soliton), or a standing wave trapped in a cavity. If an electron is to be modelled after a spinning element in continuous space it must rotate in spherical mode, surrounded by an undulating, wave-like region, related to a de Broglie wave; with elementary waves of Compton wavelength (Zitterbewegung) in the core.

4.1.1 Non-local Effects

The paper [15], often referred to by the acronym EPR, based on the initials of the three authors, describes how the probabilistic quantum model implies instantaneous non-local communication, in conflict with relativity theory. The most readable account [19] of the effect considers the separation of paired spins, carried apart by molecular fragments, but still correlated through a common wave function. A spin measurement on one fragment collapses the wave function and instantaneously communicates the outcome of the measurement to the second fragment. Without interfering with the second spin in any way its orientation is therefore fixed at a distance.

The fallacy of this argument is now exposed by better understanding of the holistic nature of a four-dimensional spinor. In this view the separated spins are not linked by a common wave function, but by two wave functions, correlated in the sense of describing two spinors of opposite chirality. This correlation remains fixed in space-time and independent measurements must always reveal, not create, paired spins. There is no further need of the postulated collapse of a wave function as if it is some physical object.

4.2 Matter and Curvature

A comprehensible world must be free of singularities, the most bothersome of which is infinity. The only way to get rid of it is to give up Euclidean geometry in favour of a system which is closed, both physically and mathematically. This is the fundamental assumption of general relativity. As a theory of the gravitational field a reciprocal relationship between space-time curvature and the existence of matter is postulated. The implication is that Euclidean space-time is devoid of matter and energy and should be viewed as a linear featureless void.

Nonlinear structure develops in curved space-time, like ripples on a pond. With increased curvature more turbulence develops as elementary units of generated action coalesce into more massive structures that cause local curvature effects and attract more matter from the vicinity to itself. The end result is the observed universe in dynamic equilibrium. Occam's razor predicts a one-sided closed system, as realized in projective topology and visualized in two-dimensional projection as a Möbius strip. The double cover of the Möbius strip demonstrates a one-sided surface with involution, and separated from itself by a two-sided interface. In four-dimensional reality

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the interface encloses the double cover on all sides to produce an isolated model universe that terminates in the vacuum, without an outside.

Like a circle, four-dimensional space-time has no beginning nor end, neither in space nor time. There is no infinity and no need of creation. Everything is just there, in energetic equilibrium and effective symmetry across the interface.
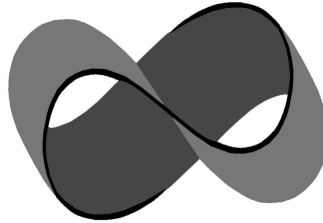
The reason why this does not rhyme with common perception is because of evolutionary conditioning to perceive the world in three dimensions. Topologists refer to perception in local Euclidean space, tangent to the underlying four-dimensional reality. The linear science formulated in tangent space, although a good approximation, fails to take into account, not only four-dimensional detail, like spin, but also nonlinear effects.

4.2.1 Non-linearity

The hydrodynamic analogy is invoked once more to emphasize the importance of the nonlinearity that characterizes all macroscopic systems. Linear, or laminar, flow is a delicate condition that develops nonlinear turbulence on the slightest disturbance.

The solutions of a linear differential equation remain valid in superposition, much like the layers of a liquid in laminar flow. Non-linear differential equations do not have the superposition property and systems of any complexity can therefore not be described correctly by linear differential equations.

The way in which solutions of the linear Schrödinger equation are routinely used in linear superposition to simulate the behaviour of complex chemical systems, is therefore not justified. The perennial problems of molecular quantum chemistry [20] are manifestations of this oversight.

4.2.2 The soliton model

The idea of a dual wave-particle nature is now rarely challenged anymore and found its way into all textbooks, although Schrödinger never abandoned the wave-packet description for an electron. The standard objection was the dispersive property of linear wave packets.

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The construction of non-dispersive nonlinear wave packets, in the form of *solitons*, as models of elementary particles, is now routinely practised [21]. The attractive idea is that a running wave transforms spontaneously into solitons when it enters a nonlinear environment.

The formation of a soliton can be understood as the balance between linear dispersion and nonlinear cresting of a wave packet.

The resulting soliton is persistent and moves without change in shape. It is described by a linear differential equation with an added nonlinear term.

Propagation of a wave through a nonlinear medium, like the restriction of laminar flow in hydrodynamics, causes cresting of the wave, resulting in a wave train of longer wavelength.
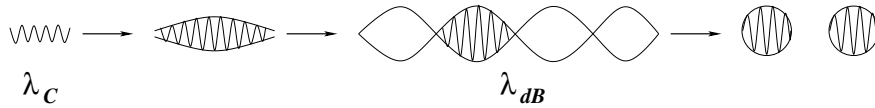
It is in this form that an electronic wave train with de Broglie wavelength that depends on electric field strength undergoes diffraction. In media at an increased level of nonlinearity, such as a Wilson cloud chamber, the wave-train separates into individual solitons, each with the mass, charge and spin of an electron, and for all practical purposes appear to behave like point particles. The same thing happens to an electromagnetic wave at a metal surface, in which case the resulting solitons cause the photoelectric effect.

Recognition of an electron as a flexible wave structure makes the concept of wave-particle duality redundant. It also disposes of the need to simulate wave motion in terms of probability particle density and of quantum uncertainty, which is frequently ascribed to the commutation properties of conjugate variables, such as position and momentum. However, this is a well-known phenomenon associated with all forms of wave motion.

4.2.3 The Quantum Limit

The perceived fundamental difference between microscopic quantum systems and macroscopic classical systems occurs because of the nonlinearity of the latter. As pointed out before the classical nonlinear Hamilton-Jacobi equation differs from the linear Schrödinger equation in the appearance of the quantum potential term and because of this difference there is no smooth transition between the classical and nonclassical regimes. The obvious remedy is to add the quantum-potential term to the traditional Schrödinger

equation. Substitution of $\Psi = R \exp(iS/\hbar)$ into the resulting nonlinear Schrödinger equation

$$ih\frac{\partial \Psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V + V_q \right)\Psi \,,$$

now transforms it directly into the HJ equation, which implies a seamless transition between quantum and macroscopic systems, without a quantum limit.

4.2.4 Antimatter

Matter and antimatter are chiral opposites that annihilate on contact. The preponderance of matter in the observable universe becomes difficult to rationalize. In a universe of projective topology it becomes a non-issue.

The effect of an involution in space-time amounts to inversion of chirality and hence conversion of matter into antimatter. Directed motion in the double cover gradually experiences the involution and conversion. After displacement of 2π the conversion is complete and after 4π the original configuration is restored. There is only matter, with pliable chirality that adapts to orientation in space-time.

5 Conclusion

There is ample evidence that the pioneers of wave mechanics aimed at formulating a model that would correctly reflect the wave nature of matter, Lorentzian invariance and nonlinearity. As a preliminary approximation Schrödinger proposed a linear non-relativistic equation that could be solved in closed form. Anticipating a nonlinear non-dispersive wave packet as a model of elementary matter he demonstrated [22] how this could be forged, using harmonic-oscillator wave functions of high quantum number.

Schrödinger's ideal was never realized in the face of serious opposition from the Copenhagen camp that favoured probabilistic particle mechanics and, by now it is all but forgotten. As a result wave mechanics as a fundamental theory of matter has never come to fruition. As it stands, it gives a convincing, but incomplete description of atomic spectra, a tolerable simulation of one-electron chemical interaction, a qualitative guide to elemental periodicity, empirical incorporation of electron spin, confusing exposition of quantum measurement based on wave-function collapse and total inconsistency with the theory of relativity.

In the hands of the chemist wave mechanics has suffered further distortion. Substitution of the orbital concept for wave functions paved the way for the introduction of fanciful ideas as quantum concepts. Some of these spurious concepts, through repetition in generations of textbooks have gained

the status of fundamental science. The creation of "real atomic orbitals" by the linear combination of complex wave functions is but one example. It is as if some authors, who appreciate the fallacy of the operation, nevertheless avoid direct mention of the deception, without giving up the result. The following quote [23] is a typical example of the way in which an unpalatable fact can be disguised.

It is usual to depict the real and imaginary components, and call these orbitals p_x and p_y:

$$p_x = \frac{1}{\sqrt{2}}(p_- - p_+) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r) \sin\theta \cos\phi$$

$$p_y = \frac{i}{\sqrt{2}}(p_- + p_+) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r) \sin\theta \sin\phi$$

... the real forms are more appropriate when $x-$ and $y-$axes are well defined, such as in non-linear molecules. All three orbitals (p_x, p_y and p_z) have the same double-lobed shape, but aligned along the $x-$, $y-$, and $z-$axes respectively.

What they neglect to point out is that all three hybrid wave functions also have the same magnetic quantum number ($m_l = 0$), in violation of the exclusion principle.

It is standard fare to claim that the real orbitals do not require quantum numbers, without admitting that this identifies them as classical constructs. It is helpful to call them *orbitals*, and not wave functions, in this instance. The reason why chemists cling to the idea of hybridization, without mentioning it by name, is because without it the LCAO procedure that underpins all of quantum chemistry has no validity.

In line with the quantum philosophy of "shut up and calculate" chemists maintain that "quantum-chemical" computations, despite obvious deficiencies, are the sole means available for the theoretical simulation of electronic behaviour in molecules. This attitude reflects no more than reluctance to abandon a profitable comfort zone and will not be pursued here any further.

The major deficiency of theoretical chemistry is a credible model of molecular structure and this is where wave mechanics is least effective. The current practice of optimizing observed structures in terms of semi-empirical principles has no future. It is not clear where improved understanding would originate, but a useful start could be a complete re-assessment of the concept of matter waves [4] against the background of nonlinear four-dimensional curved space-time. As a sobering side effect this might lead to rejection of the quasi-philosophical baggage of unreality and mysticism that clouds quantum theory.

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