

## Electronic Structure and Number Theory

Bohr's Boldest Dream

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# Preface

At the time of writing, the world of physics is buzzing with the identification of a Higgs field. In the popular press, which refers to the Higgs boson as the “God” particle, we read [1] that

It is the last unobserved piece of the Standard Model, the most convincing explanation available for the way the universe works. . . The purpose of the Higgs boson is to inculcate mass into those particles which weigh something. . . The search for the Higgs is a search for closure on the old world. Supersymmetry is the new. It might also (explain) “dark matter”.

These are brave words, which echo the expectation of another theorist [2]:

For some physicists, the end of the road is in sight, and the main question is simply, How long until we reach it?

In view of the common contention that all of chemistry is reducible to physics it may therefore seem expedient to explore the implications of this mighty discovery on our understanding of molecules and their structure. However, the immediate simple answer is zero.

The standard model of physics is based entirely on dimensionless point particles, and, whatever it may reveal about dark matter, it offers no explanation of the extension and structure of molecules. These elementary particles acquire their mass mathematically, on interaction with the hypothetical Higgs field, in a process of [2]

miraculous mass generation.

The nature and source of mass remain unexplored. Extrapolation from the Higgs field to molecular shape is just a bridge too far.<sup>1</sup>

The mathematics of the standard model relies on spontaneous breaking of a gauge symmetry, defined by the phase of an elementary-particle wave function. Theoretical chemists, guided by molecular physicists, have imprudently adopted the same model, without a thorough physical basis, primarily for computational

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<sup>1</sup>The Higgs is an incomprehensible abstraction, a partial solution to an extraordinarily rarified and perhaps always incomplete intellectual puzzle - Daniel Sarewitz, Nature 488:431 (23 August 2012).

purposes. In physics it serves for the computation of observable spectroscopic and fragmentation patterns, but in the chemical context robust molecular properties can only be simulated *empirically* as probabilistic particle distributions. As a theory of molecular structure and chemical interaction this pursuit is not very useful.

In this volume an alternative to quantum chemistry is proposed. At the outset we challenge the idea of gauge invariance associated with structureless point particles as a logical impossibility. All known phase relationships are associated with wave systems and all waves are distinguished by periodic variation specified by integers. These are precisely the properties featured as textbook characteristics of quantum systems.

The sordid infighting among quantum theorists to gain ascendancy of the particle or Copenhagen model over the wave alternative may be irrelevant. What was claimed as the final formulation of quantum physics has long since been superseded by Higgs fields and string theory. There is no longer any danger in reviving a wave model of matter in situations where it works. However, with hindsight it is now more appropriate not to reconsider a simplistic three-dimensional model, but to rather take note of the topology of space–time and the theory of general relativity at the same time.

A special theory of relativity was developed in the first place to account for the prediction of Maxwell's equations that light rays are observed to propagate at constant speed in the vacuum, irrespective of the relative motion of an observer. The resulting kinematic theory, known as Lorentz transformation, is readily shown to amount to complex rotation in four-dimensional space–time. Extension to accelerated frames requires reformulation of the theory in non-Euclidean four-dimensional space–time. Although the new emerging concepts of mass–energy equivalence, time dilation and the gravitational field have captured the imagination of the world, another important result, the equivalence of space and time variables is rarely fully appreciated. This is the seminal property that allows formulation of a wave theory of matter in four dimensions. It is also one aspect of relativity theory which is often ignored. It is difficult to properly visualize non-Euclidean four-dimensionally curved space–time, which is called for in order to take the next step forward in physics.

Some of the seven billion inhabitants of the planet still entertain the atavistic notion of an infinite flat earth, some accept a two-dimensional planetary surface, closed in three-dimensional space. However, despite the evidence from general relativity it is safe to say that, without much exception, everybody still considers cosmic space as infinite and flat in three dimensions.

As for particle physics there is also a standard model for cosmology which interprets the observed spectroscopic red shifts of galactic light as a Doppler effect caused by the expansion of three-dimensional Euclidean space, claimed to be consistent with general relativity. In actual fact general relativity demands not only the entanglement of space and time coordinates in a four-dimensional continuum but also non-Euclidean cosmic topology. The property of curvature is embodied directly in Einstein's relativistic field equations which balance the mass–energy content of the universe against its curvature. It is immediately obvious that flat space contains

no matter, and given the observable matter content of the universe, space–time has to be curved and in all likelihood topologically closed. This means that the standard models of physics and cosmology are dealing with artefacts created by the use of a dimensionally and topologically fallacious model.

Topologically closed space–time has the philosophical advantage of avoiding many bothersome infinities. The universe becomes of finite extent and eternity, like a circle, has no beginning or end. Neither the finite big-bang age of the universe nor John Locke’s beginning in the infinite past are attractive propositions.

When contemplating the formulation of four-dimensional theories the first measure would be the use of Minkowski space–time, which is tangent to the underlying curved manifold and adequate, to first approximation, for the analysis of macroscopic local phenomena. At the sub-atomic or galactic level the effects of curvature cannot be ignored.

With a wave model in mind as a chemical theory it is helpful to first examine wave motion in fewer dimensions. In all cases periodic motion is associated with *harmonic* functions, best known of which are defined by Laplace’s equation in three dimensions. It occurs embedded in Schrödinger’s equation of wave mechanics, where it generates the complex surface-harmonic operators which produce the orbital angular momentum eigenvectors of the hydrogen electron. If the harmonic solutions of the four-dimensional analogue of Laplace’s equation are to be valid in the Minkowski space–time of special relativity, they need to be Lorentz invariant. This means that they should not be separable in the normal sense of Sturm–Liouville problems. In standard wave mechanics this is exactly the way in which space and time variables are separated to produce a three-dimensional wave equation.

In the same way that two-dimensional harmonics are complex functions, four-dimensional harmonics are hypercomplex functions or *quaternions*, also known as spin functions. A spin function represents the four-dimensional analogue of the conserved quantity known as angular momentum in three dimensions. The problem with standard wave mechanics is that on separation of the variables to create a three-dimensional Sturm–Liouville system the spin function breaks down into orbital angular momentum and one-dimensional spin, which disappears in the three-dimensional formulation.

It is significant to note that the spin function also describes the complex rotation which defines the Lorentz transformation. An unexpected bonus of a four-dimensional quantum mechanics is this natural merger with relativity theory, the importance of which is beyond the scope of this work. Of more immediate relevance are the relativistic ramifications in chemical systems.

An almost forgotten issue is the proposed relativistic nature of an electron as elucidated by Lorentz. The electron was seen as a flexible spherical unit of charge which distorts as it contracts in the direction of any motion. To account for the relativistic contraction of macroscopic bodies Lorentz further assumed that the electrical forces which bind atoms together were essentially states of stress and strain in the aether. Countless prominent scientists have expressed similar views without trying to develop a coherent theory of matter. The Lorentz electron model antedates de Broglie’s postulate of matter waves and the development

of general relativity. Reinterpreted against this background the Lorentz electron emerges as a relativistic invariant wave structure which is generated as a persistent elementary distortion of the aether, due to space–time curvature, and is described mathematically by the four-dimensional spin function.

We are reminded by Bohm [3]:

... that scientific investigation is basically a mode of extending our *perception* of the world, and not mainly a mode of obtaining *knowledge* about it.

The world as perceived in four-dimensional space–time is fundamentally different from the perception in tangent space. Even the most fundamental perceptions such as the Rydberg–Ritz formula are perceived differently in four dimensions, as demonstrated by Casper Schutte in this volume. Bohm [3] identifies the problem with new ideas as

... the difficulty of enertaining new concepts which clash with older ones that we have held habitually since childhood. . .

Whoever reads this volume without rejecting the picture of a point electron that only shows up as a probability distribution has the same problem. In our perception it occurs, like other elementary entities, as a persistent, flexible, wave-like, chiral distortion of space–time. It has mass, charge and spin by virtue of a characteristic wave structure. It disperses into the vacuum on interaction with another of opposite chirality.

It is no accident that both wave motion and the fundamental theory of chemistry are best described in terms of natural numbers. However, conventional wave mechanics in three dimensions offers only a partial elucidation of the periodic table of the elements. On the other hand, a detailed reconstruction, also of the more general periodicity of stable nuclides, derives directly from elementary number theory. It shows, in addition, how the periodic function responds to the state of space–time curvature and identifies the golden ratio as a possible parameter that links perceptions in tangent space to the situation in curved space–time.

This observation is exploited in the analysis of chemical systems without formal solution of the four-dimensional problem. Most of the work in this volume reports results of this type. To be of practical use the numbertheory results, which pertain specifically to pairwise diatomic interactions, might be incorporated into algorithms that simulate more complex molecules. Molecular mechanics appears to be an appropriate model to achieve this. In the current quantum chemistry world, molecular mechanics appears to be a “low-level”, entirely empirical model which fully ignores the relevant electronic effects [4]. However, via specific atom types, the electronics may be accounted for, and there are a number of recent developments which include specific electronic terms, based on classical quantum chemistry [5–8]. More importantly, in terms of structural modeling, the quality of MM only depends on the force field and its parameterization based on experimental data [9]. The approach presented in this volume suggests that number-theory-based models may significantly reduce the parameter space and, more importantly, produce generic

parameters, which might or might not be optimized, based on experimental data in order to obtain a higher accuracy.

The development of chemical theory in terms of number theory is not new [10]. What is new is the realization that we are dealing with a four-dimensional problem, the analysis of which requires a fundamentally different mathematical treatment. Physically it means that a 3D analysis in terms of point particles is necessarily incomplete. The analysis by Schutte demonstrates beyond any doubt that the basic assumption of atomic spectroscopy, based on the traditional separation of space and time variables, is not supported by experiment. The most glaring demonstration that a 4D analysis is required is provided by the appearance of electron spin, which never emerges in any 3D model. It is important to understand that spin is not a relativistic effect, but derives from the four-dimensional conservation of angular momentum. These features were not known before and this is the first effort to take their consequences into account. It needs a radically new model of atomic electron distribution, and the exciting thing is that such a model is provided by an optimization by logarithmic spirals. The result is in striking agreement with a standing-wave model of electron density that involves the golden ratio and many other aspects of elementary number theory. Without further assumptions this model of atomic structure can be interpreted directly as the definitive basis of atomic ionization radii and electronegativity. Our reference to previous conclusions about the origin of the periodic table is done to explain the earlier empirical conclusions more logically.

What is new in the re-examination of covalent interactions is that the approach in terms of a four-dimensional wave structure leads to a precise definition of bond order, not achieved before. Together with the new freeatom ionization radii the parameters of interatomic distance, dissociation energy, stretching force constants and diatomic dipole moments can now be derived as simple functions of the ionization radii and the golden ratio. These results have nothing in common with the more approximate simulations described before.

The papers in this volume address a single theme and in order for each of them to constitute a self-contained unit a fair amount of repetition is inevitable, even with generous cross referencing. Many readers, less familiar with the concepts of number theory, the golden mean, logarithmic spirals, hypercomplex numbers, projective geometry, general relativity and quantum field theory, may actually find some reiteration to be of benefit. Not to alienate such readers at the outset the editor in chief, Mike Mingos, patiently guided the composition of the opening paper into the style of *Structure and Bonding*. His much appreciated advice is gratefully acknowledged.

We expect our proposed approach to the understanding of chemically important issues to be rejected by many readers who operate in a comfort zone defined by probability densities, Born–Oppenheimer systems, hybrid orbitals, potential-energy surfaces, ab initio theory and DFT simulations—all of them Copenhagen spin-offs. We realize, of course, that these models have been developed to standards, where they produce a very accurate optimization of structures and properties of molecular compounds and materials in many areas [11], and for application-oriented

theoreticians as well as for experimentalists, who use applied theory for predictions and interpretations, there is no immediate need to leave the comfort zone. At the same time it is interesting to note that we are not alone in advocating a rethink of theoretical chemistry. An increasing number of papers in the recent literature (e.g. [12]) call for an update of the teaching of valence theory, for the orbital concept and related ideas to be abandoned and specifically to be removed from undergraduate curricula. We do not fully agree with all those suggestions, but some ideas pioneered in this volume could hopefully find their way into a new paradigm.

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