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The Chemistry of Matter Waves

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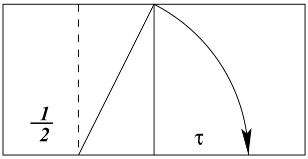
Preface

The spectacular successes such as the construction of lasers and magnetic resonance instruments, commonly credited to quantum physics and spectroscopy, make the expectation of a quantum theory of chemistry almost irresistable. Equally spectacular failures to account for high-temperature superconductivity, cold fusion, molecular diffraction, optical activity and molecular shape are conveniently ignored. Even the emergent concept of spin, correctly considered the most non-classical property of elementary matter, has never been explained in terms of first-principle quantum theory.

It is therefore not surprising to find that beyond the Bohr-Sommerfeld model of the atom quantum mechanics has caused more confusion than enlightenment in theoretical chemistry. However, to turn away from the fantasy of quantum chemistry, after a century of expectation, could be as traumatic as renouncing the prospects of alchemical transmutation.

Chemistry is the prodigy of alchemy as modified by the theories of modern physics. Even so, it still has not resolved the ancient enigma around the nature and origin of matter. Alchemy itself is the product of ancient hermenistic philosophies, traces of which have survived the metamorphosis into chemistry. Elements of the number-based Pythagorean cosmology are clearly discernible, even in the most modern theories of chemical affinity. Briefly [1]:

> The cosmic **unit** is polarized into **two** antagonistic halves (male and female) which interact through a **third** irrational diagonal component that contains the sum of the first male and female numbers $(3 + 2)$ and divides the **four**-element (earth, water, fire, air) world in the divine proportion of $\tau = (\sqrt{5/4} - \frac{1}{2})$.



In Pythagorean parlance, any chemical interaction is essentially of the type

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{NaCl} + \mathrm{H_2O}.$$

It is facilitated by the affinity between opposites to produce a product that symbolizes the principle of substantiality, in harmonious equilibrium with the total environment.

All harmonic proportions and relationships are said to derive from the roots of 2, 3 and 5, the number of life. In modern terminology, the harmony that results from the interplay of integers and irrationals manifests at all levels of reality. It is colloquially referred to as self similarity, well known to be mediated by the golden ratio and golden logarithmic spirals. Modern theories perform little better in describing ponderable matter as resulting from the interaction between cold dark matter and a universal Higgs field. The mathematical model that underpins the theory is as mysterious as the divine proportion.

Chemistry distinguishes between space and time, and between matter and energy. The seminal theories of physics, independently developed by Newton and Huygens made the distinction between particles and waves. Hamilton's refinement of classical mechanics demonstrated some common ground between the two theories, but Maxwell's formulation of the electromagnetic field revealed a fundamental difference in their respective laws of motion. It was the unified transformation of Lorentz that finally established the four-dimensional nature of Minkowski space-time and the equivalence of mass and energy. The gravitational and electromagnetic fields remained poles apart. However, both of these could be shown, by Einstein's general relativity and the notion of gauge invariance as developed by Weyl and Schrödinger, to be products of Riemann's non-Euclidean geometry. Ultimate unification of the fields was achieved in terms of Veblen's projective relativity.

Analysis of the interaction between matter and radiation and the theories of chemistry were pursued in Euclidean space and remained at variance with the theory of relativity, culminating in the awkward compromise of wave-particle duality. It is only the recognition of spin as a strictly four-dimensional concept that holds the promise of wave structures, which behave like particles. Formulated as a quaternion structure it defines the common ground between relativity and quantum theories. The electron, defined as a nonlinear construct, known as a *soliton*, recognizes the importance of space-time curvature and represents final unification of its initially antagonistic attributes.

It is the theme of this book to show how refinement of the concepts matter and wave would lead to a consistent description of chemical systems without the confusion of probability densities and quantum jumps. The final model is that of Schrödinger, extended to four dimensions in nonlinear formulation.

The major effect of this more general proposed formulation is that the procedure of linear combination of atomic orbitals, at the basis of all "quantum chemistry" completely looses its validity and it needs to be replaced by entirely new modelling strategies. One alternative, already in place, is molecular mechanics, an empirical procedure based on classical mechanics and classical notions of molecular structure. It is encouraging to note that the same number-theoretic simulations, which are effective as a basis of elemental periodicity, are commensurate with molecular mechanics.

The number-theory simulation of chemical systems originated with the observation that the periodicity of atomic matter depends on the number ratio of atomic protons to neutrons that converges to τ as a function of either A, Z, $A - Z$ or $A - 2Z$. The same pattern is revealed by the golden proton excess $x = Z - \tau N$. By demonstrating that this convergence is a function of general space-time curvature the observed cosmic self-similarity is inferred to depend in equal measure on space-time curvature, the golden ratio and the shape of the golden logarithmic spiral.

To put the whole scheme into perspective it is noted that, because of curvature, the geometry of space time is non-Euclidean and different from the commonly perceived Euclidean geometry. Topologists distinguish between an underlying, globally curved space-time manifold and the local, approximately Euclidean, three-dimensional, tangent space and universal time. Any analysis performed in tangent space, using a model such as Newtonian mechanics or Schrödinger's linear equation, produces a good, but incomplete, approximation, compared to possibly more refined descriptions in four-dimensional detail.

To compensate for the neglect of curvature the golden parameter τ, or optimization in terms of golden logarithmic spirals, provides an immediate corrective, in the simulation of chemical systems by linear procedures. The very existence of matter is seen to depend on the nonlinear deformation of a hypothetical, Euclidean, four-dimensional energy field as described by the theory of general relativity. The product is a non-dispersive solitary wave packet, known as a *soliton*. Different modes of deformation lead to the formation of solitons of different symmetry, colloquially known as elementary particles. Dependent on mass, charge and spin these units are of different stability and in combination with those of complementary affinity develop into the different forms of ponderable matter—atoms, molecules, crystals, fluids and higher aggregates. The imprint of space-time curvature and the golden ratio remains with all matter, exhibiting a common self-similar symmetry.

The periodicity of matter arises as the product of a closed numerical system with a natural involution that relates matter to antimatter. In four dimensions such a function defines elliptic space in the form of projective space-time, as used by Veblen in the unification of the electromagnetic and gravitational fields.

The hard sell of convincing chemists that quantum mechanics in its present guise is too restrictive as a theory of chemistry necessarily involves unfamiliar mathematical arguments that may turn out to be counterproductive. To be convincing it is unavoidable to introduce various aspects of physics and applied mathematics traditionally considered to be way outside the chemistry paradigm. The bland alternative of starting from "well established" mathematical physics appears equally problematical. This is the exact strategy that created the present dilemma in the first place.

The most daunting prospect is to argue convincingly for the adoption of a four-dimensional world view, against the millions of three-dimensional molecular structures derived by sophisticated experimental techniques. To complicate matters by the introduction of nonlinear effects would surely be considered as meaningless, unless it can be supported with concrete examples. The anticipated response is difficult to predict.

The conservative respect for authority creates another problem. It comes naturally to reject, without thinking, dissident views that contradict the time-honoured ideas of respected pioneers. A prime example is in the handling of high-temperature superconductivity. The BCS theory, which ascribes superconduction to the formation of bosonic electron pairs, mediated by lattice phonons, offers no insight into the mechanism that operates in ceramic materials. Even the correlation of low-temperature metallic superconduction with normal-state properties remains an empirical observation without theoretical support. A reported room-temperature superconducting state is simply denied as theoretically impossible.

The credibility of the quantum-based BCS theory rests entirely on the reputation of its authors. Reluctance to abandon the model relates to the mistaken perception that it is supported by the mathematical simulation of a superconduction transition as the breakdown of gauge symmetry on cooling. However, the symmetry model applies to all forms of superconductivity whereas the phonon interaction is an empirical conjecture for one special case only.

The readily demonstrated dependence of superconductivity on the composition of atomic nuclei favours an alternative description of the phenomenon as a nuclear, rather than a strictly electronic, property. Special stability of the nuclear composition that corresponds to the Z/N ratio of τ implies a positively charged surface shell that correlates remarkably well with anomalous nuclear spin and superconduction. With this surface excess as a guide an alternative mechanism that effects all forms of superconductivity is recognized.

At a more speculative level the phenomenon of electrolytic "cold fusion", appears to occur at cathodes, rich in high-spin isotopes of the same type. In this case the active process appears as neutron capture that converts symmetry-distorted nuclides to lower-energy forms.

These examples all point at the unpalatable conclusion that quantum theory, in its present form, falls far short of popular perceptions. It is not the all-embracing panacea that stretches beyond science and inspires the non-local metaphysics of fundamental acausality, probability and complementarity, which blossomed into multiverse cosmology. An "inner voice" told Einstein that something was amiss, but he lacked the data to support his intuition.

The central issue that defied comprehension was the apparent dual nature of both elementary matter and radiation. Efforts to account for this uncertainty resulted in concepts, universally accepted by now, such as an observer's role in creating patterns from the conceptually unknown. This confusion between subject and object resonates with the musings of psychologists and philosophers, groping for an understanding of reality in terms of medieval mysticism through quantum theory [2].

The unfortunate conviction that inspires such pursuits, although hard to gainsay philosophically, has a simple resolution:

There is no such thing as an elementary point particle.

Matter, as the product of intrinsically nonlinear four-dimensionally curved space-time, or "condensation of the vacuum (æther)", has a wave structure. Not in the form of dispersive wave packets, but as non-dispersive persistent solitary waves, or *solitons*, only known to occur in shallow water at the time when quantum theory was formulated.

Solitons are flexible and under certain circumstances may appear to behave like point particles. Futile efforts to account for a soliton's wave-like behaviour with a particle model result in the weird constructs, generally believed to reflect quantum effects. This statement is a concise summary of the argument to be developed in the following.

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Contents

Chapter 1
Of Electrons and Molecules

Abstract The discovery of X-ray diffraction promised to resolve the mystery of molecular structure, but a hundred years on it is fast receding into the fourth dimension. The contemporary development of quantum mechanics performed no better. It introduced, without explanation the notion of non-commuting dynamic variables, described by complex functions, failed to account for electron spin or optical activity and still appears to be at odds with special relativity. The confusion starts with Maxwell's formulation of the electromagnetic field, interpreted differently in quantum and relativity theories, and grows with the chemical practice of reducing complex quantum functions to real classical variables. This leaves the nature of a single molecule's structure undefined—neither classical nor non-classical.

1.1 Introduction

Chemical theory is based in the final analysis on two poorly understood concepts—*electron* and *molecule*. In principle both of these are wave-mechanically well defined, but in reality neither model reveals anything beyond the initial assumptions. The chemist's electron is a negatively charged particle and a molecule a set of atoms connected into a fairly rigid framework as dictated by classical valence forces.

The purpose of this introductory chapter is to review the theoretical problems with electrons and molecules in broad outline and to highlight important aspects to be discussed in subsequent chapters. It is necessary to recognize the problems, which are commonly ignored during unsuccessful computational simulations, in order to reformulate the wave-mechanical approach on a more fundamental basis.

1.2 Electrons in Chemistry

As the science that studies the transformations of matter, an understanding of chemistry depends on elucidating the behaviour of the electrons that mediate interaction between atomic cores. Elucidation in this sense is not to be confused with the simulation of intramolecular electron transfer, routinely performed by practising

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chemists, without appreciating the nature of electron spin, charge or mass. It is considered as sufficient common knowledge that an electron carries one unit of indivisible negative charge and half a unit of intrinsic spin, directed either up or down. The origin and meaning of these attributes are seldom contemplated and electron mass is no more than the natural property of an elementary point particle. The more surprising phenomenon of electron diffraction is considered adequately explained by the quantum-mechanical concept of wave-particle duality.

This amazing compliance can be traced back to the accepted infallibility of quantum theory, considered to underpin all of chemistry. Most theories are considered subordinate to experimental evidence, but occasionally some special theories acquire metaphysical importance by virtue of universal acclaim that results in dogmatic certainty. This recognition befell the peripatetic physics of Aristotle, Ptolemaic cosmology, the phlogiston theory of chemistry and the quantum theory according to von Neumann. Once a theory has been elevated to such a level, conflicting evidence is rationalized by the introduction of secondary concepts, not part of the seminal theory. Well-known examples include the epicycles of planetary motion and the negative mass of phlogiston. The accepted properties of the electron are immediately recognized as being of this nature.

Except for the quantum theory, all of the others had given way eventually under the pressure of experimental evidence. In the same way the prevailing theory of the electron needs replacement by another that accounts for its spin, charge and wave nature. Schrödinger's fundamental equation represents a modification of the general equation for wave motion according to de Broglie's postulate of a function $\psi = \exp(ip_x/\hbar)$ to describe matter waves.

The resulting wave-mechanical formulation of quantum theory has several defects. The most glaring is that, despite the evidence from special relativity, it is formulated as a theory in three-dimensional space. For this reason the spin function remains undefined. Solution of the resulting differential equation by further separation of the variables next reduces all electronic motion into the unrealistic classical one-dimensional vibrations of quantum chemistry.

As for all linear differential equations, superposition of any elementary solutions of Schrödinger's equation is another solution. The most general solution can hence be written as the Fourier sum of orthogonal functions

$$\psi(x) = \sum_k A(k)e^{ikx}.$$

For continuously varying k, the normalized solution

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)e^{ikx}dk$$

represents a wave packet, which is dispersive for de Broglie matter waves, *e.g.* an electron.

1.2.1 Wave-Particle Duality

Although the Schrödinger-de Broglie model failed to produce an acceptable wave description of an electron with spin, its confirmation of the Bohr-Sommerfeld hydrogen spectra instilled overwhelming confidence in the methodology. Instead of modifying the seminal equation to generate a non-dispersive electronic wave packet, the agreed remedy was to retain the equation without alteration, but supplemented by the addition of suitable *ad hoc* correction factors.

Without a stable wave packet to simulate the particle-like behaviour of an electron it was therefore redefined arbitrarily as a point particle with spin and wave properties. Of these stated attributes only the wave behaviour is consistent with the mathematical model. Spin could be introduced by the addition of a matrix operation to represent an extra two-level variability, not reflected in the seminal equation. However, the simulation of wave-like behaviour in terms of particle dynamics necessitated a drastically modified interpretation of the wave functions that characterize the eigenvalue solutions. The agreed innovation, sanctioned by neither de Broglie nor Schrödinger, was to interpret the square of the wave function $|\psi|^2 = P$, as a probability electron density. Not even this device could be argued to account for electron diffraction, which problem was overcome by the invention of the new term *wave-particle duality*. It has no operational meaning but is recommended to imply that an electron may behave as either a particle or a wave, as needed.

1.2.2 The Schrödinger Approximation

Quantum chemistry is based exclusively on the one-electron solutions of Schrödinger's equation. As a modification of Laplace's equation these solutions are modified spherical harmonics. Two-dimensional plane harmonics, better known as circular harmonics, underpin the original quantum theory of Bohr [1]. One-dimensional simple harmonics define the basis of de Broglie's postulate that relates linear momentum to wavelength.

The relationship between one-dimensional harmonic vibration and two-dimensional circular motion is demonstrated by the mechanical device known as a Scotch yoke, familiar to most as an automotive crankshaft. This device generates rotational motion about an axis perpendicular to two orthogonal vibrations that it locks into phase, as described by a complex function. In spherical rotation the phase relationship is described by a four-dimensional hypercomplex function. Mathematically the various modes of harmonic motion are all described by Laplace's equation. In one dimension it describes simple harmonic motion by a single real variable and circular harmonics by a complex function of two variables. Schrödinger's equation is obtained by separating the space and time variables of a three-dimensional wave equation [2].

Not only could this be the reason why quantum chemistry fails, but it also explains the notorious discrepancy between quantum mechanics and the theory of general relativity, which was developed as the common frame of reference for mechanical motion and the electromagnetic field. The equations of special relativity, known as the Lorentz transformation are formulated most generally as a complex rotation in four-dimensional space-time [3]. It is of the essence that this formulation does not allow the separation of space and time variables. The four-dimensional rotation operator is known as a *quaternion* and the argument as a *spinor*, which is a harmonic function in four-dimensional space-time.

There is a regular progression from one- to four-dimensional number systems. The familiar fields of *real* and of *complex* numbers are one- and two-dimensional respectively. A complex number has two real components. In the same way a four-dimensional *hypercomplex* number, known as a quaternion, has two complex components. Quaternions differ from complex numbers in not being *commutative* under multiplication. An *octonion* has two quaternion components and for it the distributative law does not hold.

Notably there is no normed division algebra in three dimensions [4]. Three-dimensional space is therefore described in terms of a complex plane, orthogonal to a linear polar direction. General, or spherical rotation, which defines a spinor is hence undefined in three-space. This explains why the important property of electron spin has to be added manually to the traditional quantum model. The standard model of quantum chemistry, which is based on three orthogonal orbital directions, is, for the same reason, undefined in Schrödinger space.

1.2.3 Four-Dimensional Waves

The appearance of an electron, as all other elementary forms of matter, cannot be reduced to a level lower than the physical vacuum, with geometrical shape defined by the space-time variables of general relativity. As a discrete object it must be seen as characteristic of a stable elementary distortion of space-time. While the nature of empty space-time remains unknown elementary objects, such as electrons, which appear in curved space-time, have been studied in detail.

To first approximation different elementary units have characteristic properties of mass, charge and spin, all of which relate to a specific mode of space-time distortion and the accumulated space-time density that results in the region of distortion.

If elliptic topology of space-time is assumed, the vacuum is represented by an equilibrium interface between material and anti-material regions and may be imagined to be in a state of gentle undulation. Space-time curvature generates interference patterns in this four-dimensional wave field with the formation of standing wave packets, recognized as electrons and other elementary entities.

To ascertain the characteristic mass (or energy) of such an entity, space-time density is multiplied by the volume in space, *i.e.* $m = \rho x^3$. In four-dimensional space-time the product of $\rho x^3 t = a$, corresponds to the more fundamental property known as *action*, $a \propto mt$. The elementary unit of action, given by Planck's constant,

$\hbar$, describes the spin, or the four-dimensional symmetry of the distortion. The three-dimensional symmetry (rotation) with respect to the local time axis, is observed as electric charge.

The more complex internal structure of hadrons is ascribed to extra symmetry (*e.g.* three-fold symmetry) of the internal wave field. It is suggested that such interactions could be described by octonions.

1.2.4 Nonlinear Schrödinger Equation

An obvious defect of wave mechanics is being based on linear differential equations. The computers to solve nonlinear equations simply did not exist in 1930 and, to a first approximation, solutions of the linear equations corresponded so well with experimentally known quantum effects that the model was generally accepted as adequate. Twenty years later when serious discrepancies started to emerge the paradigm was so firmly established that modification was considered heretical.

At the same time the theoretical analysis of chemical problems by the linear combination of atomic orbitals, which came into widespread use, was seen as the ultimate solution. A moment's sober reflection at the time should, arguably, have cautioned the numerous users of powerful new software that became widely accessible, that nonlinear effects in the handling of medium to large molecules cannot reasonably be ignored. The numerical simulation of ergodic effects at Los Alamos brutally exposed the inadequacy of linear statistical models and soon led to the recognition of soliton structures that could be of relevance in the simulation of elementary-particle models.

Computational chemists have been too slow to exploit the new techniques for the analysis of electron and molecular structures, while chemical and electrical engineers continue to make free use of nonlinear Schrödinger (NLS) and sine-Gordon equations.

It is of special importance to note that the NLS equation has the same structure as the so-called classical Schrödinger equation. This parallel identifies the quantum potential as the nonlinear term and defines a seamless transition between wave-mechanical and classical Hamilton–Jacobi systems. An exciting possibility arising from this is the recognition of a wave-mechanical basis of venerable classical concepts such as electronegativity, bond order, polarizability, valence state and molecular shape.

In order to fully appreciate the proposed modifications to the standard wave-mechanical model of chemistry it is necessary to examine the state of the art against the background of the historical developments over the previous two centuries.

1.3 Molecular Structure

The molecular-structure hypothesis originated during the 19th century in the work of Kekulé, van't Hoff and others [5]. It gained respectability as a reliable diagnostic of optical activity of molecules in solution and as the basis of the Lewis electron-pair model of chemical bonding. Final vindication of the three-dimensional structure of molecules in the crystalline state was provided by the pioneering work of J. Monteith Robertson who published a structure for anthracene as early as 1933 [6], with the significant comment that:

> It must be remembered, however, that the crystal molecule is far from being a free body in space.

On the other hand, the famous statement by Dirac [7] that:

> . . . the whole of chemistry are thus completely known. . .

signalled the prospect of deriving the molecular structure of any molecule by quantum-mechanical calculation.

The brave attempt [8] to formulate a quantum theory of chemistry during the period around the second world war, anticipating full development by powerful digital computing, has by now turned into an embarrassment. Despite the absolute confidence of quantum physicists in the enabling theory, the conviction of a few that it was incomplete must now be seriously re-examined.

1.3.1 Molecular Modelling

Despite the posturing of computational chemists the theory behind molecular modelling amounts to a computerized empirical generalization of the Lewis electron-pair model of a hundred years ago. This includes all quantum-chemical VB and LCAO-MO schemes, DFT and molecular mechanics.

Trying to understand what *Quantum Chemistry* is all about we may turn to one of its principal architects, C.A. Coulson. Two relevant passages from his monograph [9] put his vision and the ground rules of the pursuit into fair perspective:

> . . . the laws of quantum mechanics (of which wave mechanics is merely one particular formulation) allow us, in principle, to predict not only the electronic structure and the geometry of a molecule but indeed all of its properties.
>
> At the highest level, we attempt a highly accurate numerical solution of the Schrödinger equation; such calculations, which usually start from nothing more than a conjectured molecular geometry, are usually termed *ab initio*.

These two statements can, at best, be described as deliberate euphemisms to disguise the fact that quantum chemistry does not extend beyond a crude rationalization of the hydrogen atomic spectrum. The laws of quantum mechanics, whatever they are, do not, even in principle, allow the prediction of the electronic structure of a molecule and most certainly not the geometry and properties of any molecule, including H_2^+. This is confirmed by the second statement which admits the necessity of *assuming* a molecular structure in order to attempt a calculation at the highest level. It is fatally misleading to refer to such computations as *solution of Schrödinger's equation*. It is nothing of the kind.

The *solution* of any equation is exhaustive and excludes further alternatives. An *ab initio* 'solution' only demonstrates that a polynomial function can be constructed computationally to be apparently consistent with the assumed molecular Hamiltonian. For this to be considered a solution it would be necessary to repeat the exercise for the infinite number of alternative connectivities, permutations and configurations, consistent with the chemical formula of the 'molecule'.

The unspoken assumption that sanctifies the *ab initio* procedure is that once an acceptable level of agreement between the calculated electron distribution and the assumed Hamiltonian has been reached, the molecular structure has been confirmed quantum mechanically. This is utter nonsense, even in terms of the so-called laws of quantum mechanics. One of these, known as the uncertainty principle, forbids a fixed location for any quantum object, presumably including atoms and molecules.

Irrespective of the 'level of theory' no amount of hand waving or computing power can overcome this problem. A Hamiltonian based on a rigid, so-called Born-Oppenheimer, nuclear framework can never constitute a quantum-mechanical variable. The emperor simply has no clothes on.

Alternatively, a solution *ab initio* in terms of the Copenhagen laws of quantum mechanics must generate, not assume, the probability nuclear distribution, given the chemical composition of the target molecule.[1] Unless this can be achieved molecular quantum chemistry does not exist. Density-functional theory is refuted by the same argument.

Molecular mechanics has no such pretensions. Its only objective is to simulate a classical three-dimensional molecular structure according to the principles developed by Kekulé, van't Hoff, Lewis and others, using classical mechanics and Hooke's law. Within this formalism it serves the chemical community well, despite repeated efforts to belittle the technique for not being quantum based. In this respect it is no different from VB, MO and DFT methods, except for being honest about its theoretical background. In order to distinguish interactions of different order an unfortunate practice to label bonding types in orbital terminology, has developed, but this can be eradicated with little effort.

That orbital hybridization is a myth is now getting more widely accepted [10, 11]. It occurs most frequently to describe the interaction between first-period elements in terms of $s - p$ hybrid orbitals. According to Coulson [9]:

> ...we describe each electron by an orbital, or 'personal wavefunction'...
>
> The p-functions occur in *sets of three*, each set describing three alternative states in which the electron has exactly the same energy; three such p-orbitals, which we denote by p_x, p_y, p_z are said to be *triply degenerate*.

What remains unsaid is that these p-orbitals are all **real** functions; therefore all with the same wave-mechanical quantum number of $m_l = 0$. At the same time we are reminded by Coulson [9] that

---

[1] Some science writers even claim that the molecular products of chemical reactions can be predicted quantum-chemically.

> Pauli's famous exclusion principle then takes a very simple form: *in the orbital description of an atom no two electrons can occupy the same spin-orbital.*

In any other branch of science such self-contradiction would be devastating. Quantum chemists respond that in this case quantum numbers are no longer needed, which, they forget to admit, therefore defines a classical system.

We conclude that a search for the quantum-mechanical basis of molecular mechanics is a *non sequitur*. It does not exist and there is no need for it. Still, it would be useful to have a non-empirical estimate of the variables, such as ideal bond lengths and angles, stretching and bending force constants and a measure of steric rigidity; that feature in MM force fields. Many of these are provided by the number-theory approach to covalent interaction. However, in practice there is little need of recalculating the force-field parameters which, in most applications, have been established empirically with care and suitable validation.

It does not mean that the search for a wave-mechanical model of molecular structure should be abandoned. New insight based on four-dimensional and nonlinear molecular models would be of tremendous advantage in the elucidation of chemical reactivity.

1.3.2 Atomic and Molecular Structure

The 4D equivalent of Schrödinger's equation remains to be solved. In the interim the number-theory simulation of atomic structure [12] confirms a spherical standing-wave structure of electron density as first indicated by golden logarithmic-spiral optimization [5]. The interaction between such wave structures depends on the interference of (hyper)spherical waves, which cannot be reconciled with the formation of rigid chemical bonds. The familiar structural formulae of molecules can only reflect connectivity patterns and not rigid three-dimensional structures.

We conjecture that curving of the space-time vacuum generates elementary four-dimensional distortions, which, for lack of better terminology, may be described as spherical wave packets of characteristic mass, charge and spin, summarized together by a quaternion wave function. As these elementary units coalesce into larger structures they appear as the classical objects familiar to three-dimensional observers in tangent space. Free molecules are not of this class, but molecular crystals are.

Free molecules only occur in empty intergalactic space-time. Radio astronomical analysis of Rydberg atomic spectra from interstellar space indicates electronic quantum numbers of up to 350, for atomic size of $\sim$6 micron and subject to strong polarization by weak electromagnetic fields [13]. Free molecules would be affected in the same way and are not likely to occur intergalactically. Stable small molecules of high symmetry are detected in dark interstellar clouds [14]. These molecules have no structure. As the concentration of matter in an environment increases, single molecules develop structure of lower symmetry, culminating in molecular crystals.

The shape of a single molecule therefore varies from a structureless 4D symmetry to a rigid 3D arrangement—from a non-classical to a classical molecule.

Intergalactic space-time is not a void, although depleted of matter in large enough concentration to cause further aggregation. The total uniformly distributed residual elementary wave structures constitute an enormous total mass which astrophysicists refer to as dark matter and energy. The mass density in interstellar space is sufficient for the condensation of clouds hot enough for the formation of primitive molecules.

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Chapter 2
The Classical Background

Abstract The development of physical science over the last two millenia is traced from the summary of Lucretius, through the early Christian era, to the transformation into critical science after Copernicus. This revolution saw the birth of physics and chemistry to replace Aristotelian authority and alchemy, guided by the principles formulated by Isaac Newton and John Dalton. The new awareness blossomed into the formulation of a comprehensive theoretical mechanics and the recognition of seventy well-characterized chemical elements to replace the four elements of antiquity.

2.1 Introduction

Modern theories of the physical sciences have developed through several refinements from ancient philosophical models and, not surprisingly, many an outdated concept has remained hidden in modern expositions. Most persistent are those that appear self-evident to the non-critical or casual observer and therefore quietly tolerated without further analysis. Some of the most debilitating inconsistencies in theoretical science are of this type and often the hardest to gainsay.

A useful strategy to weed out hidden fallacies is by historical scrutiny of the theoretical progress of science, starting from the classical roots. Most of the authentic ancient sources have been lost, but a reliable account of physical theories in Roman times (∼55 BCE) has been preserved in poetic form, as compiled by Lucretius [1]. The poem develops around six primary propositions:

(i) Nothing is ever created out of nothing
(ii) Nothing is ever annihilated
(iii) Matter exists in the form of invisible particles (atoms)
(iv) Besides matter, the universe contains empty space (vacuity)
(v) The universe consists of matter (with its properties and accidents) and of vacuity and of nothing else
(vi) The atoms are indestructible

These are augmented by two further propositions:

(vii) The universe is boundless
(viii) The universe has no centre

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The motion and shape of atoms are described by two sets of secondary propositions.

On atomic movement:

(i) The atoms are always on the move, either falling or rebounding
(ii) They move faster than light
(iii) The atoms normally curve downwards
(iv) Occasionally they swerve slightly from the vertical
(v) They were never either more or less congested than now
(vi) The apparent mobility of matter is an optical illusion

On atomic shape:

(i) The various properties of objects are due to the varieties in the size and shape of atoms
(ii) The number of atomic shapes is large but finite
(iii) The number of atoms of any one shape is infinite
(iv) All visible objects are compounds of different kinds of atoms
(v) Only certain compounds can exist
(vi) The atoms themselves are devoid of colour, heat, sound, taste, and smell, and sentience

These propositions are supported by three general corollaries:

(i) The world is one of an infinite number
(ii) Nature is self-regulating, without interference from the gods
(iii) The world had a beginning and will soon have an end

A number of important conclusions, drawn from appropriate analysis of the basic propositions, deserve special mention:

(i) The universe is not bounded in any direction. It stretches away in all directions without limit
(ii) Solid matter results from a closer union between atoms by the entanglement of their own interlocking shapes
(iii) Through undisturbed vacuum all bodies must travel at equal speed though impelled by unequal weights. The heavier will never be able to fall on the lighter from above
(iv) There is no visible object that consists of atoms of one kind only

Many of these propositions have a surprising modern ring to them, although based on a totally outdated cosmology of a flat earth in infinite space. The disturbing reality is that precisely these objectionable features again underpin the "standard cosmology" of the West. Despite the evidence from general relativity, space is still considered in the expanding universe cosmology as Euclidean (*i.e.* flat) and of infinite extent in all directions. Despite intimate experience with the electromagnetic field, the expanding universe is modelled exclusively in terms of matter moving through vacuity, precisely as presumed by Lucretius.

It would seem that apart from trivial refinement of the atomic model, the philosophical paradigm has not changed in two millenia. Where Lucretius ascribed chemical interaction to the entanglement of interlocking atomic shapes the modern quantum chemist achieves the same in terms of entangled hybrid orbitals, and with the same conviction as Lucretius.

The first millenium after Lucretius saw little change in the understanding of the physical world, except for an infusion of theological dogma and the revival of creation myths that have survived into the present as big-bang cosmology. Instead of progressing, theoretical physics regressed to the Aristotelian model, leaving it to Galileo to rediscover the Lucretian proposition of falling bodies. As the progenitor of chemistry the art of alchemy descended into mysticism and astrology.

By the end of the first millenium CE there was total consensus in the Western World over the workings of the cosmos and the odd heretic, who dared to challenge the revealed truth, could readily be disposed of. Only two problems, destined to disturb this tranquility, remained: how to make gold and where to find the universal remedy for all disease. In searching for the philosopher's stone and an elixir to end the quest, the variety of unexpected secondary products that turned up could no longer be understood within the standard model of alchemy. The emerging scepticism soon spread to other aspects of natural philosophy and it became feasible to challenge metaphysics with real physics; alchemy with chemistry. However, the development of a new scientific paradigm had to await the emergence of a new cosmology, which was initiated by Copernicus.

2.1.1 The Copernican Revolution

Mediaeval science was liberated from its paralysis, imposed by the canonized Aristotelian and Ptolemaic systems, by the new cosmology, inaugurated by acceptance of the heliocentric model proposed by Copernicus. The awkward questions that tortured Lucretius, such as the whereabouts and status of the sun at night, the cause of seasonal changes and the support structure of the earth in space, disappeared almost miraculously, although the new system was resisted by the establishment for more than a century.

The real hero of the revolution was Johannes Kepler, who supposedly [2, p. 178], murdered his superior, Tycho Brahe, in order to gain access to the data that eventually substantiated heliocentric planetary motion without epicycles. Although Kepler's three laws of planetary motion on elliptic, rather than circular, orbits[1] were, for ideological reasons, received with scepticism, they were embraced by a new generation of scientists and eventually inspired the long-awaited new paradigm. The idea of planetary orbits, stabilized by gravity, culminated in Newton's memorable work and it finally also invalidated the notion of astrological interaction between heaven and earth and its stranglehold on alchemy. The way was cleared for the development of modern physics and chemistry.

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[1] Only circles were assumed to reflect heavenly perfection.

2.2 Newtonian Physics

The tortuous route from Kepler's laws to Newton's reformulation in terms of the mechanical concepts of inertia and force was reviewed only recently [3] and the details of Newtonian mechanics have been confirmed in writing so many times as to make another repetition superfluous. It is considered more important to concentrate on the philosophical aspects of his work, how these impacted on later developments, and still have a decisive influence on current science.

The single most important concept introduced by Newton in order to rationalize Kepler's laws was the general inverse-square law of gravity, postulated to operate between any two mass points in the universe with a force,

$$F = G\frac{m_1 m_2}{r^2}.$$

Newton was the first to admit that [4, p. 314]:

> …the Cause of Gravity is what I do not pretend to know…

and further elaborated:

> That Gravity should be innate, inherent and essential to Matter, so that one Body may act upon another at a distance thro' a Vacuum, without the Mediation of anything else, by and through which their Action and Force may be conveyed from one to the other, is to me so great an Absurdity, that I believe no Man who has in philosophical Matters a competent Faculty of thinking, can ever fall into.

The evident implication is that the mathematical formalism that correctly accounts, not only for planetary motion, but also for terrestrial gravitational effects, is by itself sufficient to uphold the general theory, without any physical understanding of the interaction.

Two and a half centuries had to elapse before a satisfactory physical explanation of gravity would emerge from the general theory of relativity. During this time constant positive scrutiny of Newton's gravitational model created the firm conviction that mathematical formalism suffices as the sole criterion to establish a physical theory. As a pertinent example, it is frequently repeated as a great virtue of quantum mechanics that it is adequately formulated on the hand of postulates with no more than mathematical meaning. It is probably fair to say that this has been the hallmark of twentieth-century theoretical physics. The delusional effects of such false security cannot be overemphasized and will be highlighted again in the course of this work. The problem does not lie with the mathematics *per se*, but with an inappropriate physical interpretation that may become established by default.

The particle concept that still dominates physical science is another spin-off of Newton's mathematical model. It arose from Newton's comment in *Principia* [4, p. 295]:

> After I had found that the force of gravity towards a whole planet did arise from and was compounded of the forces of gravity towards all its parts, and

> to every one part was in the inverse proportion of the squares of the distances from the part, I was yet in doubt whether that proportion as the square of the distance did actually hold… it might be that the proportion that was accurate enough at greater distances would be wide of the truth near the surface of the planet, where the distances of the particles are unequal, and their situations dissimilar.

The eventual mathematically inspired conclusion was that the force between two spheres

> …increases or decreases in proportion to the distance between their centres according to the same square law as applied to the particles themselves. And this is a noteworthy fact.

As paraphrased by Hall [4]:

> Once more mathematics demonstrated a physical improbability as truth: the sphere acted on any body outside it, however close, from its own centre; and this was true of any law of attraction. But if the inverse-square law applied outside the sphere, then inside it the attraction to the centre was directly as the distance.

It is remarkable how this conclusion has gone unnoticed by scores of scientists who have agonized for many years over the presumed infinite self-energy of a charged object such as an electron. Without going too deeply into further philosophical implications, the proposition that a geometrical mass-point takes the place of a physical body, has had enormous ramifications. Not least because of Newton's lack of distinction between particles and atoms. He stated [4, p. 237]:

> …it seems probable to me that God in the Beginning form'd Matter in solid, massy, hard, impenetrable, movable Particles…
>
> For the matter of all things is one and the same, which is transmuted into countless forms by the operations of nature… and hence we conclude the least particles of all bodies to be also extended, and hard and impenetrable, and movable, and endowed with their proper inertia.

It is clearly implied that all fundamental particles are alike. This proposition has evolved into the modern notion that all elementary particles are zero-dimensional points. Nothing causes more confusion in quantum chemistry than the electronic point particle.

2.3 Daltonian Chemistry

The reason why the Copernian proposal of a heliocentric system was resisted for such a long time, is because it challenged the views of the mediaeval philosopher-saints, who incorporated Aristotelian physics and the Ptolemaic Almagest as a subset of revealed biblical truth. In essence, the result was a universe, centred on the static earth, in the form of eight concentric crystal spheres that move in harmony, directed by the prime mover (God) on the ninth immovable heavenly sphere.

As all motion is interconnected, all terrestrial events are inextricably correlated with their counterparts on the crystal spheres. This awareness developed into a firm guiding principle for the early alchemists whose prospects of success was interpreted to depend equally on a correct reading of the stars as on experimental design [5].

The Copernican revolution changed all that. The earth, no longer the focal centre of the cosmos, was no longer perceived as the microcosm that merely responds to the whims of the *primum mobile*. Events on earth could now happen and be controlled, independent of the stars. As the emphasis on astrology diminished, the relationship between starting materials and reaction products started to be appreciated and alchemy gradually evolved into chemistry.

Robert Boyle, a contemporary of Newton is generally identified as the first modern chemist, whereas Newton's chemical research is usually referred to as alchemy. In this case tradition has almost certainly got it wrong. Boyle is credited with writing the book *Sceptical Chymist* and, apart from formulating a seminal gas law, had contributed very little to indicate a new direction for chemistry. On the contrary, Newton's "alchemy" was pursued in the belief [4, p. 323]:

> ...that chemistry touches on some of the fundamental properties of matter. Through chemistry knowledge might be won of the forces that hold together, or rearrange, the particles of substances.

This is still the spirit in which modern chemistry is practiced. Although Newton therefore contributed very little of chemical significance, he certainly showed the way in which chemistry was to develop.

In less than a hundred years after Newton succeeded in providing a firm foundation for new physics, the new directions in chemistry culminated in the formulation of Dalton's atomic theory which did the same for chemical science.

The formulation of Newton's laws of motion, by refuting the four-element theory of Aristotle, was of equal importance for the development of chemistry. Associated with heavenly spheres, the elements, identified as earth, water, air and fire, each had its own natural comfort zone to which it invariably returned when displaced by unnatural action. The lowest sphere was occupied by earth, always seen to fall back when raised to higher levels, The heavier an object, the faster it falls. Next came water, that preferred to float on the solid earth in the sphere where it belongs. Air occupied the next sphere, with fire at the top. This behaviour soon found a more rational explanation in terms of Newton's law of gravity, rather than each element accelerating towards its own sphere.

The properties of composite bodies could be rationalized in terms of their elemental composition. Heavy objects obviously contained a high proportion of earth and inflammable substances were full of fire. In this sense the four elements represented characteristic principles, rather than indentifiable substances and were interpreted in this way by the alchemists. For laboratory practice the alchemists identified the secondary qualities of metallicity (spirit), brittleness (body), and combustibility (soul), typified by the real 'elements' mercury, salt and sulphur.

The seven metals, astrologically linked with seven planets

> silver (Moon), mercury (Mercury), copper (Venus), gold (Sol), iron (Mars), tin (Jupiter) and lead (Saturn),

contained the three qualities in characteristic, subtly different, adjustable proportion, which enabled transmutation.

The period between Newton and Dalton saw the identification of a variety of different airs (gases) such as fixed air (carbon dioxide), acid air (HCl), alkaline air (ammonia), empyreal (dephlogisticated) air (oxygen), phlogisticated air (nitrogen), phlogiston (hydrogen), laughing gas (nitrous oxide), inflammable air (carbon monoxide) and inflammable air of marshes (methane) [6]. The confusing nomenclature was a remnant of the phlogiston theory of combustion, the overthrow of which by Lavoisier was a direct result of the discovery of new gases. The reformulation of known chemical processes in terms of mass-balanced reactions, such as

mercury calcinatus = mercury + oxygen
oxygen + hydrogen = water
oxygen + nitrogen = laughing gas
acid air + alkaline air = sal-ammonia
charcoal + oxygen = fixed air (carbonic gas)
wort of grapes = carbonic gas + alcohol

are all consistent with the conservation of matter, as conjectured by Lucretius.

The stage was set for the formulation of Dalton's atomic theory, in the form of four postulates [6]:

(i) The ultimate particles of a pure substance, whether simple or compound, are perfectly alike in size and weight.
(ii) The "simple atoms" of an elementary substance are indivisible, and can neither be created nor destroyed.
(iii) The "compound atoms" (or "molecules") of a compound are formed by the union of two or more elementary atoms.
(iv) Combination between atoms takes place in the simplest integral ratios, *e.g.* 1 atom of A with 1, 2 or 3 atoms of B.

This reads like a paraphrase of what Lucretius proposed almost two millenia earlier.

The difference is that Dalton had a responsive audience and a mass of data that could be rationalized in the form of a few simple laws of chemical combination, based on Dalton's proposals. These are the well-known laws of:

(i) Fixed Proportions
(ii) Multiple Proportions
(iii) Reciprocal Proportions

The first of these is almost self-evident, giving new meaning to the concept *element*, the second follows as a prediction from Dalton's postulates and the third implies *that each element has its own characteristic equivalent* or *combining weight*.

The third law enabled the specification of chemical formulae that reflect the relative number of equivalents of different elements in various compounds, but because of multiple proportions equivalent weights could not be assigned unambiguously. This ambiguity was finally resolved ten years later by Avogadro's Hypothesis, stating that,

> When the temperatures and pressures are the same, equal volumes of different gases contain equal numbers of molecules.

To make this generally applicable it was necessary to assume that molecules of an elementary gas might consist of groups of similar atoms, such as

$$N_2, O_2, O_3, H_2, P_4, S_8, \textit{etc.}$$

It is therefore possible to substitute molecules for volumes in any equation in which gases are involved. Thus, from the experimental result that

$$\text{(1 vol)nitrogen} + \text{(1 vol)oxygen} = \text{(2 vols)nitric oxide}$$

it follows that

$$N_2 + O_2 = 2NO.$$

The next fifty years were devoted to clear up the confusion between atoms and molecules; between equivalent and atomic weights, finally achieved by Cannizaro, resulting in a consistent set of atomic weights for elements known at the time.

2.4 The Aftermath

Newton saw himself [7]

> ...to have been like a boy playing on the sea-shore, ...now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.

The same is evidently true of John Dalton. In both cases their bold conjectures provided the foundation for continued research, aimed at the ultimate refinement of their seminal ideas, which were never in doubt.

2.4.1 Dalton's Legacy

The chemists were so single-minded in their dedication that the brilliant insight of William Prout, that made sense of their blind pursuits, was rejected with such hostility that he had to publish his theory anonymously. Noting the large number of atomic weights on the (H = 1)-scale improbably close to whole numbers Prout hypothesized [8]

> ...that *the atoms of all elements are formed by the condensation of atoms of hydrogen*, this element being the **primary matter** or **protyle**.

It is as if the mule-headed obstinacy that sustained alchemy, against all reason, for two millenia has been driving chemical research ever since. The same obstinacy upheld the phlogiston theory in the face of overwhelming counter-evidence. Even the discoverers of oxygen (Priestly) and hydrogen (Cavendish) refused to consider the experimentally proven alternative theory of combustion. At the present time one marvels at the pathological reluctance to abandon the discredited model of orbital hybridization and linear combination of atomic orbitals as an explanation of chemical interactions.

In defence of Prout's hypothesis it was pointed out repeatedly that non-integral atomic weights, such as 35.5 for chlorine, could result from a mixture of atoms with different mass, but the same chemical properties. The only reason why this proposition was rejected, was because it conflicts with Dalton's conjectures. The discovery of isotopes, almost a hundred years later, dovetailed with Prout's proposal, without lessening Dalton's contribution.

In the meantime sustained efforts to either confirm or discredit Prout's hypothesis resulted in a consensual set of accurate atomic weights. However, the revolutionary postulate of elemental gaseous molecules, consisting of aggregates of identical atoms remained a major stumbling block for many years. Such a union is explicitly forbidden in the Lucretian system and was seriously frowned upon by Dalton. The vague notion of chemical affinity, which presupposed an attraction between some type of opposites, offered no explanation for the formation of elemental molecules. It caused the same agony as experienced before by Newton and his contemporaries looking for a physical explanation of gravity. In the same way it culminated in a passive acceptance of some mysterious attraction that leads to the formation of chemical *bonds*. As a palliative it was argued that the exceptionally close approach, which can be achieved between vanishingly small atoms, would imply strong inverse-square gravitational interaction.

The discovery of electrochemical effects later in the 19th century provided a partial explanation of chemical affinity in terms of polarization effects, but also largely confined to heteroatomic interactions. Commenting on chemical affinity Alfred Stewart [9] stated in 1926, when wave mechanics was already in the air:

> In the 'nineties the whole problem lacked a generalization. On the one hand lay the metallic salts with their capacity for ionization, which suggested an electrical conception of chemical affinity; but on the other side stood the enormous host of the carbon derivatives which showed no electrical character and which could be so easily symbolized by means of graphic formulæ. Attempts to force the carbon compounds into line with the inorganic compounds proved unsatisfactory; while the converse effort to reduce the inorganic series to a graphic formulation was equally ineffective: and towards the end of the century, the whole problem seemed beyond the power of chemists to solve upon a simple basis.
>
> It cannot be asserted that, even at the present day, the chemical affinity problem is solved; but at least some change in outlook is obvious. It is generally agreed that chemical affinity is electrical in nature; and that polar and non-polar compounds differ from each other in degree rather than in kind.

> The theory of G.N. Lewis is widely accepted as a means of formulating the machinery of chemical combination and dissociation, though at present it has hardly progressed beyond the stage of being a representation of the facts rather than an explanation. Still, even with its limitations, it furnishes the best mechanical model available to depict the union of one atom with another; and it has the decided advantage of bringing a unifying conception to bear upon the whole question.

The classical concepts of chemical affinity developed from the rapid advances in organic chemistry following the introduction by Berzelius of a simplified scheme of atomic symbols and molecular formulae to replace the awkward graphical symbolism of Dalton. Many of the rules were formalized by Kekulé [10] by assigning valencies of 1, 2, 3 and 4 to H, O, N and C and their congeners, later associated with affinity centres in order to rationalize the assumed three-dimensional structure of molecules. The well-known conjecture of Jacobus van't Hoff which associates optical activity with three-dimensional molecular chirality is perhaps the most important chemical concept that can be traced back directly to Dalton's atomic theory.

2.4.2 Classical Mechanics

The heirs of Newton were equally diligent in repeatedly solving the equation

$$F = ma$$

in all possible situations, but decidedly more open-minded in accepting equivalent alternative formulations, particularly those developed by Lagrange, Hamilton and others.

An important issue left undecided by Newton and his contemporaries was the mode in which light propagates. The bland statement, repeated in many textbooks, that Newton defended the corpuscular nature of light against the wave model of Huygens, has no validity. In his mathematical analysis of *Newton's rings* [11, p. 368], Newton introduced a 'fit' parameter, not physically defined, but in exact agreement with modern values of wavelength. Hence [4, p. 271]:

> Evidently Newton's theory of light was very far from being a simple corpuscular or emission theory. The wave-concept was always essential to it—not as a hypothesis, but as a feature of a mathematical theory from which verifiable predictions could be drawn.

A brief review of classical dynamics [12] shows that the Hamiltonian refinement of Newton's laws resulted in a similar formulation that links particle mechanics to wave motion.

For a system of n mass points the Newtonian equations of force along x, as a function of kinetic energy

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{x}_i}\right) = m_i \ddot{x}_i = X_i$$

is further modified by defining the force as a function of potential energy,

$$X_i = -\frac{\partial V}{\partial x_i}$$

to yield

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{x}_i}\right) + \frac{\partial V}{\partial x_i} = 0$$

with similar expressions for y_i and z_i.

Hamilton's principle of least action requires that the Lagrangian function, $L(q, \dot{q}) = T - V$, defined as the difference between the kinetic and potential energies of a system, in terms of generalized coordinates and velocities, be an extremum, *i.e.*

$$\delta \int_{t_0}^{t_1} \left\{T(q, \dot{q}) - V(q)\right\} dt = 0.$$

After integration by parts the variation condition yields the set of equations

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0, \quad j = 1, 2, 3, \ldots, 3n.$$

The Lagrangian equations are further modified by definition of the Hamiltonian function

$$H = \sum_{k=1}^{3n} p_k \dot{q}_k - L(q_k, \dot{q}_k)$$

where

$$p_k = m_k \dot{q}_k = \frac{\partial T}{\partial \dot{q}_k}, \qquad k = 1, 2, 3, \ldots, 3n, \qquad \dot{p}_k = \frac{\partial L}{\partial q_k},$$

$$i.e. \quad \frac{\partial H}{\partial p_k} = \dot{q}_k, \qquad \frac{\partial H}{\partial q_k} = -\frac{\partial L}{\partial q_k} = -\dot{p}_k.$$

These are the Hamiltonian or canonical form of the equations of motion, with the advantage that they contain $6n$ partial differential equations of the first order rather than $3n$ of the second order. Noting that kinetic energy is a homogeneous quadratic function of velocities it is shown that $H = T + V = E$, the total energy, and $T = p^2/2m$.

In the case of a time-dependent Hamiltonian it is next demonstrated that

$$\frac{1}{2m}\left(\frac{\partial S}{\partial q}\right)^2 + V + \frac{\partial S}{\partial t} = 0,$$

the so-called Hamilton–Jacobi equation, where $H = -\partial S/\partial t$, $dS/dt = L$ and the action S is known as Hamilton's Principal Function.

The Hamiltonian in integrated form is given by $S = -Et + W$, where $W(p, q)$ is known as Hamilton's Characteristic Function. It now becomes apparent why S has been called the action of the system. It represents the energy transferred to the system over a period of time. Substitution of $-\partial S/\partial t = H$ into the HJ equation shows that

$$H = T + V = \frac{1}{2m}\left(\frac{\partial S}{\partial q}\right)^2 + V \tag{2.1}$$

to give another form of the HJ equation:

$$\left(\frac{\partial S}{\partial q}\right)^2 = 2m(E - V).$$

At any given instant the equation $S(q, t) =$ constant defines a surface in Euclidean space. As t varies the surface traces out a volume. At each point of the moving surface the gradient, ∇S is orthogonal to the surface. In the case of an external scalar potential the particle trajectories associated with S are given by the equation $m\dot{q} = \nabla S$. It follows that the mechanical path of a moving point is perpendicular to the surface of constant S for all q and t. A family of trajectories is therefore obtained by constructing the normals to a set of surfaces, each orbit being distinguished by its starting point q_0. For a single starting point the moving surface describes a spherical wavefront. This intimate connection between wave and particle formalisms is of special interest and has been used to forge a link between geometrical and wave optics. By analogy to this it was also used by Schrödinger in his original formulation of a wave equation for quantum matter [13].

The alternative approach is to describe the motion in wave formalism. In this case the wave equation

$$\nabla^2 U = \frac{1}{v^2}\frac{d^2 U}{dt^2}$$

is assumed to have a plane-wave solution of the form

$$U = Ae^{i(\omega t - k\phi)}$$

with variable amplitude A, phase $k\phi$, frequency ω, and variable velocity v. It satisfies the wave equation providing

$$\nabla^2 A - k^2 A(\nabla\phi)^2 + A\frac{\omega^2}{v^2} = 0.$$

Assuming the velocity in vacuum, $v_0 = \omega/k$ one has

$$\frac{\nabla^2 A}{A} - k^2\left[(\nabla\phi)^2 - \left(\frac{v_0}{v}\right)^2\right] = 0$$

where v is the velocity in another medium with index of refraction $n = v_0/v$. Since $\nabla^2 A = 0$ for the plane wave and $k^2 \neq 0$, it is implied that

$$(\nabla\phi)^2 = n^2.$$

The striking mathematical similarity between this so-called eikonal equation of geometrical optics and the HJ equation

$$(\nabla S)^2 = 2m(E - V)$$

is unmistakable. Setting $n^2 = 2m(E - V)/p^2$, where p has the dimensions of a momentum and assuming the proportionality $S = p\phi$, the equations become identical.

This result suggests the possibility that wave propagation can be approximated in terms of particle motion or to describe the motion of a particle in wave formalism, the basic assumption of wave mechanics. However, it is important to note that this eikonal analysis is only valid in the short wavelength region of geometrical optics and under no circumstances does it imply the popular notion of wave-particle duality.

The mechanical equivalents of the dimensionless optical parameters ϕ and n have the dimensions of momentum appropriate for wave-mechanical matter waves. These wave properties become increasingly less in evidence with increasing mass and becomes effectively unobservable for macroscopic massive objects.

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Chapter 3
Great Discoveries

Abstract The two major achievements of 19th century science that produced the periodic table of the elements and the electromagnetic theory are reviewed. A critical analysis of Prout's hypothesis, Newlands' law of octaves and Nagaoka's Saturnian model of the atom argues for a major re-assessment of the currently accepted history and interpretation of this most important chemical discovery of all time. The synthesis of concepts around chemical affinity and molecular conformation by Sommerfeld is recognized as the ultimate development of chemical theory based on Newton's particle model.

The developments that led to the unification of magnetism, electricity and optics happened during the same period. The empirical observations that resulted in Maxwell's synthesis are reviewed. The theory of electromagnetic radiation and the supporting theory of wave motion are critically examined.

3.1 Introduction

The initial burst of activity in physics and chemistry was triggered by the two new theories of Newton and Dalton. The experimental researches inspired by these theories produced such dramatic new insights that by the middle of the 19th century the emphasis had shifted to the contemplation of issues no longer understood in terms of the seminal theories. A periodic relationship, revealed by experimentally measured atomic weights, pointed at a radically different interpretation of chemical phenomena and the measurements that resulted in the recognition of an electromagnetic field demanded a complete reformulation of classical mechanics.

Such an alternation between theoretical and experimental advances has become a regular feature of scientific research. A new theory is said to establish a new paradigm to be adhered to in all subsequent experimental studies. Any result at variance with the paradigm is treated with suspicion and subjected to remorseless scrutiny. In many cases such deviant results are suspended from consideration until an acceptable correction factor for its rationalization is found. Many a new innovative suggestion is simply rejected pending conclusive proof, and promptly forgotten. Paradigm shifts, which in retrospect may appear to be natural logical developments, are never painless and may happen only gradually over a period of many years.

J.C.A. Boeyens, *The Chemistry of Matter Waves*, DOI 10.1007/978-94-007-7578-7_3,

3.2 Periodic Table of the Elements

Despite the erratic atomic weights derived by a variety of methods, based on gas densities, heat capacities (Dulong and Petite), isomorphism (Mitscherlich) and chemical analyses, before Cannizaro managed to unify the results, sufficient data were generated to reveal some regular patterns. The generalization suggested by Prout has been mentioned. At about the same time it was spotted by Döbereiner that the atomic weights of triads of related elements, such as chlorine, bromine and iodine were related in a simple numerical pattern. Like Prout's hypothesis this observation was simply ignored.

As described by Berry [1]:

> Between 1863 and 1866 a series of short papers was published in *The Chemical News* by Newlands on numerical relations between the atomic weights of the elements and their corresponding properties. He found that if the elements… were arranged in the order of ascending atomic weights, 'the numbers of analogous elements generally differ by seven', like 'the extremities of one or more octaves in music'. This relation was termed the law of octaves by Newlands. It was read before the Chemical Society and publication was refused.

The situation is further elaborated on by Stewart [2], stating that:

> He also suggested that from his scheme it was possible to predict the existence of elements as yet unknown.
>
> It is reported [Chem. News **13**, 113 (1866)] that when the Law of Octaves was propounded at the meeting of the Chemical Society, "Professor G. Foster humorously inquired of Mr. Newlands whether he had ever examined the elements according to the order of their initial letters".

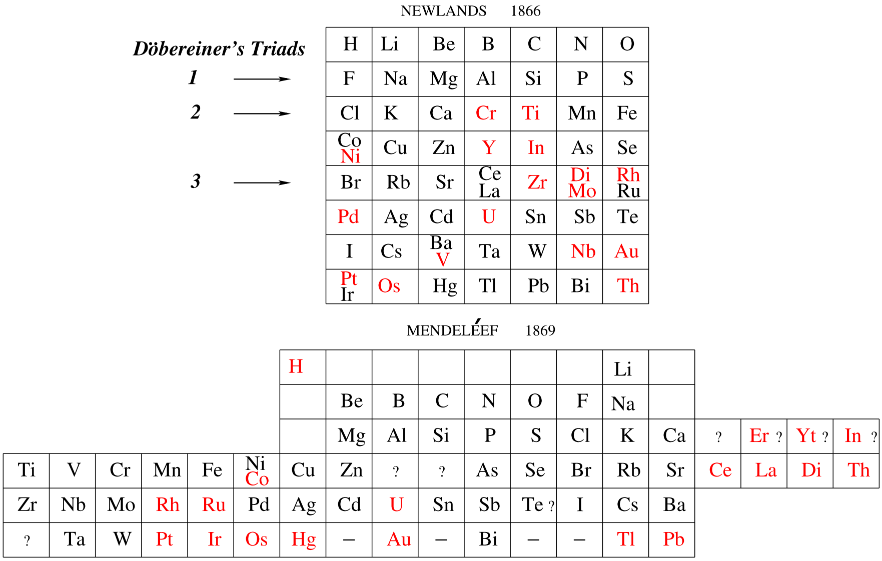
Stewart further compares the published tables of Newlands (1866), that was rejected and ridiculed, and that of Mendeléef (1869) that was received with acclaim. The comparison is reproduced from [2] in Fig. 3.1. Those elements, incorrectly placed in terms of modern concepts are printed in red.

Remarkably, the two tables list 62 and 63 elements respectively, of which each placed 45 correctly, according to the compact form of the Periodic Table based on number theory [3] for Newlands, and according to the standard long form for Mendeléef. Of those placed incorrectly 9 are in common between the two tables, evidently because of incorrectly measured atomic weights.

Modern textbooks invariably dismiss the Law of Octaves as infantile numerology compared to the scientifically mature exposition of Mendeléef. This conclusion is clearly based on the ignorant conceit of a buffoon, who was repudiated when the Davy medal of the Chemical Society was awarded to Newlands in 1887.

In comparing the contributions of Newlands and Mendeléef Stewart [2] reached the following conclusions:

> In his Faraday lecture (1889) Mendeléef summarized [his achievements in the form of 8 claims].



NEWLANDS 1866

Döbereiner's Triads							
	H	Li	Be	B	C	N	O
1 →	F	Na	Mg	Al	Si	P	S
2 →	Cl	K	Ca	Cr	Ti	Mn	Fe
	Co Ni	Cu	Zn	Y	In	As	Se
3 →	Br	Rb	Sr	Ce La	Zr	Di Mo	Rh Ru
	Pd	Ag	Cd	U	Sn	Sb	Te
	I	Cs	Ba V	Ta	W	Nb	Au
	Pt Ir	Os	Hg	Tl	Pb	Bi	Th

MENDELÉEF 1869

						H							Li					
							Be	B	C	N	O	F	Na					
							Mg	Al	Si	P	S	Cl	K	Ca	?	Er ?	Yt ?	In ?
Ti	V	Cr	Mn	Fe	Ni Co	Cu	Zn	?	?	As	Se	Br	Rb	Sr	Ce	La	Di	Th
Zr	Nb	Mo	Rh	Ru	Pd	Ag	Cd	U	Sn	Sb	Te ?	I	Cs	Ba				
?	Ta	W	Pt	Ir	Os	Hg	–	Au	–	Bi	–	–	Tl	Pb				

Fig. 3.1 Periodic Tables according to Newlands (1866) and Mendeléef (1869) redrawn in modern style (Colour figure online)

> When the first five of these statements are compared with the six claims of Newlands (1884), it will be found that the two sets are practically identical. All that Mendeléef ascribed to the Periodic Law had already been achieved by the Law of Octaves. As to the seventh and eighth clauses… neither of them was correct even in Mendeléef's day.
>
> On the face of things, then, Mendeléef had achieved nothing which Newlands had not already brought before the chemical world…

Attempts to rationalize the irrational response of the chemical world in denying Newland's rightful priority to the major chemical discovery of all time, is irrelevant in historical perspective.[1] It is properly documented that Newlands published the Law of Octaves three years ahead of Mendeléef and Lothar Meyer, albeit four years after de Chancourtois had announced the telluric screw which contained the pioneering concept of atomic numbers. The fact that a group of British chemists found the comparison with music sufficiently hilarious to discount the scientific value of the discovery is immaterial. They would probably have considered the achievements of Pythagoras and Kepler as equally ridiculous.

It is intriguing to note Mendeléef's sanctimonious denial of all knowledge about any previous mention of atomic periodicity, while openly insinuating that Lothar Meyer had plagiarized his work.

---

[1] If the Catholic church could admit and apologize for their shabby treatment of Galileo after 4 centuries, the least that the chemists of the world can do is to give Newlands his proper recognition.

The human drama that surrounded the discovery of the Periodic Table pales into insignificance compared to the scientific importance of the event. In this regard it is sufficient to note that, as more atomic weights became accurately known, a general awareness of some mysterious qualitative relationship between atomic weight and chemical properties, developed among European chemists—in Britain, France, Germany, Italy and Russia. Apart from the frivolous response in some quarters it must have been generally appreciated that Dalton's atomic model was hopelessly inadequate to account for this observation. The time had come to move beyond Newton's solid, massy, hard, impenetrable particles as an atomic model.

The problem had become more intractable than simple interatomic attraction that could be vaguely likened to the equally mysterious gravitational interaction. There is no simple understanding of how three elements like chlorine, bromine and iodine, with vastly different atomic weights, could be so alike in their special chemical behaviour. If the same trend is observed for seven elemental triads in a row of increasing atomic weight, it becomes all the more difficult to dismiss as a coincidence. The conclusion that the members of each triad must share some internal characteristic, independent of atomic weight, becomes irresistable.

Soon, the wish became father to the thought, with Faraday's experiments on electricity in mind. In 1879 Crookes discovered cathode rays, followed by Arrhenius with the publication of his ionic theory in 1887 and Stoney's proposal in 1891 of a charged particle, called *electron*, present in all atoms. The old paradigm was dead and with it all restrictions on experimental innovation. The next two decades produced spectacular results which identified new phenomena and entities such as radioactivity, the photoelectric effect, X-radiation, atomic line spectra, positive rays and isotopes.

The time was ripe for the emergence of a new paradigm, which for chemistry meant a new atomic theory to account for all the exciting new atomic properties. Such a theory was communicated to the Physico-Mathematical Society, Tokyo on Dec. 5th 1903 by the author, Hantaro Nagaoka, reported the next year in Nature [4] and communicated in full the same year [5].

The planet Saturn with its rings served as a model, which [4]

> ...will be approximately realized if we place negative electrons in the ring and a positive charge at the centre.
>
> ...at the centre of the circle is placed a large particle attracting the other particles forming the ring according to the same law of force.
>
> Such an ideal atom will not be contradictory to the results of recent experiments on kathode rays, radioactivity, and other allied phenomena.

The feasibility of this model was later confirmed by Rutherford's scattering experiments. Figure 3.2 demonstrates the scattering of a beam of α-particles on an atomic nucleus in a metal foil.

Nagaoka showed [5] how the model reproduces the spectral frequencies as summarized by the formulae of Balmer and Rydberg and added the following significant comments:

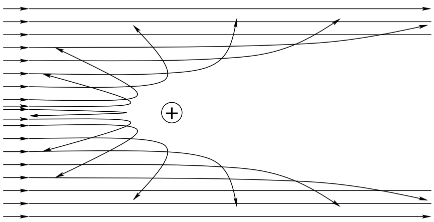


Fig. 3.2 Diagram to simulate Rutherford scattering on an atomic nucleus

> Here we notice that waves of frequency n travel around the ring in opposite senses, so long as the particles are not acted upon by extraneous forces. The frequency increases as h [integer $1, 2, 3, \ldots$] is increased, and the nature of the series shows that the spectral lines corresponding to these vibrations will gradually crowd together when h is large.
>
> If the spectra of the elements be due to the motion of electrons revolving in circular orbits, as above supposed, several rings of electrons must exist where there are different series of spectra, as in most elements.
>
> There are various problems which will possibly be capable of being attacked on the hypothesis of a Saturnian system, such as chemical affinity and valency, electrolysis and many other subjects connected with atoms and molecules. The rough calculation and rather unpolished exposition of various phenomena above sketched may serve as a hint to a more complete solution of atomic structure.

This could well be the first meaningful mention of the modern concept of *atomic structure*. As pointed out before [6]:

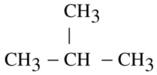
> The nuclear concentration of mass anticipated Rutherford's model of the atom, and Bohr's planetary model by a decade. The spectral integers, linked to a standing-wave pattern, predates de Broglie's proposal by two decades.

Apart from Rutherford's reference, Nagaoka's model has not received the recognition it deserves [6]. However, extension of the model by Bohr and Sommerfeld resulted in a new understanding of elemental periodicity and chemical affinity, preparing the ground for a revolutionary new paradigm.

3.2.1 *Static Model of Chemical Affinity*

Kekulé and his contemporaries derived all the empirical rules to account for the valence structure of most small organic molecules, which enabled the distinction between isomeric structures by their connectivities, according to structural formulae. A typical example occurs for the two compounds with the same formula of C_4H_{10}, known as butane and isobutane:

$CH_3-CH_2-CH_2-CH_3$ and



$$\begin{array}{c} \quad CH_3 \\ \quad | \\ CH_3-CH-CH_3 \end{array}$$

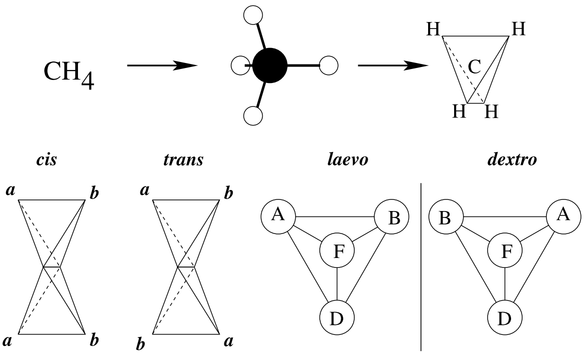
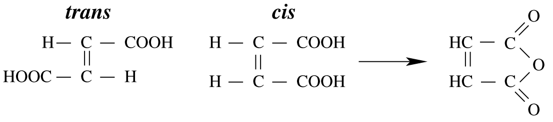


Fig. 3.3 The tetrahedral carbon atom according to van't Hoff

The question of geometrical and optical isomerism remained unresolved until 1874 when van't Hoff suggested an explanation based on an assumed tetrahedral structure for carbon in saturated compounds, such as methane, pictured in Fig. 3.3. The classical problem of the isomeric maleic and fumaric acids was solved by the postulate of restricted rotation around a double bond, which was formulated as the interaction that connects two tetrahedra joined at two corners (Fig. 3.3).



Fumaric acid **Maleic acid** **Maleic anhydride**

Only the *cis* form allows the easy formation of an anhydride.

Optically active molecules were proposed to contain at least one asymmetric carbon, having four different substituents at the tetrahedral corners, resulting in an arrangement which cannot be superimposed on its mirror image. It is emphasized that van't Hoff's proposals are precise diagnostics for stereoisomerism, without explaining the cause. Still, the scheme was successful enough to serve as a guideline towards understanding the nature of interatomic interaction.

Gilbert Lewis was the first to combine the ideas of Newlands, Stoney and van't Hoff into a single construct whereby most of the known chemical interactions could be rationalized. Discovery of the noble gases required modification of the law of octaves into a periodic arrangement of 8 elements each in the short periods Li–Ne and Na–Ar. This condition was interpreted by Lewis as defining a valence shell with the number of electrons increasing from 1 to 8 within these atomic series; *i.e.* Li and Na each with a single valence electron, and filled valence shells for Ne and Ar.

To account for Kekulé's valency rules and van't Hoff's stereochemistry the valence electrons were postulated to occupy corner sites of a cube that surrounds each atomic kernel. In order to include hydrogen into the scheme the first noble gas, He was assigned a valence shell, completely saturated by two electrons.

The success of the model relies on the assumption that the interaction between two atoms is driven by the tendency to acquire a filled valence shell of 8 or 2 electrons. This can be achieved either by the transfer of electrons from one atom to another, or by sharing a pair of electrons between the interacting atoms. As the electron carries unit negative charge the interaction between Na and Cl atoms is symbolically represented by

$$\mathrm{Na} + \mathrm{Cl} \rightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-}.$$

The structure of methane is rationalized in terms of shared electron pairs at alternate corners of the C cube, completion of an octet for carbon and a pair for each hydrogen atom. The van't Hoff double bond (Fig. 3.3) amounts to the sharing of two pairs of electrons between the carbon atoms of ethylene, $H_2C{=}CH_2$, as in the Kekulé double bond.

The Lewis mechanism, with minor embellishments, has remained the working model of practising chemists to this day. The most important additional assumption relates to the formation of bonding pairs that only happens between electrons with oppositely directed spin vectors.

The most familiar modification to the Lewis model was proposed by Irving Langmuir, lucidly summarized by Dushman [7] in [8, p. 1061], and more specifically aimed at an improved formulation of the periodic law. Starting from the Rydberg formula

$$N = 2\big(1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 +\big).$$

Langmuir is quoted [7] as stating:

> ...to determine the arrangement of electrons in atoms, we must be guided by the numbers of electrons which make up the atoms of the inert gases; in other words by the atomic numbers of these elements: 2, 10, 18, 36, 54 and 86

hence, assuming that the outer shells of krypton and xenon each contains 18 electrons while 32 are required to complete the outer shell of the radon atom. Following this scheme he arrived at closed sub-shells of 10, 10 and 24 for Ni, Pd and Pt. In line with the Lewis model the *kernel* consists of the nucleus and inner electrons, which do not play any rôle in chemical combination.

Formulated in terms of the total number of valence electrons, e, the number of octets n, and p, the number held in common by two octets, Langmuir's valence model amounts to the formula

$$p = \tfrac{1}{2}(8n - e).$$

As an example, the water molecule has $n = 1$ and with $e = 8(6 + 2 \times 1)$, $p = 0$. For carbon dioxide, $p = (24 - 16)/2 = 4$, *i.e.* O=C=O.

The formula works for all carbon compounds and proves to be more reliable than the simple octet rule for compounds of oxygen and nitrogen. In the words of Langmuir:

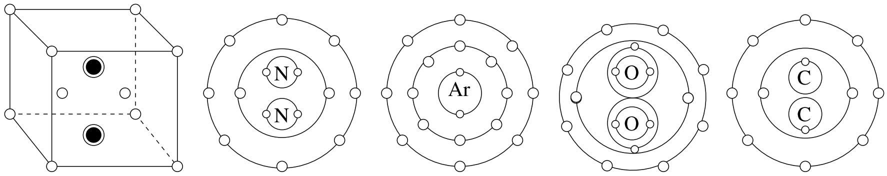


Fig. 3.4 Langmuir's model of the N_2 molecule, compared to the Ar atom, O_2 and C_2 in the same style

> If we apply the octet theory to the nitrogen molecule, by placing $n = 2$, $e = 10$, we find $p = 3$. We are thus led to the formula :N≡N: for the nitrogen molecule. Now, in acetylene we have an illustration of two atoms holding three pairs of electrons in common. Such a substance is endothermic, forms additional products easily, and even by itself is relatively unstable. A structure of this kind could not possibly account for the properties of nitrogen.

Langmuir pointed out that in most of its properties elementary nitrogen resembles argon, which is fair comment. Its freezing point lies between those of argon and oxygen, while its boiling point lies below those of either of these gases.

As an alternative it is suggested that $p = (8 - 10)/2 = -1$, interpreted as an electron pair inside the octet.

This description is directly in line with Avogadro's original conception of gaseous molecules as spherical objects of the same type as an atom. This view likens the pair of nitrogen kernels to an atomic nucleus surrounded by shells of 2, 8, 8, *etc.*, electrons, as shown in Fig. 3.4 for Ar. As remarked by Langmuir [7]:

> This structure of the nitrogen molecule explains in a perfectly satisfactory way all the remarkable properties of elementary nitrogen... The high heat of formation of nitrogen molecules from the atoms accounts for the great number of endothermic and explosive nitrogen compounds. It is also evident why elementary nitrogen is so unusually inert, while in its compounds it is one of the most active of the elements.

Other molecules with similar structures were identified as CO, NO and the CN radical. The whole series of nitrogen oxides, from N_2O to N_2O_5, are shown to obey the standard valence rule.

The previously highlighted [6, p. 70] anomalous properties of the diatomic N_2, O_2 and H_2 molecules, such as relative size, as predicted by conventional theory, are readily understood in terms of Langmuir's model. Modification of the two carbon and oxygen kernels to facilitate the formation of an inner molecular shell of 2 electrons, is shown in Fig. 3.4 to generate biradicals, in line with the observed paramagnetism of O_2, probably not appreciated in Langmuir's time, before the discovery of electron spin. Such detail and the final structure of the classical periodic table only became apparent as the refined form of the Bohr–Sommerfeld atomic model became generally known.

3.2.2 The Planetary Quantum Model

When Nagaoka proposed his Saturnian model of the atom in the very early days of the quantum era he simulated discrete atomic and molecular spectra in terms of the integers that characterize harmonic motion. In effect, he described the orbiting electrons as standing waves.

A year before Max Planck had derived the equation that describes the equilibrium radiation density in a closed cavity at constant temperature, by the assumption that the energy carried by monochromatic light is quantized in units proportional to the frequency of radiation, *i.e.*

$$E = nh\nu.$$

The universal constant h has the dimensions of *action*, the same as angular momentum.

The Bohr Model

Planck's proposition was used by Niels Bohr to develop a mathematically precise, but physically dubious, theory of atomic structure, consistent with the experimentally known details of the spectrum of atomic hydrogen. The theory assumed the absorption and emission of radiation by atomic matter to only occur if the frequency matches the difference between allowed atomic energy levels of the form

$$h\nu_{nm} = E_m - E_n$$

for integer n and m. The allowed energy levels were assumed to correspond to allowed orbits of an electron around a stationary atomic nucleus, such as a *proton*, in the case of the hydrogen atom. A radiationless stationary orbit was assumed to occur where the coulombic attraction between proton and electron provides the centripetal acceleration of the electron of mass m to maintain an orbit at a distance r from the nucleus. In electrostatic units, it means that

$$\frac{e^2}{r^2} = \frac{mv^2}{r} = \frac{p^2}{mr}.$$

In terms of the total energy

$$E = T + V = \frac{e^2}{2r} - \frac{e^2}{r} = -\frac{e^2}{2r},$$

and orbital radius

$$r = \frac{(pr)^2}{me^2}, \qquad E = -\frac{me^4}{2(pr)^2}.$$

The quantum condition, consistent with a least-action principle specified the electronic angular momentum, $L = pr = nh/2\pi$, as an integral multiple of the unit of action $\hbar = h/2\pi$, such that

$$E = -\frac{2\pi^2 me^4}{n^2h^2}.$$

The stated frequency condition then implies a Balmer-type formula,

$$h\nu = \Delta E_{nm} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{m^2} - \frac{1}{n^2}\right).$$

The predicted Rydberg constant, $R = 2\pi^2 me^4/h^3c$, corresponds well with the spectroscopic value.

The angular-momentum postulate was substantiated in 1921 by Stern and Gerlach who confirmed the magnetic moment predicted by $L = \hbar$ for Ag atoms. The discovery of electron spin, which implied $L = 0$ for H, changed all that.

This observation highlights the major problem with the Bohr atom. It predicts an orbital frequency, of $\omega = e^2/nha_0$ for an electronic particle of mass m without measurable orbital angular momentum.

As pointed out before [6] the Bohr model could be salvaged by a simple modification of the proposition $L = n\hbar$ to read $L = n(n-1)\hbar$, but the *ad hoc* assumption of a non-radiating accelerated charge remains unresolved. A solution to this problem was in fact proposed by Louis de Broglie who proposed a description of the orbiting electron as a standing wave of wavelength $\lambda = 2\pi r/n = h/p$, to account for Bohr's action conjecture of $pr = n\hbar$, without angular momentum. It is totally feasible to reproduce all results obtained by solution of Schrödinger's equation from the Bohr model, considering the electron as a spherical harmonic fluid that surrounds the nucleus. However, this was not the historical route, which saw the Bohr model, generalized by Sommerfeld with the introduction of elliptic orbits and additional quantum numbers to address the angular momentum problem and to fit the periodic table of the elements, without giving up the particle description of an electron.

The Sommerfeld Model

In the same way that planetary orbits could be shown to be a special case of the more general elliptic Kepler orbits, it was demonstrated by Sommerfeld that the Bohr model could be successfully generalized by the introduction of elliptic electron orbits. The secret was to use the more powerful methods of Hamiltonian mechanics which allowed the quantum conditions to be restated in terms of action variables. This was Sommerfeld's "royal road to quantization". The proper procedure was, first to describe electronic motion in terms of continuous classical action variables, followed by quantization, on equating the classical action to an integral multiple of h, the quantum of action. Action is defined in general as the product of canonical variables, such as $p_j\dot{g}_j$, and the action variable for a periodic system takes the form $J = \oint pdq$. It always has the dimensions of an angular momentum.

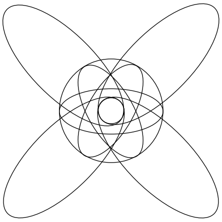


Fig. 3.5 The Ne atom with two electrons on circular orbits at an inner level, and eight electrons on four circular and four elliptic orbits in the valence shell

As an example of royal quantization it is shown [9] that modification of the Hamiltonian for a Kepler orbit,

$$H = -\frac{2\pi^2 mk^2}{J^2}$$

by substituting $k = Ze^2$ and $J = nh$, yields the quantized energy levels for a hydrogenic atom,

$$E = -\frac{2\pi^2 mZe^4}{n^2h^2}.$$

The major improvement effected by Sommerfeld lies in the introduction of two additional quantum numbers to describe the eccentricity and spatial orientation of elliptic orbits. As remarked by Sommerfeld [10]:

> (This) space quantization of the Kepler orbits is without doubt the most surprising result of the quantum theory. The simplicity of the results and their derivation is almost like magic.

The real meaning of the innovation is even more profound. Addition of the azimuthal quantum number transformed the two-dimensional Bohr model into a more realistic three-dimensional description. The two-dimensional action of the Bohr model restricts the orbital angular momentum to a single fixed direction ($L = n\hbar$) whereas the azimuthal variability introduced three-dimensional action, which correctly describes the electronic configuration of non-hydrogen atoms, in line with the structure of the periodic table.

A signal success of the system was the specification of the electronic orbits of the Ne atom, shown in Fig. 3.5 [10]. It shows a valence shell of 4 circular and 4 elliptic orbits, surrounding a first shell of two electrons on circular orbits. For the carbon atom, with four valence electrons, these were argued to occupy four degenerate elliptic orbits directed towards the corners of a tetrahedron, which ensured the quenching of the total orbital angular momentum.

The predicted tetrahedral structure for CH_4, based on this arrangement was in complete agreement with the Lewis and van't Hoff models and perfectly in line with the theory of covalent bonding. It has been remarked that [6]:

> Theoretical chemistry reached its pinnacle during the Sommerfeld era, before the advent of wave mechanics. The theoretically superior new theory,

Table 3.1 The final periodic table obtained by the synthesis of proposals from Bohr, Langmuir, Sommerfeld and Bury

Shell → Period	K	L	M	N	O	P
1	H–He					
2	2	Li–Ne				
3	2	8	Na–Ar			
4	2	8	8 + (K–Ni)	Cu–Kr		
5	2	8	18	8 + (Rb–Pd)	Ag–Xe	
6	2	8	18	18 + (Ce–Lu)	8 + (Cs–Pt)	Au–Rn

> although it eliminated the paradoxes of zero angular momentum of the hydrogen ground-state, the orbital motion in helium and the nature of the stationary states, it defined the periodic table less well and confused the simple picture of chemical bonding.

This development is discussed in the next chapter.

3.2.3 *The New Periodic Table*

By 1920 the necessary data to finalize the structure of the periodic table were in. Atomic spectra were understood in sufficient detail, the importance of atomic numbers well established and the Sommerfeld atomic model provided the theoretical framework for the final synthesis. The ultimate periodic table reflects the Rydberg formula for the atomic numbers of the noble gases. These were interpreted by Bury with the stipulation that the number of electrons in an outer shell never exceeds 8. The layout of the table over 6 shells, K–P, and 6 periods, 1–6, is shown in Table 3.1.

It closely reflects the Aufbau principle that assumes the addition of electrons in the sequence of increasing atomic numbers. It deviates from the sequence in period 6 where the elements Cs, Ba and La precede the element Ce by atomic number. In terms of spectroscopic notation the groups of ten elements in parentheses are more appropriately described as 2 + 8, *e.g.* K–Ca, Sc–Ni.

Most features of this table can be rationalized in terms of the spectroscopically assigned electronic configuration of the atoms. The major anomaly relates to a theoretical understanding of the 8-membered transition series that terminate at the elements Ni, Pd and Pt, and the relationship between the alkali and coinage groups.

It is important to note that the theoretical simulation of the periodic table in terms of the Sommerfeld model, augmented by spectroscopic analysis and assumption of a spin quantum number, $m_s = \pm\frac{1}{2}$, has never been improved upon. In this sense Sommerfeld's atomic theory is recognized as the best possible quantum description of atomic structure in terms of a particle model of the electron. The alternative wave-mechanical description of the same system, suggested as feasible by Hamilton–Jacobi theory (Sect. 2.4.2), was eventually achieved by Schrödinger.

An unbiased comparison should confirm the mathematical equivalence of the two models. It does not mean that the two formulations are equally appropriate as atomic models, as this decision would depend on different criteria of a physical nature. It must depend on whether an electron is a particle or a wave.

3.3 The Electromagnetic Field

The formulation of Newtonian mechanics and the identification of a gravitational field left three fundamental concepts unexplained. These are the propagation of light, of electricity and the nature of magnetism. Next to the development of the periodic law, the demonstration that these, apparently disparate, phenomena could be accounted for by a unified field, must rate as the other, equally important, achievement of 19th century science.

3.3.1 Wave Theory of Light

The idea that light propagates as a vibrating wave motion, which started to gain support at the time of Newton, was supported by Robert Hooke and others. It became established as a viable alternative to the more popular corpuscular theory once it had been demonstrated by Christiaan Huygens how to interpret the phenomena of reflection and refraction in terms of a propagating wavefront. The Huygens construction existed therein that each point in a wavefront acted as a source of secondary wavelets, that together constitute the wavefront.

While particle mechanics flourished wave theory remained dormant until the time of Thomas Young, who first rationalized the phenomenon of interference, assuming light to be transverse wave motion that creates a Huygens wavefront as shown schematically in Fig. 3.6.

Should this wavefront be collimated by a narrow slit, a new spherical wavefront develops around the slit. In Young's double-slit experiment this spreading wavefront was passed through two identical slits in a second screen and eventually allowed to fall on a third screen where an *interference pattern*, consisting of a set of bright lines, separated by dark spaces, is observed. The curve in Fig. 3.6 represents the decreasing intensity of the bright lines in the pattern, whose spacing depends on the wavelength of the monochromatic waves. This famous experiment has remained textbook material to this day, even to "explain" the wave-like behaviour of electronic particles.

Exploiting the same ideas the French physicist Fresnel demonstrated and explained diffraction phenomena and the optical properties of crystals. A memorable event in the development of the wave theory was Fresnel's award winning explanation of diffraction, which is succinctly summarized by Anton Amann in [11]:

> [In] the year 1818... Augustin Fresnel presented his memoir on diffraction for the prize of the French Academy. ...Poisson, Biot and Laplace were on the committee to judge the paper, and all three were declared supporters of the corpuscular theory of light. Fresnel had calculated various cases of his

Fig. 3.6 Schematic drawing of a moving Huygens plane-wavefront of coherent transverse wavelets, shown to generate an interference pattern in Young's double-slit experiment

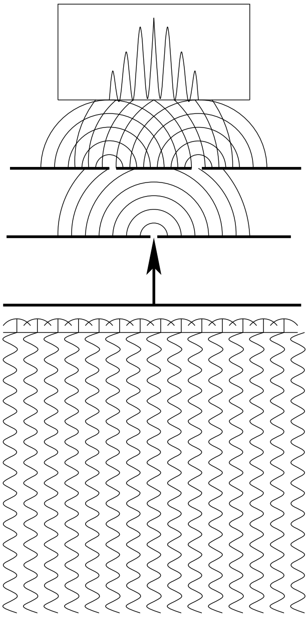
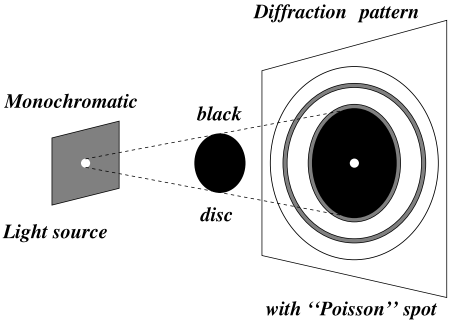


Fig. 3.7 Interference pattern of a monochromatic light source diffracted at a black disc



> formula and compared them with experiment. But Poisson noticed that one could calculate the integral for the circular disc, and came to the conclusion that there is a white spot in the centre of the shadow of a circular disc. He raised this as an objection to the whole theory, since it was patently ridiculous. However, Arago and Fresnel went and performed the experiment, and, sure enough the spot was there, whereupon Fresnel was awarded the prize.

Details of the experiment are shown in Fig. 3.7.

Amann proceeds to comment [12]:

> What we can learn from this story is, that "strange" aspects of a theory should periodically be checked again. Curious results should not be overlooked and ignored, but kept in mind for later and better understanding. Quantum theory is in some respects a strange theory in the above sense…

Some very strange quantum effects will be highlighted later on.

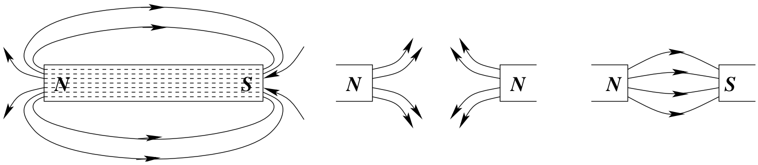


Fig. 3.8 Lines of force mapping the magnetic field of a bar magnet, the region between two north poles and between a pair of unlike poles

No other explanation of diffraction, other than the interference of waves, has ever been presented. Not only is the wave nature of light firmly established by this argument, but the observation of diffraction effects associated with electrons, neutrons and protons must be interpreted to demonstrate the wave nature of these objects. A successful theory of matter should reflect this property, which is clearly at variance with the general notion of elementary particles.

3.3.2 Magnetism

Although magnetic materials such as magnetite (loadstone) and their navigational use as compasses were known in the earliest antiquity, the phenomenon of magnetism remained poorly understood until the late 19th century. The speculations of William Gilbert in the 16th century linked this property to the proposal that the earth was a huge magnet with a pair of north and south poles like a small bar magnet. The first scientific results of practical value was obtained by Charles-Augustin Coulomb. With the use of a torsional balance he established that the attraction between unlike poles, as also the repulsion between a pair of equivalent poles, is inversely proportional to the square of the distance between the poles. He is also credited with the discovery of the same law of interaction between electric charges. This law, formulated as the force,

$$F = k\frac{m_1 m_2}{r^2},$$

for pole strengths, or charge magnitudes, of m_1 and m_2, defined in terms of the proportionality constant k, is of the same form as Newton's law of gravitational attraction.

Magnetic interaction is effectively visualized by covering a bar magnet with a sheet of paper and sprinkled with iron filings. By gently tapping the paper the filings arrange themselves along the *lines of magnetic force*, as shown in Fig. 3.8. The arrows indicate the direction in which an isolated north pole would move when placed in the *field*, defined by the lines of force. This concept of a field has proved invaluable in the mathematical analysis of electromagnetic interactions. The idea of a field of force was introduced and used to good effect by Faraday, and its use has now spread through all science.

3.3.3 Electrostatics

The term electricity derives from the Greek word $\eta\lambda\epsilon\kappa\tau\rho o\nu$ that means amber, which is a resinous substance that becomes electrified when rubbed with rabbit fur. However, like magnetism, electricity remained a curiosity until it was subjected to systematic study by Coulomb, Faraday, Ampére and Maxwell. As is the case for magnetism, the interaction between electrified objects is conveniently described as the force between positive and negative charges, giving rise to an electric field. The major difference is that positive and negative electricity may readily be separated mechanically.

Mathematical manipulation resulted in the definition of the concepts *electric field strength* and electric *potential*. The electric field at a point is defined as the force acting on a test charge at that point divided by the magnitude of the test charge. Hence the vector

$$\boldsymbol{E} = \frac{kq}{r^2}.$$

As in the gravitational field a difference in potential between two points is defined as the mechanical work required to take a test charge from one point to the other, divided by the magnitude of the test charge. The potential at a point may therefore be thought of as the potential energy of a unit charge at the point. As in the case of mechanical potential energy, electric potential is determined only to within an additive constant. This constant is arbitrary and depends on the particular choice of a zero of potential.

The work required for an infinitesimal displacement dl of a unit charge defines an infinitesimal increase in potential

$$dV = -\boldsymbol{E}.dl = -\frac{kq}{r_2}dr.$$

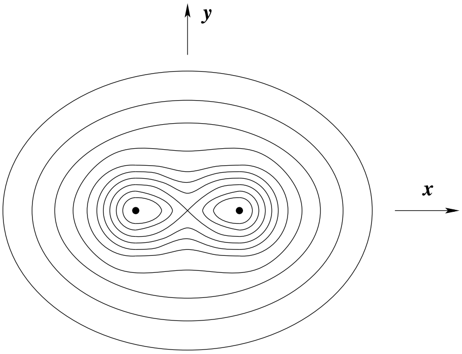
The potential difference between two points A and B,

$$V_B - V_A = -kq\int_A^B \frac{dr}{r^2} = kq\left(\frac{1}{b} - \frac{1}{a}\right).$$

It follows that the difference in potential between two points only depends on the positions of the points and not on the path between them. The work required to move a charge between two points at different potentials is known as the *electromotive force*, emf. In order to determine the additive constant it is assumed that the potential zero occurs at an infinite distance from any point of interest. This means that for $1/a = 0$ the potential V is given by the work per unit charge required to bring a test charge from infinity to $b = r$, *i.e.*

$$V = \frac{kq}{r}.$$

Fig. 3.9 Equipotentials in the plane of two positive charges



A small change in potential may be defined in terms of Cartesian displacements as

$$dV = \frac{\partial V}{\partial x}dx + \frac{\partial V}{\partial y}dy + \frac{\partial V}{\partial z}dz = \boldsymbol{grad}\, V \cdot \boldsymbol{dl}$$

which function is written in vector notation as ***grad*** V, and read, the gradient of V. The electric field strength is therefore conveniently defined as

$$\boldsymbol{E} = -\boldsymbol{grad}\, V. \tag{3.1}$$

Contour lines that represent equipotentials intersect the lines of force at right angles. Equipotentials in the field of two equivalent positive charges of q, distance d apart, calculated as [13]

$$V = kq\left(\frac{1}{\sqrt{(x-d)^2+y^2+z^2}} + \frac{1}{\sqrt{(x+d)^2+y^2+z^2}}\right)$$

are shown in Fig. 3.9.

This diagram could easily be mistaken for the electronic charge distribution obtained by a complicated quantum-chemical computation for the H_2^+ molecule [14]. The electrostatic equilibrium distribution of a uniform electric fluid of unit negative charge in the field of two positive point charges of unity should therefore describe the structure of this one-electron covalent interaction rather well. A point-charge model that simulates electrostatic interaction between positive atomic kernels and a pair of electrons has in fact been known for a long time [15] to predict the correct dissociation energy of diatomic molecules.

Electrostatic induction, which causes displacement of charges within a conductor, is illustrated in Fig. 3.10 with an *electrophorus* by lowering a metal disc held on an insulating handle on to a positively charged slab S. By inductive action across the intervening space positive electricity is displaced to the upper surface of A from where it can be discharged to earth. On raising the disc it carries the induced negative charge, leaving S positively charged.

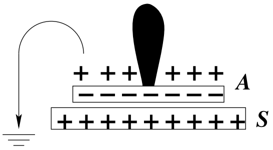
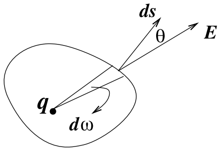


Fig. 3.10 An electrophorus

The Law of Gauss

By the same mechanism a charge within a closed surface will be displaced into the surface and from the field intensity at all points in the surface it is possible to calculate the magnitude of the enclosed charge. For each infinitesimal area ds in the surface, the vector $\boldsymbol{ds}$, perpendicular to the surface, describes the displacement of charge into the surface as $E\cos\theta ds = \boldsymbol{E}\cdot\boldsymbol{ds}$, where θ is the angle between $\boldsymbol{E}$ and the outward normal to the surface at ds.



By the inverse-square law $\boldsymbol{E} = kq/r^2$ and the sum over the closed surface

$$\oint \boldsymbol{E}\cdot\boldsymbol{ds} = qk\oint\frac{\boldsymbol{ds}}{r^2} = qk\oint d\omega.$$

The solid angle subtended at ds is given by $d\omega = ds\cdot r^{-2}$ and hence

$$\oint \boldsymbol{E}\cdot\boldsymbol{ds} = 4\pi qk = q/\varepsilon_0.$$

In the International (SI) System of units the constant k is defined as $k = 1/4\pi\varepsilon_0$, where ε_0 is known as the permittivity of free space.

In vector notation the divergence of a vector defined as

$$\nabla\cdot\boldsymbol{v} = \operatorname{div}\boldsymbol{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

describes the outward flow through a volume element $dv = dxdydz$. The integral of the flow throughout the volume must be the same as the flow through the external bounding surface, *i.e.*

$$\int_v \operatorname{div}\boldsymbol{v}\,dv = \oint_s \boldsymbol{v}\cdot\boldsymbol{ds}\,.$$

For any fluid in a region of space where there is neither a source nor a sink, the total mass flow out of a region must balance the rate of decrease of the total mass in the volume. This balance means that

$$\int_v \nabla \cdot (\rho \boldsymbol{v}) = -\frac{\partial}{\partial t}\int_s (\rho \boldsymbol{v}) ds = -\frac{\partial}{\partial t}\int_v \rho dv,$$

which leads to the continuity condition

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho \boldsymbol{v}) = 0. \tag{3.2}$$

For an electric charge density ρ the quantity $\rho \boldsymbol{v} = \boldsymbol{J}$ defines a current density. Since

$$\oint_s \boldsymbol{E} \cdot \boldsymbol{ds} = \frac{1}{\varepsilon_0}\int_v \rho dv$$

where ρ is the charge density throughout the enclosed region,

$$\mathrm{div}\, \boldsymbol{E} = \rho/\varepsilon_0, \tag{3.3}$$

also written as $\nabla \boldsymbol{D} = \rho$, where $\boldsymbol{D} = \varepsilon_0 \boldsymbol{E}$ is the displacement.

If $\boldsymbol{E}$ is eliminated between (3.1) and (3.3) the resulting equation is $\mathrm{div}\, \boldsymbol{grad}\, V = \nabla^2 V = \rho/\varepsilon_0$, where the operator ∇^2 is called the *Laplacian*.

$$\nabla \cdot \nabla \cdot V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial x^2} = \nabla^2 V = \frac{\rho}{\varepsilon_0}. \tag{3.4}$$

Equation (3.4) is known as *Poisson's equation*. In a charge-free region it reduces to *Laplace's equation*:

$$\nabla^2 V = 0.$$

3.3.4 Electromagnetism

Electromagnetic theory originated in the observations of Ørsted, Ampére and Faraday that electric currents have magnetic effects and from this it developed into the mathematical formalism that describes the interrelationships between electric and magnetic fields. The conclusion that electric lines of force stretch from a positive to a negative charge, compared to the closed lines of magnetic force, served as the guiding principle in the construction of a mathematical model. This is consistent with the observation that an isolated magnetic pole has no independent existence. In electromagnetic theory a magnetic field is always ascribed to circulating electric currents. The complete theory must therefore recognize the dynamic effect known as electromagnetic induction, in addition to the more common electrostatic induction. In the same way that electric displacement is related to the field, a magnetic field in the vacuum is defined by $\mu_0 \boldsymbol{H} = \boldsymbol{B}$, with μ_0 the permeability of free space.

Faraday's Law

Faraday's law of electromagnetic induction describes how magnetic fields induce electric effects. If the magnetic field in a region of space occupied by a conducting loop is changed in any manner, *e.g.* by changing the current in neighbouring circuits or by moving the latter when they carry steady currents or by moving a permanent magnet near the loop, an *emf* is induced in the stationary circuit. By Faraday's law: *the induced emf is equal to the time rate of change of the magnetic flux that crosses any area within the loop.*

A simple formulation of the law relates the partial derivatives of the electric field to the time derivative components of the magnetic field. The three equations:

$$\begin{aligned}\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} &= -\frac{\partial B_x}{\partial t},\\ \frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} &= -\frac{\partial B_y}{\partial t},\\ \frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} &= -\frac{\partial B_z}{\partial t}\end{aligned} \tag{3.5}$$

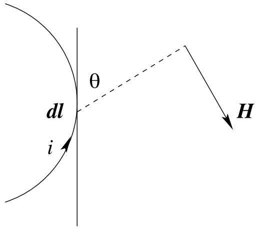
are expressed together in vector notation as

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \quad \text{or as} \quad \boldsymbol{curl}\,\boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}.$$

The vector formulation used in this discussion is largely based on Harnwell's treatise [13].

Ampére's Law

The relationship between an electric current and its magnetic effect is described most directly by Ampére's law. The law predicts the magnetic field induced by an electric current. This is the inverse of Faraday's law that accounts for the electric field induced by a circulating current. Ampére's analysis led to the result



$$\oint \boldsymbol{H} \cdot \boldsymbol{dl} = \int_s \boldsymbol{i_v} \cdot \boldsymbol{ds}$$

for current density $\boldsymbol{i_v}$. By Stokes's theorem

$$\oint \boldsymbol{H} \cdot \boldsymbol{dl} = \int_s \boldsymbol{curl\,H} \cdot \boldsymbol{ds} = \int_s \boldsymbol{i_v} \cdot \boldsymbol{ds}\,.$$

As this equation holds at every point the last two integrands may be equated, to give

$$\boldsymbol{curl\,H} = \boldsymbol{i_v} = \boldsymbol{J}\,.$$

This is Ampére's law.

Alternatively, the total induction due to the motion of a closed current-carrying circuit is

$$\boldsymbol{B} = \frac{\mu_0}{4\pi} i \oint \frac{\boldsymbol{r}_1 \times \boldsymbol{dl}}{r^2}$$

where the vector product $\boldsymbol{r}_1 \times \boldsymbol{dl} = \boldsymbol{r}_1 dl \sin\theta$ is perpendicular to both the unit vector $\boldsymbol{r}_1$ and $\boldsymbol{dl}$. The proportionality constant is fixed to $\mu_0/4\pi$ in SI units. It is readily shown by direct partial differentiation that

$$\begin{aligned} &\boldsymbol{grad}\left(\frac{1}{r}\right) = \frac{\boldsymbol{r}_1}{r^2}, \quad \text{and hence} \\ &\boldsymbol{B} = \frac{\mu_0}{4\pi} i \oint \boldsymbol{grad}\left(\frac{1}{r}\right) \times \boldsymbol{dl}\,. \end{aligned} \tag{3.6}$$

By an expansion such as (3.5) it can be shown [13] that

$$\boldsymbol{curl}\, u\boldsymbol{A} = u\,\boldsymbol{curl\,A} - \boldsymbol{A} \times \boldsymbol{grad}\, u$$

which identity simplifies the integrand of (3.6) into:

$$\boldsymbol{grad}\left(\frac{1}{r}\right) \times \boldsymbol{dl} = \boldsymbol{curl}\left(\frac{\boldsymbol{dl}}{r}\right) - \frac{1}{r}\boldsymbol{curl\,dl}\,.$$

As $\boldsymbol{dl}$ is independent of the coordinates of the point at which $\boldsymbol{B}$ is measured, this last term is zero; hence

$$\boldsymbol{B} = \frac{\mu_0}{4\pi} i \oint \boldsymbol{curl}\left(\frac{\boldsymbol{dl}}{r}\right) = \boldsymbol{curl\,A}$$

where

$$\boldsymbol{A} = \frac{\mu_0}{4\pi} i \oint \frac{\boldsymbol{dl}}{r}$$

is known as the vector potential. It plays a similar role for steady currents as the scalar potential V does in electrostatics. From another vector identity [13]: $\mathrm{div}\,\boldsymbol{curl\,v} = 0$, it follows that the divergence of magnetic induction

$$\mathrm{div}\,\boldsymbol{B} = 0. \tag{3.7}$$

3.3.5 *Maxwell's Theory*

The experimental data produced by Faraday's dexterity, restated in Maxwell's mathematical wizardry, culminated in the formulation of a single field theory that unifies the phenomena of magnetism, electricity and light. A vital factor was added by Maxwell's realization that Ampére's law was not consistent with the continuity (3.2), that requires div $\boldsymbol{J} = \partial\rho/\partial t$. By Ampére's law div $\boldsymbol{curl}\,\boldsymbol{H} =$ div $\boldsymbol{J}$ is identically zero in those situations where the charge density is constant in time. To be consistent with the continuity condition Ampére's equation was adjusted by Maxwell to read

$$\boldsymbol{curl}\,\boldsymbol{H} = \boldsymbol{J} + \frac{\partial \boldsymbol{D}}{\partial t}$$

where $\partial \boldsymbol{D}/\partial t$ is the famous displacement current.

To construct his electromagnetic theory Maxwell started from the following four fundamental equations:

$$\begin{aligned}
&\nabla \times \boldsymbol{E} + \frac{\partial \boldsymbol{B}}{\partial t} = 0, \quad \text{(Faraday–Lenz law)}\\
&\nabla \times \boldsymbol{H} = \boldsymbol{J} + \frac{\partial \boldsymbol{D}}{\partial t}, \quad \text{(Ampére–Maxwell)}\\
&\nabla \cdot \boldsymbol{B} = 0,\\
&\nabla \cdot \boldsymbol{D} = 0.
\end{aligned}$$

In the absence of charge and matter, $\boldsymbol{D} = \varepsilon \boldsymbol{E}_0$, $\boldsymbol{H} = \boldsymbol{B}/\mu_0$ and Maxwell's equations in free space become:

$$\nabla \times \boldsymbol{E} = \mu_0 \frac{\partial \boldsymbol{H}}{\partial t}, \tag{3.8}$$

$$\nabla \times \boldsymbol{H} = \varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t}, \tag{3.9}$$

$$\nabla \cdot \boldsymbol{B} = 0, \tag{3.10}$$

$$\nabla \cdot \boldsymbol{E} = 0. \tag{3.11}$$

From (3.8)

$$\begin{aligned}
\boldsymbol{curl}\,\boldsymbol{curl}\,\boldsymbol{E} &= -\mu_0 \frac{\partial}{\partial t}(\boldsymbol{curl}\,\boldsymbol{H})\\
&= -\varepsilon_0\mu_0 \frac{\partial}{\partial t}\left(\frac{\partial \boldsymbol{E}}{\partial t}\right).
\end{aligned}$$

Using the identity $\boldsymbol{curl}\,\boldsymbol{curl}\,\boldsymbol{E} = \boldsymbol{grad}\,\text{div}\,\boldsymbol{E} - \nabla^2\boldsymbol{E}$ with (3.11) it follows that

$$\nabla^2 \boldsymbol{E} = \varepsilon_0\mu_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2}.$$

Similarly, by taking the ***curl*** of (3.9) it follows that

$$\nabla^2 \boldsymbol{H} = \varepsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{H}}{\partial t^2}.$$

The product $\varepsilon_0 \mu_0$ has the dimensions of (second/metre)^2, the reciprocal of a squared velocity. If this velocity is denoted by c, its value is predicted by the theory as $c = 3 \times 10^8\ \mathrm{ms}^{-1}$. This value may immediately be recognized as the velocity of light in the vacuum. This observation strongly suggests that light is a form of electromagnetic radiation, as the two equations

$$\nabla^2 (\boldsymbol{E}, \boldsymbol{H}) = \frac{1}{c^2} \frac{\partial^2 (\boldsymbol{E}, \boldsymbol{H})}{\partial t^2}$$

are differential equations characteristic of wave motion.

3.4 Electromagnetic Radiation

To understand how electromagnetic radiation transports energy through space it is assumed that an electric or magnetic field stores potential energy to an amount that depends on the product of the field intensity and the induction at a point, *i.e.*:

$$u = \tfrac{1}{2} \boldsymbol{E}\boldsymbol{D} = \tfrac{1}{2} \varepsilon_0 E^2 \quad \text{or} \quad u = \tfrac{1}{2} \boldsymbol{H}\boldsymbol{B} = \tfrac{1}{2} \mu_0 H^2. \tag{3.12}$$

The factor $\frac{1}{2}$ arises from the balance at a point between negative and positive displacements, $D_+ - D_- = 0$, $D_+ + D_- = \varepsilon_0 E$, $\boldsymbol{D} = \varepsilon_0 \boldsymbol{E}/2$.

Without loss of generality the electromagnetic disturbance may be considered in the form of an infinite plane wave in which the vector $\boldsymbol{E}$ or $\boldsymbol{H}$ depends only on one coordinate. If z is chosen as this coordinate all partial derivatives with respect to x and y vanish. Thus $\operatorname{div} \boldsymbol{E}$ becomes $\partial E_z / \partial z = 0$, hence the electric field has no varying component along this axis. As this is the direction of propagation of the wave, (3.10) and (3.11) show that the wave is of the transverse type where the electric and magnetic vectors lie in the plane of the wave front. There will in general be both an x and a y-component of the field, *e.g.*

$$\frac{\partial^2 E_x}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 E_x}{\partial t^2}, \qquad \frac{\partial^2 E_y}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 E_y}{\partial t^2}.$$

These components are independent of each other and only one component need to be considered, and as the partial derivative with respect to y, say, is zero, it follows from the definition of ***curl*** that

$$-\frac{\partial H_y}{\partial z} = \varepsilon_0 \frac{\partial E_x}{\partial t}.$$

This equation shows that the magnetic vector of the wave is at right angles to the electric one.

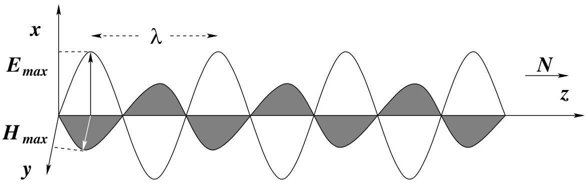


Fig. 3.11 A plane electromagnetic wave, showing electric and magnetic vectors at right angles

A wave such as that shown in Fig. 3.11, in which the electric vector (and hence the magnetic vector as well) is always parallel to one direction, is called a plane polarized wave. The plane in which the electric vector and the direction of propagation lie is called the plane of polarization.

Electromagnetic waves are usually detected through the absorption of the energy carried by them. This quantity may be calculated by forming the products

$$\begin{aligned}\boldsymbol{H}\cdot\boldsymbol{curl}\,\boldsymbol{E}-\boldsymbol{E}\cdot\boldsymbol{curl}\,\boldsymbol{H}&=-\left(\boldsymbol{H}\frac{\partial\boldsymbol{B}}{\partial t}+\boldsymbol{E}\frac{\partial\boldsymbol{D}}{\partial t}\right)\\&=-\frac{\partial}{\partial t}\left(\frac{\mu_0}{2}H^2+\frac{\varepsilon_0}{2}E^2\right).\end{aligned}$$

From (3.12) the right hand side is recognized as the rate of decrease of total electric and magnetic energy density. By the vector identity

$$\boldsymbol{H}\cdot\boldsymbol{curl}\,\boldsymbol{E}-\boldsymbol{E}\cdot\boldsymbol{curl}\,\boldsymbol{H}=\mathrm{div}(\boldsymbol{E}\times\boldsymbol{H})$$

this is equal to the divergence of the vector product of $\boldsymbol{E}$ and $\boldsymbol{H}$. By the theorem of Gauss the integral of this quantity throughout any volume is equal to the integral of the normal component of $\boldsymbol{E}\times\boldsymbol{H}$ over the bounding surface. The obvious interpretation is that the decrease of energy within the volume is accounted for by an outward flow of energy through the bounding surface, equal to the integral of $\boldsymbol{E}\times\boldsymbol{H}$ over this surface. The vector that represents this energy flow is known as Poynting's vector, $\boldsymbol{N}$. Since $\boldsymbol{N}$ is the vector product of two vectors in the xy-plane it must be directed in the z-direction, *i.e.* normal to the wave front and in the direction of motion. Absorption of this energy from short waves produces ionization, affects a photographic plate, or produces the sensation of sight. When an electromagnetic wave is incident on a conducting or absorbing surface the theory predicts that it should exert a force on the surface in the direction of $\boldsymbol{N}$.

3.4.1 General Theory of Wave Motion

Electromagnetic wave motion is governed by differential equations similar to those that apply to other forms of wave motion in Nature:

$$v^2\nabla^2\Phi-\frac{\partial^2\Phi}{\partial t^2}=0. \tag{3.13}$$

Rather than assume a specific solution it is important to examine the features that determine the most general solution. It has been shown [16] that the equation can be solved by the introduction of a single dependent variable

$$\xi = \alpha x + \beta y + \gamma z + vt$$

α, β, γ being constants, provided ∇^2 is written in Cartesian form. On substituting this into (3.13)

$$\left[v^2\left(\alpha^2 + \beta^2 + \gamma^2\right) - v^2\right]\frac{\partial^2 \Phi}{\partial \xi^2} = 0$$

which is clearly satisfied if $\alpha^2 + \beta^2 + \gamma^2 = 1$.

Subject to this condition, the substitution

$$\eta = \alpha x + \beta y + \gamma z - vt$$

will also lead to a solution $\Phi(\eta)$. The functional form of Φ is left entirely arbitrary aside from the requirement that it must permit of two differentiations. A general solution of (3.13) with constant v has the form

$$\Phi = f_1(\xi) + f_2(\eta).$$

To proceed it is necessary to assume that α, β, γ are real numbers, which interpreted as direction cosines, represent the components of a unit vector $\boldsymbol{\sigma}$. The wave function then takes the form

$$\Phi = f_1(\boldsymbol{\sigma} \cdot \boldsymbol{r} + vt) + f_2(\boldsymbol{\sigma} \cdot \boldsymbol{r} - vt).$$

Constant values of $f_1(\boldsymbol{\sigma} \cdot \boldsymbol{r} + vt)$ are defined by $\boldsymbol{\sigma} \cdot \boldsymbol{r} = -vt$; they lie on a plane travelling along $-\boldsymbol{\sigma}$ with velocity v. Likewise, constant values of $f_2(\boldsymbol{\sigma} \cdot \boldsymbol{r} - vt)$ lie on a plane travelling along $+\boldsymbol{\sigma}$ with velocity v. In this form Φ describes two plane waves that travel in opposite directions at the same speed.

This is the procedure which is used invariably for solving plane-wave problems. It depends on the two assumptions of α, β, γ real and a time variable which is independent of space coordinates; both valid in three-dimensional Euclidean space. It is noted that the absolute constant $c = 1/\sqrt{\varepsilon_0 \mu_0}$ in free space, defined by Maxwell's equations, conflicts with the two conditions above and the generality of the procedure will have to be revisited.

The solution for spherical waves suffers from the same defects. In this case the wave equation is written in polar coordinates and Φ is assumed to be a function of the radius vector and t alone. The operator ∇^2 reduces to $\partial^2/\partial r^2 + (2/r)(\partial/\partial r)$ and the equation reads

$$\frac{v^2}{r}\frac{\partial^2(r\Phi)}{\partial r^2} - \frac{\partial^2 \Phi}{\partial t^2} = 0.$$

Substitution of $\xi = r + vt$ (or $\eta = r - vt$), $r\Phi = P$, gives

$$P = f_1(r + vt) + f_2(r - vt)$$

or

$$\Phi = \frac{1}{r}\big[f_1(r+vt) + f_2(r-vt)\big].$$

This solution describes two spherical waves, one travelling in toward the origin, the other out from the origin. The factor $1/r$ accounts for the attenuation of a spherical wave as it moves out from its source. A common application, to be considered, is the formation of standing waves by a combination of f_1 and f_2.

Separation of Variables

The general form of f_1 and f_2 is established by solving the wave equation by separating the variables. Assuming that $\Phi = ST$, where S is a function of space coordinates and T a function of t only, transforms (3.13) into

$$v^2 T\nabla^2 S - S\frac{\partial^2 T}{\partial t^2}.$$

On division by TS

$$v^2\frac{\nabla^2 S}{S} = \frac{1}{T}\frac{\partial^2 T}{\partial t^2}$$

where the left-hand side (LHS) is a function of space coordinates only, while the RHS is a function of t only. This implies that each side is equal to a function neither of space nor t. That is, the two sides must each be equal to the same constant, chosen here for convenience as $-\omega^2$.

The equation

$$\frac{\partial^2 T}{\partial t^2} + \omega^2 T = 0$$

has the general solution

$$T_\omega = c_1 e^{i\omega t} + c_2 e^{-i\omega t}.$$

In this formulation the constant ω has the meaning of an angular frequency. The space part of the wave function is defined by the equation

$$\nabla^2 S + \frac{\omega^2}{v^2} = 0.$$

Interpreting the constant $k = \omega/v = 2\pi/\lambda$ in terms of the wavelength λ, implies $v = \omega\lambda/2\pi$. The equation

$$\nabla^2 S + k^2 S = 0$$

is the basis of the entire theory of vibrations. In one dimension it reduces to the Helmholtz equation

$$\frac{d^2S}{dx^2} + k^2S = 0$$

with the solution

$$S_k = ae^{ikx} + be^{-ikx}.$$

Noting that $\exp(i\theta) = \cos\theta + i\sin\theta$, the general solution of (3.13) becomes

$$\Phi = a(k)e^{i(kx-\omega t)},$$

the real part of which may be written as

$$\varphi = a\cos\left(\frac{x}{\lambda}\cdot 2\pi - \frac{t}{\tau}\cdot 2\pi\right) = a\cos(kx - \omega t).$$

This solution confirms that the profile of an harmonic wave which is periodic in both space and time is a sine or a cosine curve. The maximum value of the disturbance, viz. a, is called the *amplitude*. The profile repeats itself at regular distances $2\pi/k$, known as the wavelength λ of the wave. Periodicity in time means that the wave moves past a fixed point at a steady rate characterized by the period τ, which counts the crests that pass in unit time. Other wave variables in frequent use include:

- frequency: $\nu = 1/\tau$
- wave vector: k
- wavenumber: $\bar{\nu} = 1/\lambda = k/2\pi$
- angular frequency: $\omega = 2\pi\nu$
- There is widespread confusion in the literature over use of the symbol k, either as wave vector or wave number. As defined here $k = 2\pi\bar{\nu}$, following [17].

3.5 Conclusion

Many commentators have referred to the formulation of electromagnetic theory as the biggest achievement of 19th-century physics, if not of all time. It appears so flawless in many ways that it comes naturally to ignore and forget about a few minor inconsistencies.

All other forms of wave motion involve the oscillations of a supporting medium in response to the periodically changing wave disturbance. Electromagnetic waves are thought to represent no more than a fluctuating field in the void.[2] Still, the radiation carries momentum of N/c^2 in the direction of propagation, experimentally

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[2] Not everybody agrees with this point of view and a significant minority still finds a place for an aether [18].

observable as radiation pressure. Momentum without mass has no meaning in Newtonian mechanics.

Observations such as photochemistry, optical activity and the Faraday effect provide conclusive evidence that electromagnetic radiation also carries angular momentum related to its energy by a factor of $2\pi\nu$. However, an infinite transverse plane wave cannot carry any angular momentum even if the electric vector rotates periodically in the plane perpendicular to its propagation. It could be argued that polarized light of a *finite* plane wave might generate intrinsic angular momentum, but that calls for a meaningful modification of the general theory. This might call the assumptions of separability and Euclidean geometry into question.

The major problem with Maxwell's theory concerns the predicted absolute constant c. It emerges as a strict property of the electromagnetic field together with ε_0 and μ_0. There is no room for maneuvre and it signals a vital conflict with classical mechanics. Not only does it call for a reformulation of the relativity principle, which was addressed by Lorentz and Einstein, but for a careful scrutiny of a Euclidean basis for the entire theory.

It will be shown how some of the problems that plagued Maxwell's theory were resolved by the new theories of the next century. The same cannot be said about the periodic table. The new quantum theory, in the form of wave mechanics, although it provided an improved formulation of orbital angular momentum, performed no better than Sommerfeld's model in formulating a detailed periodic function. Furthermore it left the periodic function that includes all stable nuclides, which was recognized by Harkins [19], completely unaccounted for.

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Chapter 4
Theoretical Response

Abstract Classical science reached maturity in the discovery of the electromagnetic field and the periodic variation of the chemical properties of atoms, for which no theoretical explanations existed. The theory of relativity and quantum theory, in the form of wave mechanics, developed in response. The details are briefly discussed and critically examined. By design, the theory of relativity provided a common basis for mechanical and electromagnetic motion, which could be refined into a model for gravitational interaction. The search for an equivalent space-time origin of the electromagnetic field resulted in the recognition of gauge fields, one of which gave birth to wave mechanics. As a theory that underpins atomic periodicity and chemistry it has only been partially successful and, reduced to a scheme of quantum chemistry, based on real linear functions, has failed completely.

4.1 Introduction

As discussed in the previous chapter, nineteenth century science produced two monumental concepts—the periodic table of the chemical elements and the electromagnetic field. To gain a unified understanding of these concepts two theories to complement Newtonian mechanics were developed during the twentieth century, without reaching consensus. Quantum mechanics was developed as a theoretical model to account for the spectroscopic and periodic properties of the chemical elements and the theory of relativity was formulated as a common basis for the mechanical and electromagnetic fields. We first outline the two theories separately, followed by a comparison of the two.

4.1.1 The Electromagnetic Field

The researches of Michael Faraday and others demonstrated reciprocity between the phenomena of electricity and magnetism. In particular it was shown that these effects are transmitted differently through different media, controlled by an electrical permittivity and a magnetic permeability respectively. Both of these factors approach characteristic limiting values in the vacuum. It follows by dimensional analysis that the product of the two factors defines the inverse square of a velocity,

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which in the vacuum limit corresponds to the experimentally known speed of light. It was demonstrated conclusively by James Clerk Maxwell that a combined electromagnetic disturbance propagates as a wave motion at this characteristic speed. The implication that light propagates with a constant speed through the vacuum, irrespective of the motion of its source, is at variance with the concept of relative velocity, well known since the time of Galileo.

Redefinition of the Galilean laws of relative motion to allow for a constant speed of light, led, in the hands of Hendrik Antoon Lorentz, to a revised set of equations, known as Lorentz transformation, which underpins the special theory of relativity. The mathematical difference between Galilean and Lorentzian relativity hinges on the ratio between the relativistic particle velocity and the speed of light. At moderate velocities the Galilean formulation may appear to be adequate, but only as a special case of Lorentzian relativity, which introduces a time component in space transformations, and *vice versa*. This observation implies that the co-existence of gravitational and electromagnetic fields characterizes the world as four dimensional, rather than three dimensional as superficially observed.

4.1.2 Periodicity of Atomic Matter

The atomic and molecular models of Dalton and Avogadro focussed the course of 19th century physical chemistry on the isolation of the elements in chemically pure form and the determination of their atomic weights. The conjecture of Prout that all atoms are composites of hydrogen atoms stimulated the critical comparison of atomic weights, which resulted in the formulation of the periodic law. At the same time the need for physical characterization of the various elements stimulated the development of atomic spectroscopy. Once again the spectrum of hydrogen served as a benchmark, which, as rationalized by Balmer's integer formula for discrete line spectra, inspired all quantum models of atomic structure.

Most successful of the early proposals was Bohr's planetary model, which provided a theoretical rationalization of Balmer's formula. It is now known to be based on two-dimensional harmonics for the specification of electronic angular momentum. As modified by Arnold Sommerfeld, with the introduction of three-dimensional elliptic orbits the model correctly specifies the allowed electronic energy levels for hydrogen by two independent integer quantum numbers.

From the chemical point of view the Sommerfeld model constituted a significant advance. The more detailed specification of energy levels suggested an electronic distribution for non-hydrogen atoms which appeared to be in line with the periodic table of the elements. However, in order to demonstrate full compliance it was necessary to postulate an additional half-integer quantum number and a strict exclusion principle to regulate an *Aufbau* procedure in line with the periodic table. Equally significant was the conclusion that for the carbon atom, the highest, four-fold degenerate, energy level is characterized by elliptic orbits directed towards the corners of a tetrahedron, centred on carbon. In one fell swoop this provided a rationalization of van't Hoff's stereochemical model and the Lewis electron-pair description of chemical bonding. Chemical theory never had it so good again.

4.1.3 Theories in Conflict

The incompatibility of special relativity and quantum theory is seen as the most important unsolved problem of theoretical physics. Whereas relativity theory is interpreted to show that the speed of light cannot be exceeded in any form of motion, quantum theory in wave-mechanical formulation is interpreted to allow non-local interaction, popularly known as instantaneous action at a distance. Modern consensus favours the non-local interpretation as correlation of distant events through the collapse of a single wave function. However, in terms of the consensual quantum-particle model wave functions are poorly understood.

4.2 The Theory of Relativity

The classical, or Galilean, model of relativity allows transformation of the laws of mechanics between systems in relative motion, by an intuitive logical procedure. The transformed coordinates of a stationary object, as observed from a frame in linear relative motion in the z-direction, or *vice versa*, appear as

$$x' = x, \qquad y' = y, \qquad z' = z - vt, \qquad t' = t. \tag{4.1}$$

For a generally directed relative motion $\boldsymbol{v}$,

$$x' = x - v_x t, \qquad y' = y - v_y t, \qquad z' = z - v_z t, \qquad t' = t$$

i.e.

$$\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{v}t.$$

Since the relative velocity is constant, the time derivative

$$\frac{d\boldsymbol{r}'}{dt} = \frac{d\boldsymbol{r}}{dt} - \boldsymbol{v}$$

describes the apparent velocity of an object that moves in the primary system, as measured in the relatively moving frame of reference. Taking the second derivative

$$\frac{d^2\boldsymbol{r}'}{dt^2} = a' = a$$

shows that the acceleration is the same in both systems.

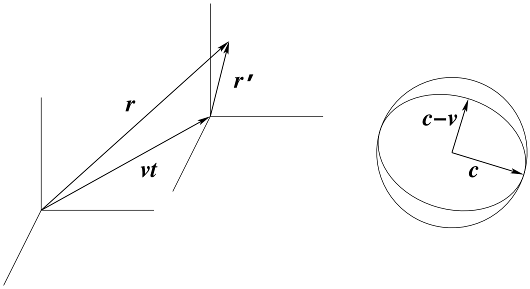

Fig. 4.1 Diagrams to illustrate relative motion

The wave front of a light beam emitted with velocity $c = d\boldsymbol{r}/dt$ in a system that moves with velocity v relative to a stationary observer should hence be observed to propagate with velocity $d\boldsymbol{r}'/dt = c - v$ in the direction of relative motion. Not only does it conflict with Maxwell's conclusion of constant c, but it also implies that the spherical wavefront becomes distorted in the direction of motion, as shown in Fig. 4.1.

Measuring the speed of light in different directions consistently failed to show up such relativistic distortion, in agreement with Maxwell's prediction.

4.2.1 Special Relativity

The relativity problem presented by the constant speed of light is readily resolved mathematically by the revised set of transformations, usually attributed to Lorentz, despite evidence that these had been used previously elsewhere [1]. The proposed equations to replace (4.1) are:

$$\begin{aligned} x' &= x, \\ y' &= y, \\ z' &= \frac{z - vt}{\sqrt{1-\beta^2}}, \\ t' &= \frac{t - vz/c^2}{\sqrt{1-\beta^2}} \end{aligned} \tag{4.2}$$

where $\beta = v/c$, the ratio of v to the speed of light. As $\beta \to 0$ at velocities $v \ll c^2$ the transformation reduces to (4.1). To demonstrate that the speed of light remains the same in both frames of reference the equation that describes a moving light-wave front

$$x^2 + y^2 + z^2 = c^2t^2, \tag{4.3}$$

after Lorentz transformation has the form

$$x'^2 + y'^2 + x'^2 = c^2t'^2.$$

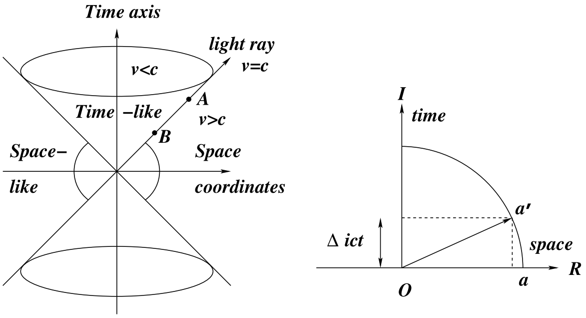

Fig. 4.2 Minkowski diagram of Special Relativity

The Lorentz transformation provides the simplest known vindication of Maxwell's wave equation. It has the virtue of being mathematically precise without specifying a definitive physical interpretation of the operation. It will be shown that the mathematical implication of length contraction in the direction of high-speed motion, accompanied by time dilation, is beyond dispute, without trying to resolve any philosophical difficulty that could arise. The common practice of disputing the theory of relativity without specifying a valid alternative to (4.2) is baseless. Whether the theory of relativity does, or does not, imply the existence of an aether is therefore considered irrelevant even though it may conflict with the exact model proposed by Maxwell.

It is significant to note that the Lorentz transformation depends on a mathematical entanglement of space and time variables. This entanglement is beautifully illustrated by Minkowski's formulation of the invariant $\tau = \sqrt{x^2 + y^2 + z^2 - (ct)^2}$, implied by (4.3), as $\tau = \sqrt{x_1^2 + x_2^2 + x_3^2 + x_0^2}$, on defining $x_0 = ict$. This proposition is visualized in two-dimensional projection by the Minkowski diagram of Fig. 4.2.

The Lorentz transformation in Minkowski space, written in the form

$$\begin{array}{llllll} x'_1 = & x_1 & & & \\ x'_2 = & & x_2 & & \\ x'_3 = & & & \gamma x_3 & + i\beta\gamma x_0 \\ x'_0 = & & & -i\beta\gamma x_3 & + \gamma x_0 \end{array}$$

with $\gamma = 1/\sqrt{1-\beta^2}$, reads in matrix notation as:

$$\boldsymbol{x}' = \boldsymbol{x} \times \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \gamma & i\beta\gamma \\ 0 & 0 & -i\beta\gamma & \gamma \end{pmatrix}. \tag{4.4}$$

The 2×2 submatrix of x_3 and x_0 resembles the rotation matrix

$$R = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix}$$

for rotation about one axis in a three-dimensional coordinate system. Correspondingly the matrix in (4.4) represents a rotation in the x_3x_0 plane of four-dimensional Minkowski space, through an imaginary angle with

$$\cos\varphi = \gamma, \qquad \sin\varphi = i\beta\gamma.$$

Successive rotations of φ_1 and φ_2 amount to a total rotation of $\Phi = \varphi_1 + \varphi_2$. Noting that $\tan\varphi = \sin\varphi/\cos\varphi = i\beta$ it follows that:

$$\tan\Phi = \tan(\varphi_1 + \varphi_2) = \frac{\tan\varphi_1 + \tan\varphi_2}{1 - \tan\varphi_1\varphi_2}.$$

Two successive Lorentz transformations with relative speeds β_1 and β_2 therefore correspond to a single transformation with relative speed

$$\beta = \frac{\beta_1 + \beta_2}{1 + \beta_1\beta_2}.$$

This is Einstein's addition law for parallel velocities. No matter how closely β_1 and β_2 may approach unity ($v = c$), their sum, β, can never exceed unity. The speed of light emitted by a source in relative motion is measured as

$$\frac{v_{obs}}{c} = \left(\frac{v+c}{c}\right) \cdot \left(\frac{1}{1 + vc/c^2}\right),$$

$$v_{obs} = \frac{v+c}{(c+v)/c} = c.$$

Vectors in Minkowski Space

A revolutionary feature of the Lorentz equations is that in order to perform a coordinate transformation between relatively moving frames of reference a complex time coordinate must be taken into account, as in Fig. 4.2. This transformation takes the form of a complex rotation in a four-dimensional pseudo-Euclidean or Minkowski space. The amount of rotation is related to the relative velocity of the observers.

A three-dimensional vector in familiar Euclidean space is represented by $\overrightarrow{Oa}$. Rotation in three-dimensional Euclidean space leaves the length

$$\left|\overrightarrow{Oa'}\right| = \sqrt{\Delta x^2 + \Delta y^2 + \Delta z^2} = r$$

invariant. However, on rotation into complex space the real part of the transformed vector is no longer invariant, as the vector acquires an extra component, such that

$$\left|\overrightarrow{Oa'}\right| = \sqrt{\Delta x^2 + \Delta y^2 + \Delta z^2 + \Delta(ict)^2} = |\overrightarrow{Oa}|.$$

The real (space) part therefore contracts by Δr, which is compensated by an increase Δict. Since c is constant this effect is observed as a *time dilation*, Δt. Clocks in relatively moving frames do not remain synchronized.

Thus, when an object moves by an amount $dx + dy + dz$ in time dt with respect to a stationary observer, the time as measured by an observer moving with the object, is $d\tau$, where

$$(d\tau)^2 = dt^2 - \left(1/c^2\right)\left(dx^2 + dy^2 + dz^2\right)$$

and $d\tau$ is known as the *proper time* for the observer in relative motion. While the velocities, such as $dz/d\tau$ remain small compared to c, there is little difference between dt and $d\tau$. However, when the relative velocity of two observers is comparable to the speed of light, their time directions are measurably not parallel.

Another consequence of time dilation is that the concept of simultaneity depends on the frame of reference. Suppose two events occur at the same time t at two points z_1 and z_2 in system S. Observed in a relatively moving reference frame S' these events occur at times

$$t_1' = \frac{t - (v/c^2)z_1}{\sqrt{1 - v^2/c^2}} \quad \text{and} \quad t_2' = \frac{t - (v/c^2)z_2}{\sqrt{1 - v^2/c^2}}.$$

Obviously $t_1' \neq t_2'$, unless $z_1 = z_2$. This inability to define absolute simultaneity also prevents the definition of an absolute universal time.

The path followed by an object in *space-time* is called its *world line* and the distance along it is seen to measure its proper time:

$$(icd\tau)^2 = dx^2 + dy^2 + dz^2 + (icdt)^2.$$

Since the apparent size of objects changes with the relative velocity of the observer, the apparent density of matter is also not an invariant under Lorentz transformation. It is inferred that the mass of a body is not a four-dimensional invariant. This is confirmed by the conservation of momentum as discussed below.

The vector dx_μ, $(\mu = 0, 3)$ represents the change in the four-dimensional position vector of a particle in differential motion along its world line. The absolute magnitude of the 4-vector, as for any 3-vector, is described by the dot product with itself and defines an invariant *world scalar*,[1]

$$ds^2 = -\frac{1}{c^2}\sum_{\mu=0}^{3} dx_\mu \cdot dx_\mu \equiv -\frac{1}{c^2} dx_\mu dx_\mu.$$

In expanded form:

$$ds^2 = -\frac{1}{c^2}\left[dx^2 + dy^2 + dz^2 - c^2 dt^2\right]$$

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[1] The Einstein summation convention applies: If an index occurs twice in one term of an expression, it is always to be summed unless the contrary is expressly stated.

or

$$ds = dt\sqrt{1 - \frac{1}{c^2dt^2}\left[dx^2 + dy^2 + dz^2\right]}$$

which is equivalent to writing $dt = d\tau/\sqrt{1-\beta^2}$ for proper time $d\tau$.

Exactly like the proper time all other vectors such as the momentum or force vectors have one time-like and three space-like components. The 4-velocity

$$\boldsymbol{u}_\nu = \frac{dx_\nu}{d\tau} = \frac{dx_\nu}{\sqrt{1-\beta^2}dt}$$

has space-like components $u_i = v_i/\sqrt{1-\beta^2}$, $i = 1, 3$ and time component $u_0 = ic/\sqrt{1-\beta^2}$. The world velocity

$$\boldsymbol{u}_\nu \cdot \boldsymbol{u}_\nu = \frac{v^2 - c^2}{1-\beta^2} = -c^2.$$

To an observer moving with a particle at constant velocity v in the z-direction the mass of the particle is m_0 and the proper time is τ. With respect to a stationary observer the particle travels a distance dz, where $d\tau^2 = dt^2 - (dz/c)^2$. To ensure that momentum is conserved it is necessary to define the components of the momentum as:

$$p_z = m_0\frac{dz}{dt} = \frac{m_0v}{\sqrt{1-v^2/c^2}}; \qquad p_t = m_0c\frac{dt}{d\tau} = \frac{m_0c}{\sqrt{1-v^2/c^2}}; \qquad v = \frac{dz}{dt}.$$

The invariant square of the momentum

$$p^2 = p_z^2 - p_t^2 = \frac{(m_0v)^2}{1-v^2/c^2} - \frac{(m_0c)^2}{1-v^2/c^2} = \frac{m_0^2(v^2-c^2)}{1-v^2/c^2} = -(m_0c)^2.$$

The momentum four-vector as measured by a stationary observer, for a particle moving with relative velocity v is

$$p_{x_i} = \frac{m_0(dx_i/dt)}{\sqrt{1-v^2/c^2}}, \quad i = 1, 3, \qquad p_t = \frac{m_0c}{\sqrt{1-v^2/c^2}}, \quad v^2 = \sum\left(\frac{dx_i}{dt}\right)^2.$$

The time component of the momentum is proportional to the total energy of the particle:

$$E = cp_t = \frac{m_0c^2}{\sqrt{1-v^2/c^2}} = mc^2$$

where $m = m_0/\sqrt{1-v^2/c^2}$ is the relativistic mass and m_0 is the *rest* mass.

Motion in Minkowski space is defined as differential change with respect to the time interval on a clock that moves with an object, which is its *proper time*.

The trajectory through space is known as the *world line* of the object. The mathematical formalism required to express dynamic variables, gradients and potentials in four-dimensional notation has been completely worked out, as briefly summarized before [1]. It is of special importance to note that, in the same formalism, the usual vector and scalar potentials of the electromagnetic field transform together as a Minkowski four-potential, related to the invariant four-vector of current and charge densities. The fourth component of such a four-vector often is the complex product of light velocity and a three-dimensional quantity such as time, mass, electric charge or scalar potential. The equivalent of the three-dimensional scalars are known as Lorentz *invariants*.

The Lorentz transformation is assumed to refer to particle motion within the time cone. Electromagnetic waves are confined to the surface of the light cone. The entire space domain is declared physically unreal. This interpretation depends on the clean separation of space and time coordinates, at variance with Lorentz transformation. The interval between any pair of points in the light cone surface, such as ***A*** and ***B*** in Fig. 4.2, is in fact zero. The so-called speed of light, c, therefore is not a speed at all, but only a conversion factor to relate space and time variables.

4.2.2 General Relativity

The common perception that the world can be described in terms of three space coordinates, orthogonal to universal time is fatally misleading. Working through the implications of Lorentz transformation demonstrates that any object in motion suffers contraction in the direction of motion, compensated for by time dilation. This effect has an important implication for an object accelerated to move on a stable circular orbit. It contracts in the direction of motion, but not in the perpendicular radial direction. The length of a ring in orbital motion must therefore decrease while its radius remains constant. This means that the geometrical relationship between the circumference and radius, known as the constant π, is no longer valid with respect to accelerated motion. This condition defines the basis of Einstein's theory of general relativity. Any acceleration, including the acceleration due to a gravitational field, is said to cause space-time to become curved, or non-Euclidean, in geometrical terminology.

The quadratic invariant of special relativity

$$ds^2 = dx^2 + dy^2 + dz^2 - (cdt)^2$$

is a special case of the more general expression for non-Euclidean Riemann geometry,

$$ds^2 = \sum_{\mu,\nu=0}^{3} \eta_{\mu\nu} dx^\nu dx^\mu$$

with $x^1 = x$, $x^2 = y$, $x^3 = z$, $x^0 = ict$ and the metric tensor

$$\eta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -c^2 \end{pmatrix}.$$

As the presence of gravity (mass) imparts a variable curvature on space the metric tensor is no longer constant. As the summation extends over all values of ν and μ, the sum consists of 4×4 terms, of which 12 are equal in pairs, hence 10 independent functions. The motion of a free material point in this field will follow a curvilinear non-uniform path.

The curved space may be considered as covered by local metric neighbourhoods and regions of overlap where the transformation law of general relativity applies. It is called a Riemannian *manifold*. Vectors transplanted to neighbouring points may change their orientation and the intuitive idea of a straight line must be replaced by that of a *geodesic*, which may be regarded as the shortest or straightest curve in that region. A manifold on which vector transplantation is described by a law of the form

$$d\xi^i = \Gamma^i_{mj} dx^m \xi^j \tag{4.5}$$

(in which the summation rule operates) is called an *affine* (or linear) space and the Γ coefficients are called the affine connections. To ensure that the length of a vector is not affected by the transplantation the metric requirement that the scalar product of two vectors be invariant is retained. This condition defines an unique connection, compatible with a given metric tensor g, and its components in any coordinate system (x) are given by

$$\Gamma^i_{jk} = -\tfrac{1}{2} g^{im} \left(\frac{\partial g_{mk}}{\partial x^i} + \frac{\partial g_{mj}}{\partial x^k} - \frac{\partial g_{jk}}{\partial x^m} \right).$$

The defining equations for a geodesic in Riemann space become

$$\frac{d^2 x^i}{ds^2} - \Gamma^i_{\alpha\beta} \frac{dx^\alpha}{ds} \frac{x^\beta}{ds} = 0$$

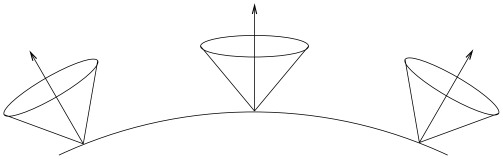
where s is the arc length of the geodesic.

An affine manifold is said to be *flat* or *Euclidean* at a point p, if a coordinate system in which the functions Γ^i_{jk} all vanish, can be found around p. For a cartesian system the geodesics become

$$\frac{d^2 x^i}{ds^2} = 0, \quad \textit{i.e.}\text{ straight lines.}$$

To specify the directions of two different vectors at nearby points it is necessary to define *tangent* vectors at these points. Stated in different terms, at each point of space-time, known as the *contact point*, there is an associated tangent Minkowski space. The theory of these spaces together with the underlying space becomes a

Fig. 4.3 Schematic drawing of a positively curved Riemannian manifold with tilted light cones in tangent space



Riemannian geometry if a Euclidean metric is introduced in each tangent space by means of a differential quadratic form.

Important tangent spaces are the light cones of Fig. 4.3. In Minkowski space these all have the same shape and orientation, but not in general relativistic curved space, where the light cones may tilt, expand or contract as one moves from one tangent space to another.

Our immediate objective here is an equation that relates a geometrical object representing the curvature of space-time to a geometrical object representing the source of the gravitational field. The condition that all affine connections must vanish at a Euclidean point, defines a tensor

$$R^{\alpha}_{\mu\beta\nu} = \frac{\partial \Gamma^{\alpha}_{\mu\nu}}{\partial x_{\beta}} - \frac{\partial \Gamma^{\alpha}_{\mu\beta}}{\partial x_{\nu}} + \Gamma^{\gamma}_{\mu\nu}\Gamma^{\alpha}_{\gamma\beta} - \Gamma^{\gamma}_{\mu\beta}\Gamma^{\alpha}_{\gamma\nu}$$

known as the *Riemann curvature tensor*, which can be contracted to the symmetrical tensor $R_{\mu\nu}$ with 10 independent components. Since this tensor has non-zero divergence it cannot feature in a conservation law (of mass and energy), but this is achieved by definition of the *Ricci tensor*

$$G_{\mu\nu} = R_{\mu\nu} - \tfrac{1}{2} g_{\mu\nu} R$$

where the doubly contracted tensor R is called the Riemann scalar. The components $g_{\mu\nu}$ of the fundamental tensor define the gravitational potential. Light rays are null curves $ds^2 = 0$ and the trajectories of particles in uniform motion are the geodesics. The geometry of space is not known *a priori*, but depends on the distribution of matter.

The Ricci tensor that represents the geometry of space is next equated with the so-called energy-momentum (stress) tensor of the matter field that defines the influence of matter and field energy

$$T^{\mu\nu} = \rho_0(x)u^{\mu}(x)u^{\nu}(x)$$

in terms of a scalar density field ρ_0 and a four-vector field of flow.

This procedure leads to the Einstein gravitational field equations, one form of which is

$$\begin{aligned} G_{\mu\nu} = R_{\mu\nu} - \tfrac{1}{2} g_{\mu\nu} R &= -\frac{8\pi\kappa}{c^2} T_{\mu\nu} \\ &= kT_{\mu\nu} \end{aligned} \tag{4.6}$$

where k is Newton's gravitation constant, or equivalently

$$R_{\mu\nu} = -\frac{8\pi\kappa}{c^2}\left(T_{\mu\nu} - \tfrac{1}{2}g_{\mu\nu}T\right) \tag{4.7}$$

where the Laue scalar T is the doubly contracted stress tensor.

The most important feature of Einstein's general relativistic field equations is the obvious symmetry between $T_{\mu\nu}$ and $R_{\mu\nu}$ as shown in (4.6) and (4.7). Both of these tensors vanish in empty Euclidean space and a reciprocal relationship between them is inferred: The presence of matter causes space to curl up and curvature of space generates matter. As the curvature of Euclidean (flat) space is zero by definition, the known universe, full of matter and energy fields, must therefore have positive curvature. Our perception of a three-dimensional world with universal time is a delusion, which only appears valid in local context. Topologists refer to this local Euclidean space as *tangent* to an underlying four-dimensional non-Euclidean space-time manifold in which space and time coordinates are intimately entangled.

In summary—existence of the electromagnetic field demands that any valid mathematical description of the world should be formulated in terms of the entangled parameters of four-dimensional non-Euclidean space-time. To first approximation the theory of special relativity, formulated as Lorentz transformation in Euclidean four-dimensional Minkowski space, describes an entangled whole. Any attempt to interpret the theory in tangent space destroys the relativistic effects that support the electromagnetic field, and reduces the theory to the classical Galilean approximation.

Motion always occurs in response to a potential field which is mathematically described by a second-order differential equation, the solutions of which are known as harmonic functions. The harmonic equation in Minkowski space is traditionally interpreted as a three-dimensional wave equation. When solved in this form by the separation of space and time variables the solutions are three-dimensional harmonic waves.

Three-dimensional wave motion is described by *linear* differential equations, with the remarkable property that any superposition of two or more solutions of an equation is another solution. In the development and interpretation of wave-mechanical quantum theory, especially in quantum chemistry, extensive use is made of this property. The procedure of linear superposition no longer holds in non-Euclidean spaces, which means that the results of quantum theory can only be approximately correct in the space-time of general relativity. This complication is not easily overcome as the solution of nonlinear differential equations presents a non-trivial problem.

4.3 Quantum Theory

The first convincing rationalization of the postulated stationary states of the Bohr model came with Louis de Broglie's wave model,[2] which pictured the hydrogen

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[2] De Broglie's argument is outlined in Chap. 7.

electron as a standing wave on the Bohr orbits. This postulate was exploited by Schrödinger when modifying the general three-dimensional wave equation to describe de Broglie's matter waves. This new *wave mechanics*, which requires three quantum numbers, predicted energy levels equivalent to the Sommerfeld model, with an improved characterization of orbital angular momentum in terms of spherical harmonics. According to this description the electron now finds itself in a truly unaccelerated, non-radiative, stationary ground state with zero orbital angular momentum.

The real impetus behind the search for a quantum theory based on more fundamental principles than the Bohr–Sommerfeld atomic model, was provided by Herman Weyl's proposal of a new world geometry with a gauge field.

4.3.1 Global Gauge Invariance

The concept of a gauge field and the notion of gauge invariance originated with the suggestion [2] how to accommodate electromagnetic variables, in addition to the gravitational field, as geometric features of a differential manifold.

Vector transplantation in an arbitrary coordinate system, formulated in differential form, is described by (4.5)

$$d\xi^i = \Gamma^i_{mj} dx^m \xi^j$$

where the Γ are symmetric connections of the manifold, ξ^i are the components of the vector and dx^m the local displacement vector. In Riemannian space the length of the vector ξ, specified as

$$l^2 = |\xi|^2 = g_{\mu\nu}\xi^\mu \xi^\nu$$

remains invariant under transplantation. The suggestion made by Weyl was that a differential manifold which allows transplantation with non-constant l could be considered instead. If the vector ξ is interpreted as the length of a measuring rod it means that this length (gauge) could change under displacement. Assuming that the increment in length is proportional to the length itself and a linear homogeneous function of the displacement vector, then

$$dl = \left(\phi_m dx^m\right) l$$

where the covariant vector ϕ_m takes the role of the connection Γ.

For a time-independent gauge vector ϕ_0, like an electrostatic field, the gauge transformation after time x^0 would yield

$$l = l_0 \exp\left[\int_0^{x^0} \phi_0 dx^0\right] = l_0 \exp\left(\phi_0 x^0\right).$$

Since the gauge factor is in general dependent on the path and therefore not integrable, circulation vectors defined by the ***curl*** operator (3.5):

$$f_{ik} = \frac{\partial \phi_i}{\partial x^k} - \frac{\partial \phi_k}{\partial x^i}$$

will be non-zero. The divergence

$$\frac{\partial f_{ik}}{\partial x^l} + \frac{f_{kl}}{\partial x^i} + \frac{\partial f_{li}}{\partial x^k} = 0, \quad i \neq k \neq l,\ i,k,l = 0,3.$$

The formal resemblance with the electromagnetic field equations *e.g.* (3.8) and (3.11)

$$\boldsymbol{curl\ E} = -\frac{\partial \boldsymbol{B}}{\partial t},$$
$$\mathrm{div}\,\boldsymbol{E} = 0$$

prompted Weyl to identify the gauge factor with the potentials of the electromagnetic field.

Although Weyl's conjecture could not be substantiated in its original form it was pointed out soon afterwards by Schrödinger [3] and London [4] that the classical quantum conditions could be deduced from Weyl's world geometry by choosing complex components for the gauge factor, *i.e.*

$$l = l_0 \exp\left[\frac{2\pi i}{h} \int \phi_m dx^m\right].$$

In view of this new insight Weyl [5] reinterpreted his world geometry as a change of phase rather than scale. In the original proposal the scale was proposed to change from unity to

$$1 + S_\mu dx^\mu \tag{4.8}$$

in going from a point x^μ to a neighbouring point $x^\mu + dx^\mu$ of space-time. In the new interpretation the factor S_μ is replaced by the complex quantity iS_μ. This has the far-reaching consequence of changing (4.8) into[3]

$$1 + i\alpha \rightarrow e^{i\alpha}$$

which is a phase change, not a change of scale. The terms gauge invariance and gauge field were retained, have persisted to this day and should be understood to mean phase invariance and phase field respectively.

In the theory of special relativity the gauge factor α is a constant since there exists only one coordinate system for all space. The transformation

$$\psi(x) \rightarrow \psi'(x) = e^{i\alpha}\psi(x) \tag{4.9}$$

is called a global gauge transformation and it has the special property that the derivative of the field

$$\partial_\mu \psi \rightarrow e^{i\alpha} \partial_\mu \psi$$

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[3] For small α $\cos\alpha \rightarrow 1$ and $\sin\alpha \rightarrow \alpha$, hence $e^{i\alpha} = \cos\alpha + i\sin\alpha \rightarrow 1 + i\alpha$.

transforms like the field itself. It is assumed here that the complex field $\psi(x)$ describes an electron, following the suggestion of Schrödinger [3].

A charge (q) is therefore associated with the wave field $\psi(x)$ and the charge density is given by

$$\rho(x,t) = q|\psi_t|^2$$

which is clearly invariant under the phase transformation (4.9). This invariance implies the global conservation of the total charge, and shows that the overall phase factor is not measurable. The phase can be chosen arbitrarily, but is a constant and, once chosen it remains fixed over the entire universe and for all time. The relevance of the gauge concept to quantum theory was convincingly demonstrated by Fritz London [4].

4.3.2 Wave Mechanics

Accepting the Bohr postulate of an electronic orbit on a hydrogen atom, stabilized by a balance between mechanical and electrostatic forces,

$$\frac{mv^2}{r} = \frac{e^2}{r^2}$$

London calculated the orbital velocity $v = e/\sqrt{mr}$ and period $\tau = 2\pi r/v$ for an electron at a distance r from the proton. At constant r the Weyl gauge parameters are $\varphi_0 = a/r$, $\varphi_1 \equiv 0$, where a is a dimensionless proportionality constant, and describe the variation of scale as

$$l = l_0 \exp\left(\int_0^{x^0} \varphi_0 dx^0\right) = l_0 e^{\varphi_0 x^0}$$

in terms of the time coordinate x^0. Assuming that the change of scale vanishes for special orbits specified by an appropriate choice of a, it follows that

$$\exp(\varphi_0 c\tau) = 1, \quad \varphi_0 c\tau = 2\pi i n$$

where n is an arbitrary integer, such that

$$\frac{ac\tau}{r} = ac \cdot \frac{2\pi\sqrt{mr}}{e} = 2\pi i n$$

or

$$r = -\frac{n^2 e^2}{a^2 c^2 m} \equiv a_n,$$

for the first Bohr orbit,

$$a_0 = \frac{h^2}{4\pi^2 e^2 m}.$$

Hence

$$a^2 = -\frac{4\pi^2 e^4}{h^2 c^2} \quad \text{and} \quad a = i\alpha,$$

where α is the Sommerfeld fine-structure constant. By this analysis a complex gauge factor leads directly to the quantization conditions for the hydrogen atom.

From de Broglie's postulate of electron waves of wavelength $\lambda = h/p$, an even simpler derivation of the Bohr formula follows from the argument that limits the wavelength of a standing wave on a circular orbit by the condition, $n\lambda = 2\pi r$, *i.e.* $nh/p = 2\pi r$; $pr = n\hbar$.

From this result, and the unexpected appearance of a complex gauge factor, the logical conclusion to describe electronic motion by a wave equation is almost self-evident. The only impediment was the incorporation of a massy, hard electron into such an equation. The problem was overcome by Schrödinger on appealing to Hamilton's demonstration of material motion as mathematically equivalent to a propagating wavefront, (2.1).

The modern interpretation of Schrödinger's equation considers the link with the wave equation, shown here in one dimension,

$$\frac{\partial^2 u(x,t)}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2 u(x,t)}{\partial t^2} = 0 \tag{4.10}$$

as no more than a formal resemblance. Fact remains that the solution

$$u(x,t) = f(x) \cdot e^{-i\omega_0 t}$$

leads directly to Schrödinger's equation. Forming the derivatives

$$\begin{aligned}
\frac{\partial u}{\partial x} &= e^{-i\omega_0 t}\frac{\partial f(x)}{\partial x}, \\
\frac{\partial^2 u}{\partial x^2} &= e^{-i\omega_0 t}\frac{\partial^2 f(x)}{\partial x^2}, \\
\frac{\partial u}{\partial t} &= -i\omega_0 f(x) e^{-i\omega_0 t} = -i\omega_0 u, \\
\frac{\partial^2 u}{\partial t^2} &= -\omega_0^2 f(x) e^{-i\omega_0 t} = -i\omega_0 \frac{\partial u}{\partial t}
\end{aligned}$$

substituted back into (4.10) leads to two new equations:

$$\text{(i)} \qquad \frac{\partial^2 u}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 f(x)}{\partial x^2} + \left(\frac{\omega_0}{c}\right)^2 f(x) = 0,$$

which is the Helmholtz equation

$$\left(\frac{d^2}{dx^2} + k_0^2\right) f(x) = 0, \quad \text{where } k_0 = \omega_0/c.$$

$$\text{(ii)} \qquad \frac{\partial^2 u}{\partial x^2} + \frac{i\omega_0}{c^2}\frac{\partial u}{\partial t} = 0.$$

By introducing the quantum postulate $\hbar\omega_0 = E - V$, the energy in excess of a constant potential, and the velocity of a matter wavefront, in Hamilton–Jacobi formalism [6], $c = \sqrt{T/2m}$, these equations (in 3D) transform into the familiar set of Schrödinger equations:

$$\frac{\hbar^2}{2m}\nabla^2\psi + (E - V)\psi = 0, \tag{4.11}$$

$$\frac{i\hbar}{2m}\nabla^2\Psi = \frac{\partial\Psi}{\partial t}. \tag{4.12}$$

Equation (4.12) in Ψ, the so-called time-dependent wave equation, is often considered to be a diffusion equation, as it shows only a first time derivative.

In the axiomatic approach to quantum mechanics these equations are obtained by substituting differential operators for the classical variables of momentum and energy

$$p \to -i\hbar\nabla, \qquad E \to i\hbar\frac{\partial}{\partial t}$$

into the Hamiltonian expression

$$H = \frac{p^2}{2m} + V.$$

Schrödinger's Equation

Schrödinger's amplitude equation in three dimensions reads

$$\left(\nabla^2\psi = \frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2}\right) + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0.$$

It can be solved in principle for any system of physical interest on specification of the two parameters m and V, representing mass and potential energy respectively. Its most conspicuous success as a theory for chemistry occurred as the solution of electronic motion in the hydrogen atom. Not only does it reproduce the numerical results of the Bohr model without further assumption, but also provides a convincing explanation of the quantum integers of Sommerfeld's model.

The hydrogen atom is handled as a spherically symmetrical central-field problem. In the simplest formulation the electron is treated as a spherical wave with unit negative charge in interaction with a stationary proton of opposite charge. The potential energy of the electron, as a function of radial distance, is given in SI units as

$$V = -\frac{e^2}{4\pi\varepsilon_0 r}.$$

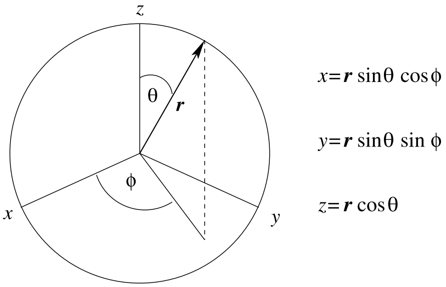

Fig. 4.4 Definition of spherical polar coordinates

Since cartesian coordinates are not appropriate to handle problems in spherical symmetry it is necessary to transform to the more appropriate spherical polar coordinates r, θ and ϕ as defined by Fig. 4.4.

An expression for the Laplacian operator ∇^2 can be obtained directly by forming the appropriate derivatives. The result, given without proof is

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2.$$

The term in Λ contains the total angular dependence, independent of r. The radial wave equation, without angle dependence is

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi = 0. \tag{4.13}$$

For large r the equation becomes

$$\frac{d^2\psi}{dr^2} + \frac{2mE\psi}{\hbar^2} = 0.$$

This equation is familiar in the form $k^2 = 2mE/\hbar^2 < 0$, with solutions $\psi = \exp(-kr)$. Substitution of this solution into (4.13) gives

$$\frac{d\psi}{dr} = -ke^{-kr} = -k\psi,$$
$$\frac{d^2\psi}{dr^2} = -k\frac{d\psi}{dr} = k^2\psi$$

and hence

$$k^2 - \frac{2k}{r} + \frac{2mE}{\hbar^2} + \frac{me^2}{2\pi\varepsilon_0\hbar^2 r} = 0.$$

Since this equation is valid for all r the respective sums that are dependent and independent of r should individually be equal to zero, *i.e.*

$$k^2 + \frac{2mE}{\hbar^2} = 0 \quad \text{and} \quad -2k + \frac{me^2}{2\pi\varepsilon_0\hbar^2} = 0.$$

Thus

$$k = \frac{me^2}{4\pi\varepsilon_0\hbar^2} = \left(\frac{1}{r_1}\right)_{Bohr} \quad \text{and} \quad E = -\frac{k^2\hbar^2}{2m} = (E_1)_{Bohr}.$$

Solution of Schrödinger's three-dimensional differential equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi = 0$$

is achieved by separation of the variables, writing

$$\psi(r,\theta,\phi) = R(r)\cdot Y(\theta,\phi).$$

The two separated equations, with separation constant $l(l+1)$ are

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + l(l+1)Y = 0 \tag{4.14}$$

and

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{8\pi^2\mu}{h^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r}\right) - \frac{l(l+1)}{r^2}\right]R = 0. \tag{4.15}$$

The angle-dependent equation is separated into two equations by introducing the separation constant m_l^2, *i.e.*:

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0$$

with the solution,

$$\Phi = Ae^{\pm i m_l \phi}$$

and the Θ equation:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0.$$

The separated equations are all of the Sturm–Liouville type

$$L(x)y(x) = \lambda y(x)$$

with differential operator $L(x)$ and real eigenvalues λ, [1]. The condition

$$\Phi_{m_l}(2\pi m_l) = \Phi_{m_l}(0)$$

for single-valued $\Phi(\phi)$ restricts the values of m_l to positive or negative integers. The normalization condition

$$\int_0^{2\pi} \Phi\Phi^* d\phi = 2\pi A^2 = 1$$

implies

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\Phi}, \qquad -i\frac{\partial\Phi}{\partial\phi} = m_l\Phi.$$

The operator $L_z = -i\hbar\partial/\partial\phi$ defines a set of action eigenfunctions

$$L_z\Phi = m_l\hbar\Phi,$$

traditionally interpreted as orbital angular-momentum vectors.

The more complicated radial and Θ equations are solved by the Frobenius method in terms of infinite series that terminate for integer n and l in Sturm–Liouville systems with operators H and L^2:

$$HR_{nl}(r) = \frac{1}{n^2}E_1 \cdot R(r),$$

$$L^2 Y_{m_l l}(\theta,\phi) = l(l+1)\hbar^2 Y_{m_l l}(\theta,\phi).$$

The three numerically related *quantum numbers* are commonly designated as:

Principal quantum number: $n = 1, 2, 3, \ldots, \infty$
Angular-momentum quantum number: $l = 0, 1, 2, 3, \ldots, (n-1)$
Magnetic quantum number: $m_l = -l, \ldots, 0, \ldots l$, $(2l+1$ values).

Electronic states of wave functions with common n, but different values of l and m_l have the same energy and are said to be *degenerate*. Wave functions with $l = 0, 1, 2, 3$ describe the electronic states referred to as s, p, d, f states in accordance with spectroscopic notation. The degeneracy of these states depend on allowed values of m_l and therefore amount to 1, 3, 5, 7 respectively.

4.3.3 Local Gauge Invariance

Weyl's seminal attempt to relate electromagnetic effects to gauged motion of matter through space-time, as modified by Schrödinger into a complex phase factor, provided the link for the development of particle physics.

The fundamental concept is embodied in the equation

$$\Psi' = \Psi e^{i\alpha}$$

that describes the transformation of a state function on transplantation through the vacuum. For constant α the equation defines a *global* gauge transformation, with the special property that the derivative of the field

$$\partial\Psi' = e^{i\alpha}\partial\Psi$$

has the same form as the gauge transformation. If, in the case of a charged particle, the complex field Ψ describes an electron, a charge of $\rho = |\Psi|^2$ is associated with its wave field, which is clearly invariant under the transformation and implies conservation of the total charge.

In the curved space-time of general relativity the gauge factor α is no longer globally fixed, but changes as a function of the local coordinates of the curved space-time manifold,

$$\Psi' = \Psi e^{i\alpha(\mu)} \equiv \Psi e^{i\alpha(x,t)}. \tag{4.16}$$

By forming the derivative

$$\partial_\mu \Psi' = \partial_\mu \Psi \cdot e^{i\alpha} + \partial_\mu \alpha \cdot i\Psi e^{i\alpha}$$

it is seen that the conservation of charge now depends on the appearance of a compensating gauge field.

In the case of an electron the transformed wave function (4.16), on substitution into Schrödinger's equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \Psi}{\partial x^2}\right) \tag{4.17}$$

yields

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2 \Psi}{\partial x^2} + 2i\frac{\partial \alpha}{\partial x}\frac{\partial \Psi}{\partial x} - \Psi\frac{\partial^2 \alpha}{\partial x^2} - \Psi\left(\frac{\partial \alpha}{\partial t}\right)^2\right] + \hbar\Psi\frac{\partial \alpha}{\partial t}.$$

Abbreviated in vector notation it reads

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= -\frac{\hbar^2}{2m}\left[(\nabla + i\nabla\alpha)^2 - \nabla\cdot\nabla\alpha - \frac{2m}{\hbar}\frac{\partial \alpha}{\partial t}\right]\Psi \\ &\equiv -\frac{\hbar^2}{2m}\left[(\nabla + i\boldsymbol{A})^2 - \nabla\times\boldsymbol{A} - V\right]\Psi. \end{aligned} \tag{4.18}$$

The form of (4.17) is recovered by defining the vector $\boldsymbol{A} \equiv \partial\alpha/\partial x$ and the scalar $V = (2m/\hbar)(\partial\alpha/\partial t)$.

Equation (4.18) is recognized as Pauli's equation that describes an electron in an electromagnetic field. $\boldsymbol{A}$ and V are known respectively as the vector and scalar potentials of the electromagnetic field.

The central idea of particle physics is inspired by this successful description of an electron in terms of the electromagnetic gauge field. Having recognized the appearance of strong and weak interactions in atomic nuclei it was argued that these could also serve to characterize the corresponding elementary particles by specifying the appropriate interaction as a gauge field. Whereas Schrödinger's equation correctly describes electronic interaction, the starting point in the analysis of strong and weak interaction is to ensure that the Lagrangian function, which describes the interaction of these particle wave functions, remains invariant under the symmetry transformations that reflect known conservation laws [7].

The next important step is to identify asymmetric solutions of the symmetrical Lagrangian. This procedure corresponds in principle to the modification of global gauge invariance by the recognition of a local gauge field, as before [8]. The process has become known as *spontaneous symmetry breaking* of gauge theories. The most important application in the present context is the broken symmetry that generates the Higgs field, characterized by a massive boson.

This result is important within elementary-particle physics as a mathematical procedure to simulate the effect of space-time curvature, which is known to produce matter. In this sense it is neither unexpected nor mysterious. However, the common interpretation of the effect as a transition between two symmetry states of the vacuum has no observational support. More obviously, the high-symmetry Lagrangian is the correct formulation in hypothetical Euclidean space, whereas the 'broken' symmetry represents physically real curved space-time. Another way of distinguishing between the two symmetry states is in terms of linear and nonlinear formulations.

It is emphasized that the Higgs mechanism does not refer to two physically realizable vacuum states in that pseudo-Euclidean Minkowski space-time is no more than a local tangent approximation to the curved manifold of general relativity [9, 10]. It has no independent existence.

'Symmetry breaking' only has mathematical meaning and it makes no sense to associate it with a phase transition between two possible vacuum states. A Higgs field is one mathematical manifestation of space-time curvature.

4.3.4 Space-Time Manifold and Tangent Space

In four-dimensional space-time space and time coordinates are entangled and there is no difference between time-like and space-like events. Furthermore, point particles are without extension in both space and time, and therefore have no existence. The two-dimensional Minkowski diagram therefore becomes meaningless. It will be argued that the light cone in 4D now defines an interface between a world and an anti-world in projective space-time. In this model there is no difference between relativity and quantum theory, providing the latter is described in quaternion notation, without the separation of variables and the former abandons the notion of a limiting speed. It follows that special relativity and wave mechanics are both flawed. Wave mechanics because Schrödinger's equation describes a situation in three-dimensional tangent space (Fig. 4.5) and relativity because it is traditionally *interpreted* in tangent space. A common failure of both theories is the reluctance to abandon the notion of point particles.

The primary cause of this reluctance was Einstein's interpretation of the photoelectric effect in terms of light quanta, *i.e.* photons or *particles* of light, in interaction with particulate electrons in metal surfaces. An equally convincing interpretation in terms of interacting electromagnetic and electronic waves, offered by Schrödinger, has never been accepted. The unfortunate interpretation of electron density as a probability function developed from this oversight.

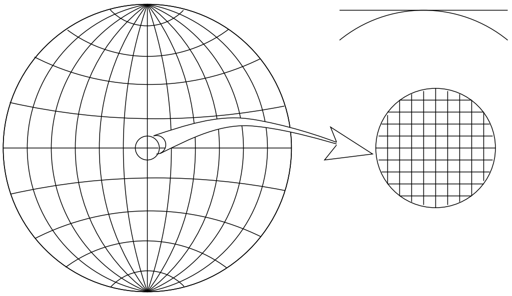

Fig. 4.5 Schematic diagram to show the relationship between a local Euclidean surface tangent to a spherically curved surface embedded in three dimensions. The tangent to a curve in a plane is a straight line

4.3.5 The Periodic Function

The wave-mechanical quantum numbers for the hydrogen atom specify a strict hierarchy of energy levels, no longer open to empirical adjustment in order to fit the elemental periodic sequence. The predicted *Aufbau* procedure stays in register with the periodic table up to atomic number 18, where it breaks down in an unpredictable complicated way. At the same time the slick description of tetrahedral structure in terms of elliptic orbits also disappeared. The laboured reformulation in terms of *hybrid orbitals* has been shown to have no validity [11].

On first discovery the wave-mechanical solutions in the form of non-commutative complex variables appeared to be foreign and mysterious. However, the simple truth is that these are the normal properties of angular momenta. As remarked by Herbert Goldstein [6]:

> The introduction of the quantum commutation relations was a great act of physical discovery by the pioneers of quantum mechanics.

He goes on to show the formal resemblance with the classical Poisson bracket formulation.

The most sensational aspect of quantum theory, the so-called uncertainty principle has been over-interpreted by the philosophers of science into an insiduous ideology of acausality and unpredictability. In reality there is nothing non-classical about the concept. It is a common feature of classical mechanics associated with conjugate pairs in Fourier analysis and wave motion [6]. Recent experimental studies [12] failed to find evidence of uncertainty induced by disturbance during measurement. The quantum version was developed in support of the unrealistic interpretation of Schrödinger's wave equation in terms of particle motion, which resulted in the concept of probability density, causing hopeless confusion in the theory of molecular structure.

The theory is therefore incomplete in its failure to account for electron spin, the periodic table and molecular structure. The reason for this failure becomes evident on closer scrutiny of the periodic function. Using the distribution of prime numbers as a guide [13], periods of 24 and 8, empirically related to composition of stable atomic nuclei and atomic number, respectively, are readily identified [14].

Elemental periodicity emerges from this analysis as a function of space-time curvature [15]. Four well-defined periodicities, which have been identified, can be associated with four special space-time structures. The periodic function defined by the wave-mechanical hydrogen spectrum correlates with the void and the observed periodic table correlates with space-time curvature characterized by the golden ratio. Periodic functions that reflect inverted electron configurations of the above are correlated with conditions of extreme curvature that induce nuclear synthesis by α-particle fusion and/or conversion into antimatter.

The well-known fact [16] that the spin function is defined by square-root quaternion rotation raises the expectation that four-dimensional hypercomplex characterization of atomic electrons could solve the periodicity and structure problems at the same time.

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Chapter 5
State of the Art

Abstract The theory of chemistry is the theory of matter—how it is constituted and how it behaves in interaction. Theories to address these issues emerged early in the previous century. Their impact on chemical thinking is discussed in this chapter. The theory of relativity that explains the origin of matter in the geometry of four-dimensional space-time has been completely ignored. Quantum theory in the form of Schrödinger's three-dimensional wave equation is claimed as fundamental to the computational scheme, widely known as *quantum chemistry*, considered to represent the "highest level" of chemical theory. It relies on the ubiquitous linear combination of real atomic orbitals, in direct conflict with the complex functions of wave mechanics. The flawed models of chemical bonding, periodicity, molecular structure, stereochemistry, point particles, molecular modelling and reaction mechanism, formulated in terms of this approach, are critically analyzed. All of these urgently need serious reconsideration.

5.1 Introduction

Quantum theory may have revolutionized physics, but in the process has destroyed chemistry, at least its theoretical basis. The two major areas in which quantum theory impacted on chemistry are traditionally known as *chemical bonding* and *molecular structure*. These two concepts are closely related and before the advent of quantum mechanics both of them were understood in terms of well-defined empirical models.

The idea of covalence, which emerged as one of the classical models of chemistry, has, despite persistent efforts never been successfully adapted as a non-classical description of chemical interaction. It gained general acceptance about a hundred years ago when formulated as the sharing of an electron pair between two atoms. The name of Gilbert Lewis is most prominently associated with this development. When it became fashionable to declare interatomic cohesion as a strictly non-classical quantum phenomenon several bizarre suggestions to glorify electron pairs had come and gone. One of the more bizarre has managed to survive into the 21st century. An electron is still regarded as a point particle that occurs probabilistically in a flexible bag, known as an atomic orbital, that protrudes from an atom. When two orbitals are fused together they form a bonding orbital which encloses the shared pair of electrons. The only new feature of this "quantum" theory, com-

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pared to the classical Lewis model, is a rich, but incomprehensible, jargon. At the point where even primary-school pupils find the model too ludicrous to consider a career in chemistry, quantum chemists are hiding behind group theory and computer software to disguise the orbitals of bonding theory.

The simple truth is that the particle concept is, and remains, a classical idea. It is not only teachers of chemistry that battle with the notion of a quantum particle; the entire physics community shares the dilemma. The founding fathers of quantum mechanics were well aware of this fact, and in order to avoid the classical idea they created the monster known as a particle with wave properties, which they proclaimed a quantum object. The respectability of the so-called wave-particle duality may be traced back to Einstein's work which was recognized for award by the Nobel committee. As physicists struggled to understand the mechanism whereby the energy, which is spread over an electromagnetic wavefront, is miraculously concentrated to interact with a single point electron in a metal surface, Einstein cut the Gordian knot by redefining electromagnetic waves as a stream of energetic particles, which became known as photons. When subsequently, the wave nature of an electron beam was demonstrated experimentally the idea of a wavicle became firmly established.

Had Einstein gone the other way by recognizing an electron as a standing wave, the present problem would have been avoided a century ago. Only Schrödinger offered an alternative explanation of the photoelectric effect as two waves interacting, but the German establishment refused to humour the Austrian. As their reward the whole world pretended for a century to understand probability densities and quantum uncertainties.

It is remarkable how often Einstein arrived at a correct conclusion for the wrong reason. When he asked in 1935 [1]:

> Can quantum-mechanical description of physical reality be considered complete?

he argued on the perceived premises of incompatibility between quantum theory and special relativity. He should have done the opposite. It now transpires that quantum mechanics appears incomplete because its equivalence to the theory of relativity is overlooked.

The irrefutable evidence of special relativity is that we live in a four-dimensional world in which the transformation between moving frames of reference amounts to a complex rotation that implies the equivalence of space and time coordinates. Furthermore, the extended theory of general relativity identifies four-dimensional space-time to be positively curved and topologically closed. This means that a mathematical description, which separates space and time variables, is no longer consistent with physical reality. It is well known that the first step in the analysis of wave-mechanical problems, is precisely that—separation of the variables by the definition of product functions that destroys the holistic entanglement of space and time.

In mitigation it is noticed that this response is the human thing to do. In the world that we experience, time and space do not appear entangled. In the same way, the two-dimensional world, as it appears in Flatland, is not entangled with any third dimension and the idea of a spherical earth has no meaning. In the same way that a flat earth is tangent to the curved planetary surface, the flat three-dimensional space, which we understand, is tangent to curved four-dimensional space-time. Events in this tangent space are described by classical Newtonian mechanics, whereas the actual four-dimensional space-time is described by the mathematical model of general relativity. This is where traditional quantum theory falls short. It tries to describe four-dimensional space-time events, best perceived as phase-locked matter-wave packets, by the mechanics of three-dimensional particles. Rather than using hypercomplex algebra it endeavours to simplify the problem by using the algebra of real numbers. The result is a disaster.

Efforts to coerce four-dimensional matter waves into reflecting the properties of three-dimensional point particles resulted in the appearance of unanticipated complex functions and dynamic variables with unforeseen commutation properties. In order to rationalize the weird mathematics an equally weird physical model, based on quantum uncertainty, wavicles and probability density, became entrenched in the lore of an acausal and unpredictable quantum world. This is the price we pay for projecting four-dimensional reality into tangent three-dimensional Euclidean space. Sadly, the result is the old classical world superimposed with non-Boolean logic. It makes no sense.

Chemistry itself is assumed to be securely underpinned by wave mechanics. However, in order to generate a model in line with classical valence theory a number of assumptions, completely at variance with quantum theory, had to be invoked.

5.2 Chemistry at the Crossroads

Several authors have tried for decades to caution the chemistry world against a malaise at the roots of the subject that threatened the credibility of chemistry as a science. The problem may be traced back to the 1950's when the idea of developing a theory of chemistry from the principles of quantum mechanics gained worldwide popularity with spirited debates between conservative and progressive theorists on the subjects of resonance, orbitals, hybridization, directed valency, π-bonds, multiple bonds, back bonding, physical methods of molecular-structure elucidation, and many other exciting developments. The new developments and ideas were eagerly accepted at face value in the chemical world, truly believing that a new dawn had broken.

Over the years small chinks appeared in the armour of quantum chemistry, but reluctance to see a few ugly facts spoil a beautiful theory had them conveniently ignored. As it turns out the half-truths confidently preached by thousands of glossy textbooks had been faithfully copied from the works of the masters.

There are basically two fallacies that bedevil chemical education. The first of these concerns the structure of the periodic table of the elements. It is taught that the general sequence of energy-level occupation follows the wave-mechanical solution of electronic energy levels in the hydrogen atom:

$$1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p < 4p < 4f \quad etc.$$

Because of interelectronic interaction in many-electron atoms some of these levels may cross to yield:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f \quad etc.$$

giving rise to an s^2 block, followed by d^{10} and p^6 blocks, with an f^{14} block inserted within the third d-block.

In reality there are no d^{10} blocks of so-called transition elements. The transition series consist of ^{21}Sc→^{28}Ni, ^{39}Y→^{46}Pd and ^{57}La→^{78}Pt—eight elements each. The block consisting of Cu, Zn; Ag, Cd; Au, Hg; is part of the s-block, as originally placed by Mendeléev. It is interesting to note that this observation was highlighted by Bohr [2], but deliberately ignored on the advent of wave mechanics, although there is no quantum theory to explain this structure. Why not be honest about this?

Another failure is to account for the periodicity amongst all stable nuclides, first observed by Harkins in 1921, and which contains the periodic table of the elements as a special case. Again there is no quantum-theoretic explanation of this fact, which is conveniently ignored by all chemists.

5.2.1 The Bonding Model

In the euphoria of discovering a quantum basis to theoretical chemistry Pauling and his followers exploited observed periodicities in atomic ionization potential, electron affinity and electronegativity to create the illusion that these quantities have a firm quantum-theoretic basis. This exercise resulted in the absurdity of three linearly related electronegativity scales, based on the square root of an energy, an energy and a force, respectively [3]. Must we assume that quantum uncertainty overrides dimensional analysis?

Undeterred, the assumed quantities are next accepted as the basis of a quantum-mechanical model of chemical bonding. The theme is developed around the known geometries of methane, ethylene and acetylene. These structures were first rationalized in terms of Sommerfeld's proposed electronic structure of carbon. Consisting of two spherical and four elliptic orbits, directed towards alternate vertices of an enclosing cube, it neatly fits the tetrahedral structure of methane. The wave-mechanical solution, on the other hand suggests four electrons in spherically-symmetrical distribution and two more of lower symmetry, assuming hydrogenic energy levels. To arrive at an orbital rationalization Pauling proposed the valence-state excitation

$$1s^2 2s^2 2p^2 \rightarrow 1s^2 2s^1 2p_1^1 2p_0^1 2p_{-1}^1$$

with four unpaired electrons to explain the tetravalency, but without accounting for the conservation of angular momentum. The four valence sub-levels correspond to a spherically symmetrical state ($2s$), another with polar symmetry (p_0) and a complex pair with combined rotational symmetry $(p_{\pm1})$. Noting that a tetrahedral structure is vectorially defined by Cartesian unit vectors $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$ in the combinations:

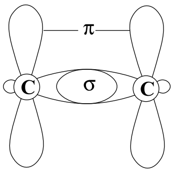
$$\begin{aligned} c_1 &= x + y + z,\\ c_2 &= -x - y + z,\\ c_3 &= x - y - z,\\ c_4 &= -x + y - z \end{aligned}$$

the complex pair was assumed reducible to unit vectors x and y by the linear combinations $p_1 \pm p_{-1}$, resulting in one real and one imaginary function, proportional to x and iy respectively. By choosing a complex coefficient for iy and defining the polar axis as z, the required unit vectors are obtained in the form of three real wave functions p_x, p_y and p_z. In order to accommodate four, rather than three electrons, the $2s$ function is added to each linear combination of p functions without changing the vectorial properties of the (in)famous sp^3 hybrid orbitals.

This construction has a fatal flaw, which probably was first pointed out in a failed MSc thesis at the University of Manchester in 1956 [4]. Fact is that any linear combination of p-type degenerate eigenfunctions defines a specific rotation of the coordinate axes. In particular, the combinations $p_1 \pm p_{-1}$ define rotations of 90° about the y and x axes respectively. The net result is two new choices of the polar axis along x and y, redirecting the p_0 eigenfunction. The real eigenfunctions p_x, p_y and p_z are in fact identical, except for orientation, which is an arbitrary choice in any case. The magnetic quantum number m_l is not affected by the rotation and remains at zero. Some textbooks [5] assign quantum numbers $m_l = \pm1$ to the p_x and p_y orbitals while others claim that quantum numbers are no longer relevant in this operation. Both of these arguments are invalid.

We conclude that sp^3 hybridization has no quantum-mechanical meaning as the existence of three eigenfunctions with identical quantum numbers $(n, l, m_l) = (2, 1, 0)$ are forbidden by the exclusion principle. On previous mention [6, 7] this statement was greeted with derision, as due to "not understanding quantum theory", and pointing out that "the exclusion principle should not be taken too literally". Not being told how to take it, one still stands to be corrected by a valid counter argument.

The only positive aspect of sp^3 hybridization is that it "predicts" the correct structure for methane, no different from van't Hoff's proposal of half a century earlier. It is also supposed to predict the correct structure for ethylene and acetylene. In the case of ethylene it is argued that through the medium of sp^2 hybridization the two carbon atoms interact through two bonds, $\sigma(sp^2)$ and $\pi(p_z)$, in direct and indirect overlap respectively.



The amazing result is that, experimentally, the π-bond is significantly stronger than the σ-bond [8], despite the guiding principle that bond strength is a linear function of orbital overlap. In this case faith is stronger than logic.

The selling point of the ethylenic π-bond is the barrier to rotation that goes with π-overlap. In the acetylene molecule there are two pairs of overlapping π-orbitals, at right angles, suggesting double the steric rigidity. Although this is not directly measurable, one finds that in the case of dimetal triple bonds, defined in exactly the same way, there is no barrier to rotation. The handwaving to gloss over this unpleasant fact is all but convincing.

In more modern analyses, especially in molecular-orbital (MO) theory, hybridization is no longer mentioned explicitly. However, the basis sets that feature in these computations are all functions of "real" spherical harmonics. Like sp^3 hybrids such things have no physical meaning. As before, any linear combination of spherical harmonics defines rotation of the coordinate axes. Even the elaborate efforts to disguise the hybrid orbitals as elements of a symmetry group cannot turn the assumed classical basis into quantum theory or impart physical meaning to these arbitrary functions. It is important to realize that the group structure has only mathematical meaning, unless it operates on *physically real objects*. Applied to linear combinations of orbitals it becomes an exercise in futility. The treatment may be advanced to higher and higher "levels of theory", without exorcizing this evil.

Even computational chemists could be hard-pressed to explain the utility of an *ab-initio* MO LCAO HF SCF CI MP4 STO-6-31++G* calculation. In this, each syllable of the acronym modifies the algorithm which, as part of a modern software package, incorporates contributions from scores of independent programmers. It is questionable if any mortal could actually keep track of the logical structure of such computer code. It is besides the point that such a calculation can be massaged by skilful selection of basis sets and convergence criteria to produce results that match experimental data. The entire procedure that manipulates mathematical functions without physical meaning, neither classical nor non-classical, is completely baseless. One of the main objectives of the scheme is to calculate molecular structure. It is fairly successful in this pursuit, provided it starts with the known structure as a classical boundary condition. The Born-Oppenheimer approximation serves as theoretical justification of the method.

5.2.2 *Molecular Structure*

Quantum mechanical solution of the problem consists of finding the molecular wave function from the eigenvalue equation

$$H\Psi = E\Psi$$

over all nuclei and electrons. However, beyond this statement no mathematical progress is possible, unless the molecular Hamiltonian is known, but that presupposes the tautology of successful solution of the equation. The tension is said to be eased by the BO assumption that splits the problem into electronic and nuclear parts by noting that, on the scale of electronic motion, the heavy nuclei remain stationary for all practical purposes. The strategy is to assume an appropriate nuclear framework as the boundary condition in solving the quantum-mechanical electronic problem. This by itself is a miracle, considering that a two-body system is the most complicated problem that has ever been solved in classical mechanics. However, computational chemists claim the ability to solve a quantum-mechanical many-body electronic problem. As a final step the computed electronic structure is then used as the boundary condition also to solve for the nuclear motion quantum-mechanically. It is in these operations that the multi-syllabic acronyms come into their own. As it all happens on a computer the need to explain the procedure that solves the many-body problem falls away.

Surely this is all a joke. In order to invoke the BO procedure it is necessary to have an algebra of observables that can be decomposed into two sub-algebras, for instance a W*-algebra. This is mathematically feasible, but there is a price to pay. The mathematical requirement is that at least one of the sub-algebras be commutative. In physical terminology it means that at least one of the sub-systems must be a classical one. The message is clear: the nuclear framework of a molecule cannot be simulated by quantum-mechanical computation.

What about the electronic structure? We are back to the problem that, even if the molecular Hamiltonian is known from the assumed molecular framework, the molecular equation can only be solved for a single electron. The most complicated molecular system that can be solved quantum-mechanically therefore is H_2^+, with clamped nuclei. Why not admit it and stop pretending to do the impossible? The only alternative is to resort to a linear combination of atomic orbitals, substituted into the equation as a trial solution, but that brings us back to hybridization, already shown to be a meaningless operation.

By ignoring the physical meaning associated with mathematical functions the chemists brought the dilemma of orbital hybridization upon themselves. What they failed to appreciate is that the eigenvectors of a degenerate set, such as the $2p$ functions with $m_l = -1, 0, 1$, are mathematically connected. Modification to any member of the set therefore affects the other partners as well. Creation of the real p_x function, by whatever means, cannot be done without generating a complex pair in the yz-plane, so as not to disrupt the degeneracy. On performing the mathematical operation by linear combination, the effects on the physical situation can therefore not simply be ignored. Choosing p_x, p_y and p_z as an orthogonal basis has mathematical meaning only, but this meaning no longer pertains to the physics.[1] All of a sudden the information about angular momentum has just disappeared. This means loss of the only function with the necessary vectorial quality that can possibly generate a three-dimensional molecular structure. Minimization of scalar energy can never generate such structure *ab initio*.

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[1] It seems plausible that the original authors of the method must have intended this as a first classical approximation, whereas later commentators failed to appreciate the difference.

5.2.3 Stereochemistry

At one stage the stereochemical postulates of van't Hoff appeared to be adequately explained by Sommerfeld's atomic model with its well-defined set of angular-momentum vectors. Electromagnetic theory associates a magnetic field with a circulating electric charge. This means that the angular momentum of an electron on an elliptic orbit must generate a magnetic field. This field should affect incoming radiation in the same way as an applied magnetic field. As shown by Faraday, chemical substances in a magnetic field interact measurably with polarized light. This phenomenon is known as the Faraday effect. At the same time it was known that some special substances retained this property even in the absence of an applied field. This, so-called, optical activity could, arguably, be caused by an intrinsic magnetic field, presumably due to orbital electronic motion. The observation by van't Hoff that all of these special optically active substances were endowed with an asymmetric structure, based on the tetrahedral carbon atom, can be correlated with Sommerfeld's model.

Two electrons that rotate in opposite sense on elliptic orbits should generate equal but oppositely directed magnetic fields, with an overall resultant of zero. This happens whenever the angular momenta of the orbiting electrons are quenched. In van't Hoff's tetrahedral model the angular-momentum vector of each orbit will be modulated by the electrochemical nature of each substituent, such as H·, Cl·, *etc.*, associated with that orbit. In a fully symmetrically substituted derivative such as CR_4 it is readily shown [9, 10] that the angular momentum remains quenched, as for any arrangement of substituents that defines a molecule which can be superimposed on its mirror image. *Chiral* molecules, such as Cabde do not have this property and are found to be optically active because of a non-zero residual angular momentum vector.

In the Pauling–Coulson model of chemical interaction, and in all other schemes that rely on LCAO, orbital angular momentum vectors and magnetic quantum numbers (m_l) are no longer defined. Optical activity is therefore undefined in quantum chemistry and treated as another of those 'mysterious' quantum effects to be accepted in good faith [11].

5.2.4 The Particle Problem

Not only have the ill-conceived concepts of orbitals and hybridization created a distorted picture of chemical interaction in the minds of many students, but an uncritical acceptance of the Copenhagen interpretation further contributed to an alienization from quantum theory itself. The original Copenhagen scheme was a deliberate effort between Bohr and Heisenberg to refute the obvious interpretation of wave mechanics and Schrödinger's denial of quantum jumps. Their main objective was to explain wave phenomena in terms of dimensionless particles. This approach may be adequate in physics. For instance, to formulate the laws of celestial mechanics the sun and its planets may be represented as point particles, without loss of generality. In this case there is nothing to be gained by dragging the physical dimensions of these bodies into the equation. Such point objects are probably better represented by the mathematical notion of an open point.

In chemistry this approach is disastrous. Entities like electrons, atoms and molecules, despite their quantum nature, are well known not to be of zero extent. Anybody who has ever carried out a crystallographic analysis or an experiment in gas kinetics should know better.

The obvious response is to recognize electrons, and the like, for what they are—flexible wave packets that interact through the medium of standing waves, known in physics as either photons or virtual photons. The size of an electron depends on its environment and may vary between that of an open-point particle or the dimensions of a macroscopic conductor. From a chemical point of view there is nothing to be gained by trying to represent an electron by a probability density of point particles or as a hybrid between a wave and a particle. The wave picture eliminates the mystery of quantum jumps, action at a distance, half-dead cats and other ghostly features ascribed to quantum systems.

5.2.5 Reaction Mechanisms

There is nothing that popularized the hybrid-orbital picture more so than the rules for predicting the stereochemical outcome of pericyclic organic reactions. The guiding principle in all instances is the observation that the stereochemical results are invariably inverted when reactions are carried out under photochemical, rather than thermal, conditions [12]. The rules are formulated in terms of what became known as frontier molecular orbitals; more specifically the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO)—always the p_z π-orbitals on the interacting C atoms. To differentiate between thermally activated and photochemical reactions the former is assumed to involve ground-state HOMO and the latter excited-state HOMO's. Although the rules that derive from this assumption correctly predict the stereochemical outcome of all relevant reactions and rearrangements, the difference between thermal and photochemical activation is never explained. In fact, there is no explanation in terms of the orbital picture. Recall that the polar p_z direction in a real Cartesian set is not fixed, but may be assigned arbitrarily.

To make sense of these rules it is noted that photochemical activation implies the transfer of electromagnetic angular momentum of $\hbar$, resulting in an activated state, not accessible to thermal activation, by inversion of the spin axis:

$$2p(\uparrow) + \hbar \rightarrow 2p(\downarrow)$$

that directly explains the different effects of thermal and photochemical activation. Favourable spin pairing in thermal activation depends on whether the reaction sites are separated by an odd or even number of double bonds, as set out in the empirically established stereochemical rules. These rules remain the same as before, but now they depend on the direction of the orbital angular-momentum vector, which is undefined in the hybridization scheme.

To put the situation into proper perspective it is important to note that a polar direction, associated with a rotating radical such as $-CR_2\cdot$, is defined by the orientation of the spin axis of the unpaired electron, with respect to the set of quenched angular-momentum vectors, $m_l = \pm 1$. This direction remains correlated with all similarly paired vectors in a conjugated system, to constitute a theoretical basis for the empirical stereochemical rules.

In the hybridization model a p_z-orbital is assumed to define the polar direction while it remains fixed by overlap within a π-bond. Once the π-bond is ruptured, as in the postulated valence state, the polar direction disappears, and with it the "symmetry of the frontier orbital". The assumed algebraic signs of the orbital lobes therefore have no meaning and cannot underpin the stereochemical rules.

5.2.6 Atomic Periodicity

At the risk of labouring a point it is emphasized once more that the key to an understanding of chemical structure and change is locked up in the details of the function that determines the periodic properties of atomic matter and the nature of spin. It is abundantly clear from the foregoing that chemistry itself lacks this understanding.

Turning for guidance to the more fundamental discipline of elementary particle physics we learn that [13]:

> …quantum theory describes a world in which a particle really can be in several places at once and moves from one place to another by exploring the entire Universe simultaneously…

but we are reassured

> …that everything is constructed out of a handful of tiny particles that move around according to the rules of quantum theory. The rules are so simple that they can be summarized on the back of an envelope… we do not need a whole library of books to explain the essential nature of things… the more we understand about the elemental nature of the world the simpler it looks.

About the periodic table of the elements we are told how to approach the problem by

> …science rather than numerology… elements 'like' to have all their energy levels neatly filled up.

The experts continue:

> Of course we have not made any attempt to actually compute the energy levels, so we aren't really in a position to rank them in order of energy. In fact it is a very difficult business to calculate the allowed electron energies in

> atoms with more than two electrons, and even the two-electron case (helium) is not so easy. The simple idea that the levels are ranked in order of increasing n comes from the much easier calculation (sic) for the hydrogen atom, where it is true that the $n = 1$ level has the lowest energy followed by the $n = 2$ levels...

It is not made clear how, in this instance, science outperforms numerology or particle physics chemistry. It is hard to spot the "simple" quantum picture of periodicity revealed by the particle model, and we leave it at that.

5.3 Conclusion

The simple fact is that the accepted electron configurations of all atoms are known empirically from the results of atomic spectroscopy. The familiar atomic states dubbed s, p, d, f summarize the most important spectroscopic analyses. They had been correlated with known features of the periodic table before the development of wave mechanics, not with more nor less success. There is no quantum-mechanical prediction of the periodic law—not even a description to rival that of numerology.

It becomes evident that the discovery of the electromagnetic field resulted in the formulation of a theory that accounts for the discovery in detail. On the other hand, the theory that was formulated to rationalize the periodic table has been less successful. This is not the biggest failure of quantum theory. Its most glaring defect is non-compliance with the theory of relativity. At first glance it is obvious that the major discrepancy between the two theories is one of geometry. The theory of relativity only has meaning in four-dimensional space-time, whereas wave mechanics derives from a three-dimensional wave equation. It will be shown how reformulation in space-time eliminates the discrepancy with relativity, and appropriately developed must surely obviate the assumption of a particle that occupy all of space for all time. As the seminal theory of chemistry it further calls for a complete redefinition of wave mechanics in a form appropriate for a new quantum chemistry, free of linear combinations of real orbitals. If this could be achieved in four-dimensional space-time the spin function would appear naturally and not by empirical addition.

History shows that paradigm shifts are initiated by exciting new ideas. That is how it happened in the 1950's. A brave new world, inspired by the "triumphant" quantum theory that revolutionized physics, was opening up for a new breed of chemists, with enough momentum to last them for half a century. Where this initiative is now running out of steam with unfulfilled promises, turning back the clock is not an option. To break the shackles of sterile "quantum chemistry" new horizons have to beckon and that is the real challenge facing chemistry in the 21st century.

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Chapter 6
The Forgotten Dimension

Abstract Henri Poincaré, one of the pioneers of relativity theory predicted that, for the sake of simplicity, physicists would never abandon Euclidean geometry. It is argued here that chemical theory has stagnated for the same reason. It is pointed out how a fresh approach in four-dimensional non-Euclidean space-time could eliminate most of the conceptual stumbling blocks that inhibit the growth of a non-classical theory for chemistry. Immediately foreseen benefits include an understanding of four-dimensional action, recognized as the spin function, to replace the unrealistic concept of orbital angular momentum associated with standing electron waves. The controversial issues of non-local interaction and the discrepancy with relativity resolve themselves, giving new meaning to the concept of quantum potential energy. Without the debilitating assumption of point particles problematical issues such as the exclusion principle, wave-particle duality, quantum probability, the measurement problem, uncertainty principle, molecular shape and the mysterious fine-structure constant, also disappear. An alternative wave model is introduced and shown to be consistent with elemental periodicity as it occurs in projective space-time, which is briefly discussed.

6.1 Introduction

Scientific evidence that we live in a four-dimensional world has been around for more than a hundred years. Manifestations of a 4D space-time continuum include the electromagnetic field and the generation of nuclear power. Although the technological byproducts are utilized worldwide, theoretical science is practiced in apparent ignorance of this reality. The space-time concept, which underpins electromagnetism and the interconversion of mass and energy, belies the notions of absolute space and absolute time. However, when time is colloquially referred to as the 'fourth dimension' it is invariably treated as a unique measure, orthogonal to, but distinct from, three-dimensional Euclidean space. This is no different from Newton's world view.

Subconscious efforts to deny the continued adherence to classical ideas generate a lot of learned nonsense about the nature of time. In reality the arrow of time is an illusion, created in the human mind, conditioned to experience the world in three dimensions. During a previous flat-earth epoch the third dimension, which had a

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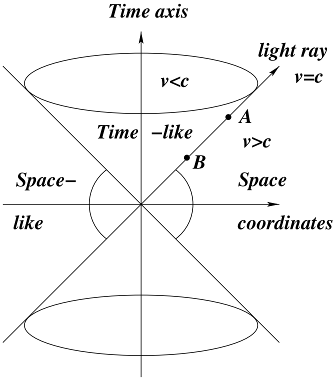

Fig. 6.1 The conventional two-dimensional representation of Minkowski space-time [1, 2]. In four dimensions the light-cone surface appears as a three-dimensional interface that separates time-like and space-like domains, interpreted to be populated by matter and anti-matter respectively

similar function as time today, was confused with the illusion of eternal heaven (above) and hell (below). One-dimensional perception probably consists of reality *here*, in magical interaction with an illusive *there*. The zero-dimensional world (of plants and animals) is static for all practical purposes.

It is obvious that $3 + 1$ dimensional science has reached its logical limit. Theoretical physics arrived at this conclusion long ago and decided to make a bold jump to many-dimensional hyperspace of string theory, apparently without getting to terms with 4D space-time first. To my mind the chemistry community would be ill-advised to blindly imitate physics again. A more prudent response would be conservative progress, not to $10 + \mathrm{D}$ theories, but towards a better understanding of 4D space-time. The most difficult concept to digest is that in such a 4D world there is no past and no future, only the dynamic present. Motion acquires a subtle new meaning distinct from the vulgar perception described by Newton's laws in three dimensions. This strange notion is illustrated most vividly with the aid of a two-dimensional Minkowski diagram shown in Fig. 6.1. The 4D interval between any two points (A and B) within the surface of the time cone,

$$d = \sqrt{(\Delta x)^2 - (\Delta ct)^2} = 0. \tag{6.1}$$

What is described in 3D as a running wave that moves from A to B with velocity c is represented in 4D by a standing undulation that connects A to B. The constant c in this context is a simple dimensional conversion factor, required to express time and space variables in the same units, *i.e.* $x_0 = ict$. The recognition of *bradyons* and *tachyons*, traditionally defined by reference to entities that propagate through three-dimensional space with speeds of $v_b < c < v_t$, relate in 4D to their location with respect to the surface of the time cone, occurring at radial distances of $d_b < 0 < d_t$ from the origin; identified in 3D parlance as time-like and space-like.

The major advantage of the 4D interpretation is the uniform description of standing and running waves. In 3D analysis running waves propagate against boundary conditions at infinity. In contrast, the 4D equivalent occurs as standing waves between emitter and acceptor. The zero-point motion of 3D vibrators relates to the time component of any event in 4D space-time.

6.2 The Classical World

Strange as it sounds, traditional wave mechanics is based on the same world structure of absolute space and time assumed by Newton. It is inherent in both cases that beyond the mathematical principles of their philosophies there is no further understanding of matter and its interactions. The main purpose of Newtonian mechanics was to account for gravitational attraction whereas wave mechanics was aimed at intra-atomic interaction. In both cases the mathematical model accounted for the important characteristics of the interaction without elucidating the underlying physics at all. The unpalatable inference in both instances was that the source of interaction mysteriously resided within the elementary particles of which matter is made up.

The wave functions, assigned to elementary particles, did very little to explain the nature of quantum-mechanical interaction and the origin of matter remained an unsolved mystery. In fairness it should be pointed out that Schrödinger conducted a spirited defence of a proposed wave model of matter [3–5] as an alternative to the uncertain particle model, in a devastating, though ineffectual, demolition of the positivist concepts such as 'probability waves', energy parcels, quantum jumps and the creation of observable states through measurement; but finally overruled by the Copenhagen orthodoxy—the standard model of quantum mechanics.

6.3 Non-classical World

The final break with Newtonian science should have occurred with the announcement of the general theory of relativity (GTR). However, in the euphoria generated by the discovery of a mathematical model that accounted for elementary atomic spectra, it was seen as the final and definitive model of quantum events—at the same fundamental level as GTR, despite a serious interpretational problem.

A series of debates around the probabilistic Copenhagen interpretation was considered to be settled by consensus in favour of Bohr [6] and the Copenhagen model. As this was followed by an empirical modification of Schrödinger's equation [7] to render it Lorentz invariant, and mathematical 'proof' of quantum theory as the ultimate rubric of physical reality [8], the issue became beyond dispute. This delusion has dominated theoretical physics to this day, with chemistry and cosmology dutifully in tow. As a result chemistry is without a theory and cosmology in chaos [9].

The fatal, but rarely recognized, defect of quantum mechanics, that accounts for all its aberrations, lies in its failure to reflect, not only the 4D nature, but also the positive curvature of space-time as revealed by GTR. Although standard analyses of GTR traditionally only emphasize the importance of space-time curvature as the generator of gravitational fields, it is equally important as a source of ponderable matter. The reciprocity between curvature and matter is the telling argument that elucidates the nature of elementary stuff. Whatever the essence of the space-time medium, whether described as vacuum or the aether, it is the only possible source of matter and energy. The field equations of GTR show that flat Euclidean space of zero curvature is matter free and that non-zero space-time curvature is balanced by the appearance of matter.

Existence of the material universe confirms that space-time is permanently curved. As a heuristic exercise the curving of flat Euclidean space may be considered to generate persistent space-time wrinkles, observed as elementary wave-like units of matter. Empirical evidence points at the occurrence of localized units with characteristic mass, charge and spin, depending on intrinsic wave structure. These material units may be likened to 4D wave packets immersed in, and interacting with, an energetic field of standing waves.

In agreement with Schrödinger's interpretation [3] photons, as energy parcels, are undefined in this model which has more in common with the interaction theory of Wheeler and Feynman [10]. The standing wave between two electronic wave packets at the same potential is known as a virtual photon in elementary-particle physics. Energy transfer between electrons at different potentials (states of vibration [3]) occurs according to Schrödinger's resonance model [3], limited by space-time resistance of $c = 1/\sqrt{\epsilon_0\mu_0}$.

The conjecture that both gravitational and electromagnetic fields could be due to space-time curvature developed in the hands of Weyl and Schrödinger into the concept of gauge symmetry. The seminal demonstration [11] that an electron, endowed with a variable complex phase, must develop the vibrational states in a central field commensurate with the energy levels that occur in the Bohr model of the hydrogen atom, enabled the textbook formulation of the electromagnetic field as a Minkowski four-vector, $\boldsymbol{V} = (A_x, A_y, A_z, i\phi/c)$.

Reformulation of GTR on projective space-time topology, in which the gauge principle appears naturally, was shown [12] to define a combined potential field of 15 variables that represents both gravity and electromagnetism. Of these the gravitational field requires 10, the electromagnetic field 4, and the extra parameter distinguishes between the worlds of matter and antimatter. The indisputable 4D nature of the electromagnetic field is interpreted as a firm indication that electronic behaviour can only be understood by its response to a 4D potential field. Projection of the projective electromagnetic potentials into three-dimensional tangent space revealed the interesting result that the golden ratio appears as conversion factor [9]. This property will be shown to underpin the utility of the golden parameter in the modelling of chemical interaction.

6.3.1 Potential Theory

Potential energy in mechanics is described by a scalar field represented by a simple number at any space-time point. Familiar examples include the displacement of a string or a membrane from equilibrium; the density, pressure and temperature of a fluid; electromagnetic, gravitational and chemical potentials. All of these fields have the property of *invariance* under a transformation of space coordinates. The most important property of a scalar field is expressed in terms of its second derivatives. From the definition of a force, defined as

$$X = -\frac{\partial V}{\partial x}, \quad \text{the gradient of the force follows as} \quad \frac{\partial X}{\partial x} = -\frac{\partial^2 V}{\partial x^2}.$$

Laplace's equation $\nabla^2 V = 0$, or its equivalent in any number of dimensions, therefore describes a system of balanced forces in a potential field.

The solutions of Laplacian equations are known as harmonic functions. The one-dimensional equation

$$\frac{d^2 V}{dx^2} = 0$$

has the general solution, $V = mx + b$, the formula of a straight line. The two arbitrary constants are fixed by appropriate boundary conditions. This simple solution illustrates two important properties of general harmonic functions: The value of V at x is the average of its values on opposite sides of x, and secondly there are no local maxima or minima—extreme values of V only occur at the end points. An example of a two-dimensional harmonic system is represented by a thin rubber sheet or a soap film stretched over an irregular support, such as a distorted ring. The most celebrated solution was obtained by Laplace to model the tidal wave motion of a flooded planet. We look for solutions of the equation

$$\frac{\partial^2 V}{\partial x_0} + \frac{\partial^2 V}{\partial x_1} + \frac{\partial^2 V}{\partial x_2} + \frac{\partial^2 V}{\partial x_3} = 0$$

to model the behaviour of a 4D electronic wave packet at equilibrium.

6.4 The Spin Function

Jean d'Alembert's equation:

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 \Phi}{\partial t^2} = 0$$

considered to define a product function

$$\Phi = X(x) \cdot Y(y) \cdot Z(z) \cdot T(t)$$

with the Minkowski condition $ict = x_0$, *i.e.*

$$\Box^2 X_\mu = 0 \tag{6.2}$$

rearranges into:

$$\sum_{\mu=0}^{3} \frac{1}{X_\mu} \frac{\partial^2 X_\mu}{\partial x_\mu^2} = 0.$$

Each term is a function of a single variable and independent of all others, which implies that it equals some constant.

The individual terms therefore resemble Helmholtz's equation

$$\frac{\partial^2 X}{\partial x^2} = k^2 X,$$

which can be solved directly. The overall condition for solution of (6.2) is

$$\sum k_\mu^2 = 0.$$

For all k_μ real it is therefore required that $k_0 = k_1 = k_2 = k_3 = 0$, whereby the overall solution is obtained as the product of four simple harmonic functions.

Alternatively with $k_0 = k_1 = 0$, $k_2 = ik_3$ the standard wave solution is obtained as the product of a Laplacian and a temporal Helmholtz function, *i.e.*: $\Psi = \psi \cdot e^{i\omega t}$. The Laplacian is the product of a two-dimensional and a simple harmonic function. This is the form in which it appears in Schrödinger's equation, interpreted in the central field as the three-dimensional angular-momentum function. There are several problems associated with this interpretation:

1. In polar coordinates the Laplacian is separated into functions of the angular variables θ and φ, with eigenvalue solutions characterized by the quantum numbers l and m_l, such that m_l ranges from $-l$ to l. The quantum number $l = 1$ defines the three-fold degenerate set of eigenfunctions, designated p. The quantum number $m_l = 0$ defines a real function ($k_1 = 0$), whereas $m_l = \pm 1$ corresponds to a pair of complex functions ($k_2 = ik_3$) which describe axial rotations in opposite sense. The interpretation of non-zero orbital angular momentum for the function with $m_l = 0$, which defines zero angular momentum, has caused considerable agony amongst quantum theorists [13]. The fact is that $m_l = 0$ describes simple harmonic motion, which consists of vibration rather than rotation, as explained above.
2. It is well documented [14] that quantum-mechanical orbital angular momentum is not a conserved quantity. A proposed remedy [14] is the *ad hoc* addition of spin angular momentum as a mysterious non-classical component on noting that classical angular momentum, $\boldsymbol{L} = \boldsymbol{q} \times \boldsymbol{p}$, vanishes for a point particle ($r = 0$).

The anomaly is explained much better as a consequence of the separation of variables in the Schrödinger analysis. Conservation of non-classical angular momentum is a manifestation of the isotropy of space-time. By separating out the time variable only the three-dimensional Laplacian harmonic function, which describes the isotropy of tangent space only, survives, and the time-like component is lost.

An alternative strategy for solving (6.2) is by defining two pairs of complex function on setting $k_0 = ik_1$, $k_2 = ik_3$. The second pair defines the classical angular momentum as before and the first pair, which combines one space coordinate and the time coordinate, defines a rotation that involves the time coordinate. This leads to the appearance of *spin* angular momentum in the form [15] of the spinor

$$\begin{pmatrix} 0 & e^{-i(\omega t - kx)} \\ e^{i(\omega t - kx)} & 0 \end{pmatrix}$$

which is traditionally added by hand to account for the spin quantum number $m_s = \pm\frac{1}{2}$. In this formulation one of the space directions is arbitrarily selected as a polar direction in space, traditionally defined as the z-axis. Dirac's equation [7] describes point particles in terms of a relativistic Hamiltonian with assumed plane-wave solutions and linearized by choosing Pauli's spin matrices as coordinate coefficients. This procedure relies effectively on the separation of space and time variables.

The most general solution of (6.2) does not provide for any such polar direction, which may be assumed to occur only in a magnetic field. This solution, obtained without separation of the variables has the form of a quaternion [15]:

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

in which $\boldsymbol{i}$, $\boldsymbol{j}$ and $\boldsymbol{k}$ are generalizations of $\sqrt{-1}$ in the form of quaternion units, in matrix notation: $\mathbf{1} = \left(\begin{smallmatrix} 1 & 0 \\ 0 & 1 \end{smallmatrix}\right)$, $\boldsymbol{i} = \left(\begin{smallmatrix} i & 0 \\ 0 & -i \end{smallmatrix}\right)$, $\boldsymbol{j} = \left(\begin{smallmatrix} 0 & 1 \\ -1 & 0 \end{smallmatrix}\right)$, $\boldsymbol{k} = \left(\begin{smallmatrix} 0 & i \\ i & 0 \end{smallmatrix}\right)$. These units define the rotations of $\mathbb{C}^2$, known as the special unitary Lie group SU(2), which describes the four-dimensional spin function.

The spin function has no polar direction. It describes rotation about a point rather than an axis, and is known as *spherical rotation*. It is demonstrated in three dimensions by the famous 'plate trick' of a dexterous waiter with a plate of soup. Another well-known characteristic of an object in spherical rotation is that, although it initially gets entangled with the medium, it unwinds periodically on completion of each cycle of rotation through 4π radians. The half-frequency undulation in a supporting medium is correctly described by the half-integer quantum number [16]. This means that a four-dimensional wave packet (*e.g.* an electron) with spin moves freely through the vacuum without shearing.

Finally, four-dimensional quaternion rotation also describes the Lorentz transformation of special relativity, which demonstrates its equivalence with quantum theory.

6.4.1 Four-Dimensional Action

In the atomic models of Bohr and Sommerfeld, which describe the motion of orbiting particles, it is appropriate to interpret the action of the system as angular momentum. The unfortunate practice to impose this concept on the Schrödinger model has caused a lot of unnecessary confusion. The Schrödinger equation describes an electron as a standing wave, without kinetic energy or angular momentum, and represents a spherical charge distribution. Interaction of the wave with an electromagnetic field, in either absorption or emission, is described by a change in the action of the system, and observed as a distortion of the spherical symmetry. The effect of such interaction may be visualized by analogy with the tides created by the gravitational field of the moon.

Four-dimensional action, defined here by the spin function, is to be understood in exactly the same way as describing the process of electromagnetic interaction, observed as the transition between different action states. In the Copenhagen interpretation this process is called a quantum jump.

6.4.2 Spin Correlation

Without understanding spin as a four-dimensional effect it is not surprising that another debate, about the mooted non-locality of quantum theory, has remained inconclusive. It started out as an argument about the predicted behaviour of a previously correlated system according to special relativity and quantum mechanics respectively. The succession of contradicting thought experiments presented by Einstein [17] and Bohr [18] makes interesting reading [19] but never revealed anything fundamental about the presumed quantum-measurement problem. After the intervention of Bell [20] the moot point was redefined as the alternative between non-local quantum theory and local realistic theory. Countless analyses of the problem have been published from many different points of view, including a contribution by the present author [16]. In view of the new insight gained into the four-dimensional nature of quantum events those conclusions can no longer be supported and the entire debate is now considered irrelevant.

In this context it is the Copenhagen interpretation of quantum measurement which is once more at issue, rather than non-locality. According to Bohm [21] and Bell [20] only one of the three independent orthogonal components of electron spin can be resolved at any time and according to Copenhagen each of them acquires a sharp value of $\pm\hbar/2$ only when measured. Any correlation between $\sigma_x(A)$ measured at point A and $\sigma_y(B)$ at B, for a previously associated pair, must then be ascribed to non-local communication between A and B.

This argument only holds if the 4D spin function is mathematically separated into one-dimensional projections for which there is no physical justification. The decomposition of a binary unit, stabilized by 4D spin pairing, must result in two complementary quaternion spinors. Unless one of them is disturbed by some external agent their spin functions must remain correlated, irrespective of locality. It follows that simultaneous, even non-aligned, spin measurements at A and B must both reflect the characteristics of the original complementarity, which for some creates the illusion of non-local communication.

6.5 The Time Enigma

One of the strangest results of special relativity shows that some velocity, $v < c$, can always be found such that the time difference between any two space-like events must vanish [22]. For light-like events ($v = c$) this means that two world points receding at the relative three-dimensional speed of light remain in physical contact, which amounts to the standing wave, commonly interpreted as photon-mediated interaction in an electromagnetic field. On the other hand, two general space-like events can only occur simultaneously for relative velocities $v < c$. For time-like separations between events there is no Lorentz transformation that will make them simultaneous.

The popular explanation of EPR-type correlations in terms of the non-local collapse of a wave function is therefore ruled out both ways. This result supports the previous conclusion that correlated spin measurements do not imply nor need an explanation in terms of non-local interaction. In this connection it is instructive to note the final sentence of the EPR paper [17]:

> While we have thus shown that the wave function does not provide a complete description of the physical reality, we left open the question of whether or not such a description exists. We believe, however, that such a theory is possible.

The prescription proposed here for non-classical chemical systems in 4D Minkowski space-time comes close to such an alternative. Probably even closer than Bohm's hidden-variable proposal [23, 24] on which Einstein commented in a letter to Born[1] [25, p. 252]:

> Hast Du gesehen, daß der Bohm (wie übrigens vor 25 Jahren schon de Broglie) glaubt, daß er die Quanthentheorie deterministisch umdeuten kann? Der Weg scheint mir zu billig.

In Bohr's response [18] to the EPR analysis it was argued that the experimental arrangement and results constitute a whole that is not further analyzable. Hence it is impermissible to attribute independent reality to the properties of separate particles. This view, although in line with the natural correlation proposed here to persist in unseparated Minkowski space-time, does not eliminate the locality problem as the measurements may be spread non-locally.

The entangled time component makes all the difference. It resolves the EPR paradox, vindicates the view that quantum theory is incomplete, but shows that the presumed non-local EPR correlation is an illusion created by projection into three dimensions.

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[1] Have you noticed that Bohm believes (as de Broglie did, by the way, 25 years ago) that he is able to interpret the quantum theory in deterministic terms? That way seems too cheap to me.

6.5.1 Quantum Potential

In view of the foregoing, designation of the quantum potential, implied by the hydrodynamic [26] and hidden-variable [23, 24] interpretations of Schrödinger's equation, as a non-local phenomenon, should also be reconsidered. Quantum potential is defined in terms of the amplitude function, R, as

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

It is generally agreed that as the potential contains R in both numerator and denominator it does not necessarily fall off with distance. In the case of a many-body system it therefore means that the interaction between the bodies in the extended system can be described as *non-local* [27].

For an object like a free electron, confined to a sphere of radius r_0, the ground-state energy $E_0 = h^2/8mr_0^2$, interpreted [28] as $V_q = E_0$, implies

$$\nabla^2 R + (\pi/r_0)^2 R = 0$$

which is solved by spherical Bessel functions, the Fourier transform of which describes a limiting sphere of uniform density. It is readily shown [9] that for a sphere of radius r, $V_q = \hbar c\alpha/2r = K/r$, where α is the usual fine-structure constant.

This result may be interpreted to define a non-local quantum-potential field, inversely proportional to the radial extent of the system of interest. It only disappears at infinity, which will be argued to be cosmologically undefined in curved space-time. In the case of a many-body system V_q depends on the coordinates of all bodies. Disturbance of one part therefore affects the entire system holistically and interaction in the extended system may be described as non-local. However, it is debatable whether it also means *instantaneous* interaction at a distance.

There is no apparent reason why these conclusions should be radically different in four-dimensional analysis. In view of (6.1) it appears likely that the holistic interaction amounts to all parts of the system being in effective contact, which defines the quantum potential also as a four-dimensional relativistic phenomenon. It therefore needs to be emphasized that such non-local 4D interaction, mediated by the quantum-potential field, is fundamentally different from the postulated EPR-type interaction, which is understood to impose a previously non-existent attribute on some system by an unrelated remote measurement.

We now conjecture that a 4D quantum potential pervades any isolated holistic unit at a constant level, inversely proportional to the radial extent of the system. Holistic units such as electron, atom, molecule and nanoparticle are stabilized by progressively weaker quantum potentials that operate over increasingly longer ranges. This trend extends to larger units such as solar system, galaxy and the observable universe as $V_q \to 0$. It is an interesting possibility that telepathic interaction and telekinesis through a universal information field could be of this type.

On a more practical note the quantum potential of an atom, activated into its valence state, can be shown [29] to define the classical empirical concept of electronegativity. Reduction of this useful concept to a fundamental basis immediately elucidates the nature of covalence and of chemical affinity at the same time. Recall that quantum potential represents the essential difference between classical mechanics as embodied in the Hamilton–Jacobi equation and non-classical wave mechanics according to Schrödinger. Explanation of electronegativity in terms of V_q therefore contradicts the popular notion, often stated by quantum theorists [30], that traditional chemical concepts such as molecular chirality and chemical potential

> . . . have served a noble purpose in the past but. . . they are now obsolete

and without meaning in modern quantum chemistry. As a possible remedy it was proposed [30] to formulate an algebraic theory of chemistry that recognizes both classical and non-classical variables, noting that

> [p]ioneer quantum mechanics in any of its proposed interpretations has an agonizing shortcoming: *it cannot describe classical systems*. [Original emphasis.]

This pessimistic view is effectively refuted if it can be demonstrated that a non-classical 4D formulation eliminates most of the irrational features of conventional quantum theory.

6.5.2 Time Flow

The elementary demonstration that independent observers in relative motion through Minkowski space-time cannot agree on the simultaneity of events is of fundamental importance for the understanding of time flow. It means that certain events in the past of one observer lie in the future of another, and *vice versa*. This observation conflicts with the common understanding of the recorded past as being fixed and for ever beyond dispute, whereas the unknown future is totally uncertain and unpredictable. In other words, what may appear to be completely uncertain could already be firmly established by observation elsewhere.

The only logic behind this paradox is that there is no difference between past and future. Any two points in time, whether past or future, coexist in the same way as two points separated in space. Transplantation between time-separated points appears equally feasible in both directions, but the situation may be more complicated in a non-Euclidean space-time manifold. Not only the ‘arrow of time’, but also the quantum-mechanical ‘uncertainty principle’ may hence be recognized as illusions created by projection into Euclidean tangent space.

The equation $\Box^2 V = 0$ describes a 4D potential field with a constant gradient tensor. In physical reality such a field has no maxima or minima, except at its boundaries, if any. A closed system, such as the surface of a sphere has no boundaries and the gradient defined by the curvature of the surface (known as the curvature tensor) is constant at all points and in all directions in the surface. Any object, which responds to the gradient, once activated, will maintain indefinite inertial motion in the surface.

The four-dimensional equivalent is topologically known as either a 4D hypersphere or a *3-sphere*. Using this as a model of space-time the GTR predicts the generation of matter that would locally modify the gradient. The accumulation of elementary matter into massive units causes distortion of the potential function, resulting in local minima, which act as attractors for other matter, observed as a gravitational field.

Newton's law of gravity treats the gravitational potential as an inverse-square function of space coordinates only. This implies that inertial displacement in the direction of the time axis (ict) continues unabated. This is consistent with the sensation of time flow and the basis for postulating an arrow of time. The argument is certainly valid at a high level of approximation, but mathematical analyses of the interactions in a black hole suggest that non-inertial time flow occurs in strong gravitational fields [31].

The concept of motion is not to be confused with time flow. Motion only acquires meaning by reference to other objects which respond differently to a potential field and act as coordinate markers. An isolated observer has no means of distinguishing between different states of inertial motion, including quiessence. For such an observer time has no meaning. The sensation of time flow is therefore best described as an emergent function of the environment. In this sense it has much in common with the three-dimensional structure of a molecule. Not surprisingly, both concepts are intimately related to the mysterious notion of entropy, another manifestation of space-time curvature.

Chemical practice happens in tangent space, but theoretical analysis of the data, like sub-atomic physics and astronomy can no longer afford to ignore the effects of space-time curvature.

6.6 Space-Time Curvature

A regular one-dimensional object without beginning or end is defined as a circle or a 1-sphere. The equivalent two-dimensional object, represented by the surface of a globe is called a 2-sphere. The surface of a 4-dimensional globe or hypersphere is known as a 3-sphere. This is the construct that Einstein envisaged as a model of the universe [32]. It is important to note that this object is defined in terms of four orthogonal spatial coordinates, to which Einstein added a universal time coordinate as a fifth dimension in order to formulate a sensible geometrical model.

Einstein's contemporary, Willem de Sitter, considered a 3-sphere defined by 3-space and one time coordinate, embedded in 5-dimensional space [33]. As an alternative Herman Weyl suggested a four-dimensional analysis in which the 3-sphere is separated into one-dimensional time and a 2-sphere in 3D space.

In order to stabilize Einstein's model it was necessary to introduce an additional parameter, the so-called cosmological constant. To stabilize de Sitter's model it is necessary to eliminate all matter and to modify the assumed 3-sphere into projective space [9]. Weyl's proposal leads to the Robertson-Walker metric which forms the basis of expanding universe cosmology and the big bang. Of these it is only de Sitter's model that incorporates the idea of curved space-time. However, the non-appearance of matter shows that 3-sphere topology does not represent the universe as observed.

6.6.1 Space-Time Topology

The topology of space-time is another of those concepts presumed to defy comprehension. However, behind the folklore there are some powerful indicators identifying a simple logical resolution of the problem. By the GTR space-time is **known** to be four-dimensional and curved. The Euclidean alternative favoured by standard cosmology can therefore be rejected out of hand. The only alternative that avoids mathematical infinities is a closed system which allows only one of two possibilities: the 3-sphere and elliptic (or projective) space with a continuous group structure in the form of the Hamiltonian quaternion [34], encountered before as the rotation that defines both the Lorentz transformation of special relativity and the spin function of 4D quantum theory. In addition, the periodicity of atomic matter has been shown [35] to be a function of projective geometry. Internal evidence from mathematics, physics and chemistry therefore points at a universe closed in projective space-time.

It becomes increasingly evident that the non-classical theory of chemistry is anchored in a four-dimensional potential function of projective space. Although a mathematical formulation may be moderately feasible, physical visualization borders on the impossible. At the risk of oversimplification a two-dimensional analogue may provide a qualitative illustration of some important points. The most convenient illustration is provided by a Möbius strip which may be considered as sliced from a projective plane.

A Möbius surface is mathematically described to be of zero thickness and considered to turn into itself through an involution. As a practical model it is more appropriate to consider a Möbius band as consisting of a double cover on the mathematical surface as interface to define a single, non-orientable surface that covers the interface on two sides as in Fig. 6.2.

Not only does a Möbius band have a single surface, but also a single edge, which is readily ascertained by inspection. In order to create a closed projective surface from a Möbius band it is only necessary to start from any point in the edge and stitch the two sides together, all the way back to the starting point. This operation, which requires that the band eventually intersects itself, turns out to be impossible in three-dimensional space.

Transplantation of a vector, oriented with respect to the surface, along the double cover, results in the inversion of the vector as it rotates through 2π to a point

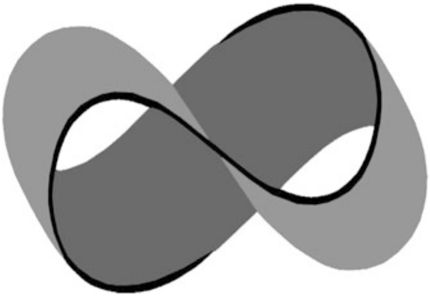

Fig. 6.2 Three-dimensional section through a four-dimensional projective plane to illustrate the property of a one-sided non-orientable surface

on the opposite side of the interface. The original orientation is restored after another 2π rotational displacement. The formal relationship with the spin function is immediately obvious.

Because of the involution a projective model of space-time would be self-destructive. More appropriately, the double cover has several attractive advantages as a 4D model universe, wrapped around a three-dimensional interface that separates a chiral world from an enantiomeric anti-world [36]. Longitudinal displacement within the double cover causes a gradual change of chirality, transforming matter into antimatter after rotation of 2π. The interface which is achiral by definition may be identified with the Minkowski light cone in curved space-time [9]. In this sense it is the abode of boson radiation which separates fermions and bradyons from anti-fermions and tachyons.

Projective geometry differs from its Euclidean counterpart by redefinition of parallelism as the intersection of straight lines in a single point at infinity. This modifies the stipulation of point positions through the addition of an extra coordinate in a homogeneous set. Four-dimensional projective space-time is thereby described in terms of five homogeneous coordinates. The effect of this is that the geometry has no metric and hence any parameter may be multiplied by an arbitrary factor without affecting its meaning. This so-called gauge factor turns out to be the same as the complex phase of wave mechanics [11] and the electromagnetic field.

The power of projective geometry in the unification of the gravitational and electromagnetic fields was recognized many years ago by Oswald Veblen [12]. At about the same time a regular five-dimensional model, shown by Kaluza [37] and Klein [38, 39] to effect the same unification, was considered less complicated than the projective model, which lapsed into oblivion. Where Kaluza's model failed the projective formulation produced a relativistic wave equation in tensor notation [40] which could be reduced to the standard form in affine space. What went unnoticed at the time was the relationship between the factors that convert potential functions from projective to affine space and the golden ratio [9]. This opens up an entirely new perspective on the relationship between four-dimensional space-time and tangent three-dimensional Euclidean space, which suggests the modelling of self-similar chemical and astronomical systems by the methods of number theory.

Support of this idea is provided by the successful simulation of the periodic table of the elements as a subset of a more general periodic function, conditioned by space-time curvature, in terms of Farey sequences and the golden ratio [35]. It reveals the same Möbius involution between matter and antimatter noticed before.

The only known attempt to derive an atomic model from GTR is due to Einstein and Rosen [41] who defined physical space as consisting of two congruent sheets connected by "bridges". Massless particles (bosons?) are identified to occur within these bridges (interface?). To quote:

> ...the electrical particle is a portion of space connecting the two sheets [...] consider the electron or proton as a two-bridge problem. [...] the "charges" of the electrical bridges are numerically equal to one another and only two different "masses" occur for the mass bridges...

Although the conclusions are rather tentative and the physical model rather vague, a close parallel with the projective model proposed here is clearly evident.

6.7 Quantum Effects

When a leading philosopher of science [42] declares that,

> quantum theory—the deepest discovery of the physical sciences—has acquired a reputation of endorsing practically every mystical and occult doctrine ever proposed,

it sounds a warning which cannot responsibly be ignored. When the same savant continues to *explain* quantum theory, in even more bizarre terms, as the histories of an elementary particle over an infinitude of inaccessible multiple universes, one stands aghast. This is the theory that was borrowed in good faith from physics and relied on by the chemists of the world as the infallible quide that underpins their pursuits.

In reality theoretical chemistry has not advanced beyond the models of chemical affinity and molecular structure developed during the 19th century. There has been a lot of handwaving with brave talk about quantum chemistry that found its way into all modern textbooks, to the annoyance of a small minority who tried in vain to encourage the development of alternative relevant theories. The constant stumbling block has been the proclaimed magic and mystique of quantum mechanics. We now re-examine a number of the concepts that sit uneasily with the practice and theory of chemistry and, where possible, show how these are avoided in the four-dimensional approach.

6.7.1 Exclusion Principle

The exclusion principle was established in an effort to bring quantum theory in line with the periodic table of the elements. The relationship was correctly formulated by Stoner [43] as follows:

> The number of electrons in each completed shell is equal to double the sum of the inner quantum numbers.

This is to be interpreted as double the total number of levels corresponding to the allowed values of the quantum number m_l for each value of the principle quantum number n. This rule was empirically ascribed by Pauli [44] to the appearance of a new two-valued quantum number for each electron, which effectively doubled the number of energy levels per shell. An improved formulation of the effect was provided by Dirac [45] on demonstrating that the two-valuedness was implied by an anti-symmetrical total electronic wave function.

The implication is that the interchange of any two indistinguishable electrons in a system must result in the inversion of their eigenfunctions,

$$\psi_T = \psi(q_1, q_2)\psi_4 = -\psi(q_2, q_1)\psi_4.$$

Equating $q_1 = q_2$ implies $\psi_T = 0$, which shows that two electrons in the same quantum state cannot be at the same point in three-dimensional space. The standard form of the exclusion principle is still stated as the requirement that electrons be described by anti-symmetrical eigenfunctions, compared to photons in symmetrical states. The fourth quantum number ψ_4 is now equated with the spin quantum number $m_s = \pm\frac{1}{2}$, but there is still no fundamental explanation of the anti-symmetry of the wave function and the exclusion principle remains an emergent property of fermions [46, 47].

Viewed as a four-dimensional effect the exclusion principle assumes a completely different complexion. Solution of the 4D potential problem leads directly to an exposition of electron spin as a spinor, which is known to reverse sign on rotation through an odd multiple of 2π [48]. Such a rotation is the natural equivalent of what is commonly referred to as the interchange of indistinguishable objects. In this case the operation is mathematically characterized as anti-symmetrical, without assumption and the exclusion principle appears as a fundamental property of fermions in 4D space-time.

It needs to be reiterated that the quaternion operation that defines the spinor is characteristic of four-dimensionally curved projective space-time.

The analysis of covalent interaction in terms of dimensionless variables of interatomic distance and interaction energy [28] reveals the exclusion principle as a restriction on electron density in space as a function of the golden ratio—*ipso facto* as a function of space-time curvature.

6.7.2 Wave-Particle Duality

The conclusion that the exclusion principle allows two electrons with paired spin to occupy the same space should immediately have eliminated the particle description as an acceptable model for fermions. It is an ancient truism that two solid objects cannot be in the same place at the same time. Indeed, the earliest known model, proposed by Lorentz [49] considered an electron at rest as a small rotating flexible sphere, subject to deformation when in a state of motion.

The major difficulty with the Lorentz model was seen as the lack of a mechanism to hold the charge together against Coulomb repulsion and so prevent spontaneous dispersal. The alternative of a point charge was shown by Dirac [50] to generate a problem of equal magnitude in the form of an infinite self energy. To overcome the problem a finite size of the electron with an interior through which signals propagate with superluminal speeds, had to be assumed. Evidently, classical theory has failed completely to postulate an acceptable structure for the electron. Quantum mechanics performed no better.

The only proposal of electron structure to come out of quantum theory occurred in the hydrodynamic model of Madelung [26]. It is identical to the Lorentz model and was rejected for the same reason—failure to account for the non-dispersal of the elementary sub-electron charges of which the electron fluid was assumed to consist.

Although theory failed to account for the structure of an electron, not even the experimental evidence that an electron diffracts like a wave was sufficient to successfully uphold the wave-mechanical model of de Broglie and Schrödinger. As a matter of fact, all of the mystical features associated with quantum theory can be traced back to a stubborn obsession to account for the wave properties of an electron, using a point-particle model. This obsession can now be traced back to the innocent assumption that the wave-mechanical action, defined by Schrödinger's equation, represents orbital angular momentum. Having failed in this and faced with conflicting experimental evidence the only way out, short of abandoning the particle model, was to declare an electron to be a particle and a wave at the same time.

6.7.3 Quantum Probability

During the early 20th century physics was driven by a single-minded urgency to find the ultimate explanation of the quantum phenomenon, which was discovered at the turn of the century. There is no better description of this obsession than by the word *ecstacy*, defined in the Collins dictionary as

> abnormal mental excitement when the mind is ruled by one idea, object or emotion.

Not surprisingly an early success in this quest was greeted *ecstatically*—

> in a state of enthusiastic frenzy or rapture.

What is surprising is that this enthusiasm has still not subsided. Despite well-known defects of the resulting theory, such as its failure to account for electron spin; its irrational account of physical measurement; its definition of a quantum object of non-zero volume (wave) as a localized (zero-volume) object (particle) at the same time; and its discrepancy with the fundamental theory of relativity, a modern quantum physicist [42] declares:

> Quantum theory is the deepest explanation known to science. [...] There is no other.

The problem with quantum theory is rooted in the frenzied search for a fundamental explanation of the stationary states of the Bohr-Sommerfeld atomic model. The ecstatic announcement from Göttingen of a matrix formulation as the final (*endgültig*) truth, almost immediately received a body blow on the publication of the more logical and user-friendly wave mechanics, based on a differential eigenvalue equation. And the gloves came off. To protect their turf the Göttingen school declared wave mechanics an inferior subset of their own *quantum mechanics*. The only problem was to demonstrate how the wave model was a flawed approximation of the more logical quantum jumps of a particle, correctly described by a matrix eigenvalue formulation. All of the mystical features associated with quantum theory originated with this stubborn obsession to account for wave properties, using a point-particle model. Such a particle is obviously required to be in more places than one at any given time. Not quite, but perhaps—probability density was born.[2]

There is nothing in Schrödinger's equation to justify the probability postulate. In fact, a lucid interpretation of quantum effects in terms of *wave packets* to represent both material objects and energy flow was presented early on [3]. Although the concept still features in numerous discussions of quantum events it stands officially discredited because of the dispersion of Schrödinger matter-wave packets. Instead of a careful examination of wave-packet dispersion, the leading quantum theorists adopted an artificial model, designed to simulate a non-dispersive wave packet by a random distribution of mass points.

Dispersion analysis [51] for a system governed by a linear differential equation such as (6.2), is based on the four-dimensional Fourier representations with harmonic functions $e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}$. Whenever a linear *dispersion relation* connects ω and $\boldsymbol{k}$ the system is *non-dispersive*. Such a linear relationship holds for electromagnetic waves in the vacuum. However, in the treatment of matter waves the equation

$$\frac{\partial^2 u(x,t)}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2 u(x,t)}{\partial t^2} = 0 \tag{6.3}$$

is modified according to de Broglie's prescription and solved by separation of the variables, assuming $\Psi(x,t) = \psi(x)\cdot e^{-i\omega t}$. The second derivative

$$\frac{\partial^2 \Psi}{\partial t^2} = -\omega^2 \psi e^{-i\omega t} = -i\omega\frac{\partial \Psi}{\partial t}$$

when substituted into (6.3) yields

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{i\omega}{c^2}\frac{\partial \Psi}{\partial t} = 0$$

---

[2] No pun intended.

and eventually, with $\omega = c\sqrt{2mT}/\hbar$ and $c = \sqrt{T/2m}$, there follows:

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2},$$

the standard time-dependent Schrödinger equation.

As demonstrated before this equation no longer reflects the correct four-dimensional spin function and with its first-order time derivative it has a non-linear dispersion relation, $\omega = k^2/c^2T$. A wave packet constructed from such waves must therefore be dispersive, as reflected in standard textbook statements like, [52] that

> …unfortunately… in general, wave packets change their shapes and flow apart with time…

or more precisely demonstrated [53] that a wave packet, obtained by the superposition of matter waves with $\lambda = 2\pi/k$ and frequency $\nu = (\hbar/4\pi m)k^2$,

> …does not retain its spatial distribution.

The "explanation" [54] that

> [t]he packet… spreads out because of the Uncertainty Principle…

simply puts the cart before the horse.

Commenting on the wave packet, constructed by the superposition of Hermite polynomials, David Bohm [55] states that

> …there is an unusual feature of the motion of this packet, namely it does not change shape with time. Normally, we expect wave packets to spread out with time, but this particular packet does not.
>
> …for a harmonic oscillator and only for a harmonic oscillator can we expect periodic wave packets.

This conclusion is based on the result mentioned by Schrödinger [3] on first proposing the electronic wave model. However, a one-dimensional harmonic oscillator hardly provides a convincing model of a free electron in motion. It remains necessary to formulate a non-dispersive four-dimensional matter-wave packet that resembles classical particles while correctly simulating the behaviour of elementary quantum objects without the need to invoke probabilities. That would eliminate the probability postulate and finally resolve the first Einstein-Copenhagen debate [6], confirm[3] [25, p. 127]:

> …daß der [Alte] nicht würfelt,

explain the quantum measurement problem and rationalize the so-called uncertainty principle.

---

[3] That the Old One does not play dice,

6.7.4 Measurement Problem

The measurement problem of quantum theory is the primary source of a body of pseudo-scientific philosophical fall-out that pervades many fields of enquiry and criticism. In essence, it concerns the subjective role of an observer in the outcome of an objective measurement. It is argued that a quantum system is inherently unpredictable and yields information only through the invasive action of an observer. Such intervention is said to collapse the wave function into one of its eigenstates, irrevocably changing the system in the process.

The exact role of an observer in effecting the collapse of the wave function (or wave packet, according to some sources, *e.g.* [55]) is the subject of intense speculation. There seems to be consensus that some measuring device by itself, without an intelligent operator to register the observation, is not sufficient. It remains mysterious how the measurement of a probabilistic particle's position can produce a sharp result. Copenhagen logic stipulates that it only happens on conscious intervention. That is why [56]

> the moon is demonstrably not there when nobody looks.

Or, even more extreme [57, 58]:

> Observers are necessary to bring the Universe into being.

Others [42] would say that a measurement favours one member of the multiverse, leaving the rest high and dry. However, if all but one of the probability points are fungible, but inaccessible in the universe of interest, then why bother? The result is no different from that predicted by Newtonian mechanics.

With each further step into the unknown quantum models based on the Copenhagen orthodoxy create more problems than they solve. In the case of chemistry, where this theory dictates a point description for molecules with demonstrable non-zero extension, the situation borders on the absurd. Reluctance to challenge authority has created a computational edifice, completely divorced from reality, but dutifully supported by educational institutions around the world. The sad fact is that *quantum chemistry* further dilutes the dictates of elementary wave mechanics to the extent where it operates at the classical level, using unnecessarily complicated algorithms with a vague resemblance to quantum formalism. Mindless extension of such practice to the life and behavioural sciences results in the grotesque philosophies widely claimed to be quantum based. Although quantum effects are real the supporting theories have gone haywire. Blind belief with ecstatic fervour is not the way forward. The time has come to critically re-examine the hasty conclusions of the pioneers and, not only for an alternative explanation, but for a more appropriate formulation of non-classical theory.

In their incisive analysis of the quantum-mechanical measurement problem Bohm and Bub [59] identified as a root cause of the problem the presumed notion of probability which is implicitly incorporated into the standard axiomatic formulation of wave mechanics, *i.e.*:

> The wave function determines the probabilities of the possible results of any measurement on the system.

A measurement, which selects one of the probabilities, is therefore said to “collapse” the wave function into a specific eigenstate. The dilemma exists therein that in the case of an electron passing through a slit system

> *…the electron is somewhere in the region where the wave function is appreciable.*

However, when analyzed in terms of “classical” probabilities, defined as $P(x) = |\psi|^2$, it is shown unequivocally that

> …the particle model fails as a description of the details of the motion of an individual electron…

Without disclosing their operational understanding of an electron the authors continue to state that,

> …since the electron acts like an individual particle […] the wave model also fails to describe the order and structure of this motion adequately.

Although details of the wave model being discounted here are not disclosed it is inferred that

> …a precise conceptual description of the process of measurement in quantum mechanics becomes in principle impossible, so that one gives up all hope of ever being able to obtain a clear conception of the *nature* of the individual electron or how it moves.

Their despair can be appreciated if the authors have in mind the model of the electron as a particle-like localized inhomogeneity, or a small stable vortex, in a continuous fluid [60] that obeys Schrödinger’s equation. The conclusion that [59]:

> There is, however, no solution to the measurement problem within the framework of classical mechanics.

must be endorsed as the only logical one. Classical mechanics is based on the particle concept, identified here as the very item responsible for the measurement confusion. Small wonder that a leading theorist states [61]:

> …I think it is safe to say that no one understands quantum mechanics.

The situation is entirely different in terms of Schrödinger’s interpretation of the wave equation, which is not based on the axiomatic approach. In this case the wave function has more than mathematical significance as it describes a wave packet with postulated physical meaning and well-defined properties of mass, charge and spin. Then there is no need to collapse a wave function in order to perform a measurement and certainly not to collapse a wave packet. The flexible wave packet simply contracts into a virtual point in the field of the measuring device and responds naturally to the electromagnetic field of the probe. A charged wave packet moves through a cloud chamber like a classical particle and leaves a track that maps out the path of its centre of mass, unlike the random walk predicted by the probability model.

An electron on an atom or a crystal does not jump around from point to point. It occurs as a wave packet which is spread across an extended domain in equilibrium with the field of atomic cores. The variation of charge density as measured by X-ray diffraction is described by the wave function as $\rho = |\Psi|^2$, in terms of the internal wave structure of the wave packet. The only problem is to identify a non-dispersive wave packet that correctly models an electron. This problem is addressed in the next chapter.

6.7.5 Uncertainty Principle

Quantum uncertainty is almost as notorious as the measurement problem. It started out as a statement of the way in which a quantum system is disturbed in an unpredictable way by any measurement. However, as this could imply a definite state of the system before measurement it was necessary to redefine measurement as the process of selecting a specific eigenstate from an uncertain set.

Although Schrödinger's interpretation of particles as wave packets was promptly rejected, the model was adapted to rationalize the uncertainty principle, not as a wave characteristic, but as a particle property, for which it makes no sense. In its most abstract formulation the uncertainty principle argued to represent an inherent lack of knowledge about quantum systems, which eventually led to [62]

> …subjectivist rejection of realism, motivated by the belief that a *fundamentally and irreducible statistical physics has to be explained by a fundamental and irreducible barrier to our* (*subjective*) *knowledge…*

The only effect of the hot air produced, by scientists and laymen alike, in countless efforts to decode the uncertainty principle is to cause more confusion. Maybe the time has come to accept the fact that quantum theory has no need of this principle, which in any case carries no new information. At the end of the day all that remains is evidence of the confusion among the scientists who first stumbled upon the spectroscopic formulae at the basis of quantum mechanics. What caused their consternation was the appearance of commutators of the type

$$[p,q] = pq - qp = i\hbar,$$

foreign to classical macroscopic systems. Instead of investigating the mathematics of commutators the founding fathers resorted to metaphysical explanations resulting in what Popper [62] referred to as "the great quantum muddle".

It is now known that the hypercomplex algebra of quaternions is not commutative and the variables that feature in a four-dimensional harmonic equation would hence not commute. There is nothing left to explain. Even in three dimensions any pair of conjugate variables related by Fourier transformation do not commute. Conjugate variables x and k are related by a conjugate transformation specified by the Fourier inversion formulae:

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx} f(x) dx,$$

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{ikx} g(k) dk.$$

Comparing [63] the spread, or dispersion Δx, of a Gaussian function $f(x) = Ne^{-cx^2/2}$ and Δk for its Fourier transform $g(k) = (N/\sqrt{c})e^{-k^2/2c}$, the product $\Delta x \Delta k = \frac{1}{2}$. On demonstrating that no other function has a smaller uncertainty product it is concluded that in general, $\Delta x \Delta k \geq \frac{1}{2}$.

In the case of matter waves where x represents position, k the wave number and $p = \hbar k$ the momentum, it follows that the relationship $\Delta x \Delta p \geq \hbar/2$ occurs as the natural property of any wave. Again, given a viable matter-wave model, there would be nothing to agonize over. The muddle starts when trying to explain this as a particle property.

6.7.6 Fine-Structure Constant

Another item which is often mentioned to highlight the mysterious nature of quantum mechanics is the fine-structure constant, with the provocative value of $\alpha = 1/137$. An award-winning theorist writes [64, p. 129]:

> It (α) has been a mystery ever since it was discovered more than fifty years ago, … is it related to π, or perhaps to the base of natural logarithms? Nobody knows. It's one of the greatest damn mysteries of physics: a magic number that comes to us with no understanding by man. You might say the "hand of God" wrote that number, and "we don't know how He pushed His pencil".

The constant was first introduced by Sommerfeld [65, p. 107] as $\alpha = v_1/c = e^2/4\pi\epsilon_0 c\hbar$ ($=e^2/c\hbar$, in esu), where v_1 is the velocity of an electron in the first Bohr orbit. The joke is that without the Bohr model the meaning of α is indeed unclear, but not as mysterious as made out. Although the unphysical probability particle model offers no alternative explanation a valid interpretation is anticipated to emerge as the property of a non-dispersive wave packet that correctly models an electron. The search for such a model, defined by nonlinear wave functions, continues in the next chapter.

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Chapter 7
Nonlinear Chemistry

Abstract The sensational aspects of quantum theory, from the wave-particle nature of electrons to Schrödinger's cat, are the artefacts that result from describing nonlinear systems by linear differential equations. As linear waves are dispersive, a wave model of the electron is still being rejected, whereas a nonlinear wave model is shown to account for electronic behaviour in all conceivable situations. This chapter introduces the distinction between linear and nonlinear systems with examples from hydrodynamics and mechanics and applied to the wave mechanics of wave packets, solitons, electrons and lattice phonons. Special topics for discussion include the motion of free electrons, the fine-structure parameter, electron diffraction, photoelectric and Compton effects, X-ray diffraction, metallic conduction, superconductivity and elementary covalent interaction. A new innovation, introduced here, is recognition of the quantum potential as a nonlinearity parameter that enables a seamless transition between classical and non-classical systems.

7.1 Introduction

It has been argued [1] that because complex phenomena are so ubiquitous in Nature the common concepts, characteristic of nonlinear behaviour, are not discipline dependent but pertain equally well to problems in physics, chemistry, biology and engineering. Although the general validity of this perception is readily demonstrated, the value of mathematical models that describe nonlinear behaviour has not been recognized to a significant extent in chemistry.

To highlight the chemical relevance of the nonlinearity paradigms developed elsewhere there is no better starting point than the analysis of electronic behaviour, which underpins all of chemistry.

Most electron models, from Lorentz [2] to the present have stumbled on the problem of non-dispersal. Despite the early realization, first verbalized by Stoney in 1891, that an electron features an indivisible unit charge, it has been argued repeatedly that it should blow up under coulombic repulsion. The standard response has been to reduce the electron to a zero-dimensional point object. The problems associated with this as a physical model are infinitely worse; with infinite gravitational and electrostatic fields.

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More recent analyses of nonlinear waves led to renewed interest in wave models of elementary particles, including electrons, in quantum field theory. Nonlinear waves are different, not because they are non-oscillatory, but also because their velocity is amplitude dependent. For linear waves the speed is always independent of amplitude. Any two solutions of a linear equation can be added together to form a new solution. This, so-called, superposition principle enables the solution of essentially any linear problem. Fourier transformation, for instance, depends on such superposition of solutions. In contrast, different solutions of a nonlinear equation cannot be added together to form another solution. A nonlinear problem can therefore not be reduced to smaller solvable problems and without a general analytic approach they are more difficult to solve.

7.2 Wave Model of the Electron

To specify the kinematics of a macroscopic system it is traditionally decomposed into elementary components of rectilinear, rotational and oscillatory motion, described by a set of linear classical equations. In Hamilton–Jacobi theory, aimed at a unified description of many-particle systems, characteristic moving surfaces are shown to propagate through space in the same manner as wave fronts of constant phase [3, p. 487]. It is therefore possible, even in classical mechanics, to recognize a duality of particle-like and wave-like aspects in the motion of macroscopic objects. This conclusion has no implication on the physical structure of the moving object and it is generally conceded that a particulate description is the more appropriate.

The same duality applies to microscopic systems, but in this case the wave nature predominates. Mathematically the only instance where wave and particle descriptions are equally valid is in the case of geometrical optics. Again, this dual formalism does not confer particle nature to physical waves or *vice versa*. On describing wave motion in Hamilton–Jacobi formalism, which is the basis of wave mechanics [3, p. 490], the appearance of particle-like behaviour must be anticipated, without implying that the wave is a point particle.

As commonly conceived a wave is theoretically of infinite extent and a particle has no extent. In this sense the two alternative descriptions of an electron commonly defined as either a particle or a wave are equally unrealistic. Maybe it is for this reason that the Copenhagen notion of an entity with both wave and particle properties is generally more readily accepted. This compromise hints at an object of finite size, widely, but vaguely, rationalized as a wave packet.

The unrealistic wave-particle model of the electron has an interesting history that dates back to the 19th century and Faraday's electrochemical research. It was found that a chemical equivalent of any substance reacts with a fundamental quantity of electricity, $\mathcal{F}$. Interpreted as an electrochemical equivalent it amounts to a charge of $e = \mathcal{F}/L$ per atom, where L is Avogadro's number. Observation of discrete particles with the same elementary charge during radioactive decay confirmed that electric charge is not indefinitely divisible but occurs as discrete units, now known as electrons.

Assuming that the electrostatic charge carried by an electron of rest mass m, is spread over a spherical volume of radius r_0, *i.e.* $mc^2 = e^2/4\pi\epsilon_0 r_0$, the electron is defined as a sphere of mass m and radius r_0 that carries a unit of electric charge. This so-called "classical" radius of the electron is confirmed in scattering experiments.

7.2.1 Wave Mechanics

The simplest example of a linear wave is the so-called sinusoidal wave

$$\phi(x,t) = a\sin(kx \pm \omega t)$$

where a is the amplitude, k and ω, wave number and angular frequency, are related to the wavelength λ and frequency ν by $k = 2\pi/\lambda$, $\omega = 2\pi\nu$. The ± sign specifies waves progressing to the left and right respectively. The speed of the wave is given by $v = \omega/k$. If the velocity of the wave is independent of k and ω, these may be eliminated by differentiation to give

$$\frac{\partial^2\phi}{\partial t^2} = c^2\frac{\partial^2\phi}{\partial x^2} \quad (c = \text{constant}), \tag{7.1}$$

the general wave equation in one dimension. Except for electromagnetic waves in vacuum, all waves in nature show some deviation from (7.1).

Equation (7.1) is linear, which means that if both ϕ_1 and ϕ_2 are solutions, then the superposition $\phi(x,t) = \phi_1(x,t) + \phi_2(x,t)$ is also a solution of (7.1). For linear waves, it is more convenient to use superposition of complex functions

$$\phi(x,t) = a(k)\exp\bigl[i(kx - \omega t)\bigr].$$

The most elementary linear wave is the harmonic wave for which a is independent of k.

The requirement that $\phi(x,t)$ satisfies a linear wave equation depends on the functional relationship between k and ω, known as a dispersion relation. If this relationship is nonlinear the wave is *dispersive*. The phase velocity is defined as $v_\varphi = \omega/k$ and describes how a surface of constant phase moves. The group velocity $v_g = d\omega/dk$ shows how fast the bulk of the wave propagates.

Given some initial data $\phi(x,0) = f(x)$ it is possible to calculate $\phi(x,t)$ for all t [4]. Even though the initial data may not have harmonic form, it may be represented by a Fourier integral

$$\phi(x,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} a(k)e^{ikx}dk$$

where

$$a(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \phi(x,0)e^{-ikx}dx.$$

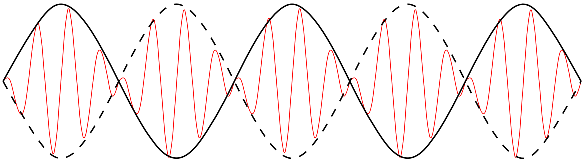


Fig. 7.1 Wave train defined by the superposition of two harmonic waves

For a linear system, $\omega = \omega(k)$, so a solution for all $t \geq 0$ is

$$\phi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} a(k) e^{i[kx - \omega(k)t]} dk.$$

However, in practice neither of these integrals can be evaluated in terms of elementary functions.

Dispersion

The general form of a harmonic wave is conveniently defined as

$$\varphi = a e^{2\pi i(kx - \nu t)}$$

in terms of an amplitude a, wave number $k = 1/\lambda$ and frequency ν. The real part of a complex wave is represented by

$$\varphi = a \cos 2\pi(kx - \nu t)$$

and for simplicity we consider the combination of two such waves with equal amplitudes and nearly equal frequencies [5]. The total disturbance is given by

$$\begin{aligned} \Phi &= a\cos 2\pi(k_1 x - \nu_1 t) + a\cos 2\pi(k_2 x - \nu_2 t) \\ &= 2a \cos 2\pi\big[(k_1 + k_2)x/2 - (\nu_1 + \nu_2)t/2\big] \\ &\quad \times \cos 2\pi\big[(k_1 - k_2)x/2 - (\nu_1 - \nu_2)t/2\big]. \end{aligned} \tag{7.2}$$

The first cosine factor represents a wave, very similar to the original waves with frequency and wavelength at the average of those of the original waves and it moves with a velocity of $(\nu_1 + \nu_2)/(k_1 + k_2)$. For electromagnetic waves this is the same as the velocity of the initial waves, $c = \nu_1/k_1 = \nu_2/k_2$. The second cosine factor changes more slowly with respect to x and t and may be regarded as a varying amplitude. The resultant is a wave of approximately the same wavelength and frequency, but with an amplitude that changes with both time and distance. In Fig. 7.1 the outer profile represents the second cosine term in (7.2).

The dotted profile is the reflection of this curve in the x-axis. The actual disturbance Φ lies somewhere between these two boundaries, cutting the x-axis at regular intervals, and touching alternately the upper and lower profiles. Since the velocity of the two component waves are the same, the wave train moves steadily forward without change in shape.

If the velocities of the component waves are not the same, $\nu_1/k_1 \neq \nu_2/k_2$, the profiles move with a speed $(\nu_1 - \nu_2)/(k_1 - k_2)$, which is different from that of the more rapidly moving oscillating part, whose speed is $(\nu_1 + \nu_2)/(k_1 + k_2)$. In other words the individual waves advance through the profile, gradually increasing and then decreasing their amplitude, as they give place to other succeeding waves. This phenomenon is strikingly illustrated by a wave on the seashore which may look large when it is some distance away from the shore, but gradually reduces in height as it moves in, and may even disappear before it is sufficiently close to break.

This situation arises whenever the velocity of the waves, *i.e.* their *wave velocity* v_φ, is not constant, but depends on the frequency. This phenomenon is known as *dispersion*. The actual velocity of the profiles is known as the group velocity, v_g. It follows that if the two components are not too different, $v_\varphi = \nu/k$, and $v_g = (\nu_1 - \nu_2)/(k_1 - k_2) = \frac{d\nu}{dk}$. In terms of the wavelength

$$v_g = \frac{d\nu}{d(1/\lambda)} = -\lambda^2 \frac{d\nu}{d\lambda} \quad \text{or}$$

$$v_g = \frac{d\nu}{dk} = \frac{d(kv_\varphi)}{dk} = v_\varphi + k\frac{dv_\varphi}{dk} = v_\varphi - \lambda\frac{dv_\varphi}{d\lambda}.$$

Wave Packets

The wave train of Fig. 7.1, even apart from the problem of dispersion, is not suitable as an electron model. It may be improved by the superposition of more waves, selected so as to produce a large amplitude over a small region of space and nowhere else. Such an accumulation of waves is known as a wave packet. It may be constructed by forming the integral

$$\int_{k_0-\Delta k}^{k_0+\Delta k} a \exp\bigl[i(kx - \omega t)\bigr] dk = \Phi(x,t)$$

assuming that the wave numbers of the component waves form a continuous distribution. Noting that ω and k are functionally related the integral may be evaluated as [6]:

$$\Phi = \int_{k_0-\Delta k}^{k_0+\Delta k} e^{ik(x-x_0)} dk = 2\sin\frac{\Delta k(x - x_0)}{(x - x_0)} e^{ik_0(x-x_0)}. \tag{7.3}$$

Plotted as a function of $(x - x_0)$ the real part looks like the curve shown in Fig. 7.2. The amplitude of oscillation is seen to reach a maximum at $x = x_0$, and goes to zero where $x - x_0 = \pi/\Delta k$. After that it is a rapidly decreasing oscillatory function.

The wave packet moves with the group velocity defined as $v_g = d\omega/dk$, which may be interpreted as the velocity of an electron as defined by the matter-wave model of de Broglie.

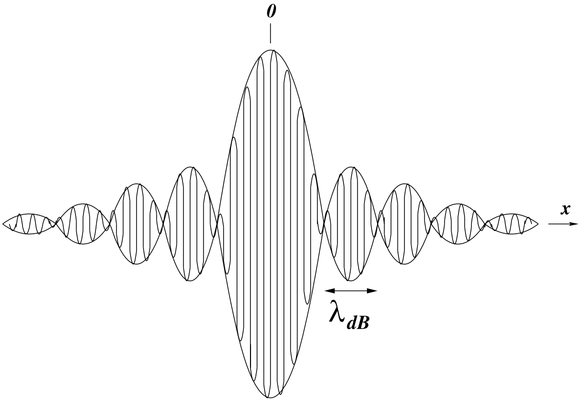


Fig. 7.2 Wave packet obtained by the superposition of harmonic waves over a limited wavelength range

7.2.2 Matter Waves

The demonstration that Hamilton–Jacobi theory favours a wave model for motion at the sub-atomic level is in line with the notion that matter in all its forms is a manifestation of space-time curvature. According to this point of view elementary matter does not appear as massive point particles in a void, but rather as local geometrical distortions of some featureless continuous medium, traditionally known as the aether. Such distortions are generated by the curving of 4D space-time and occur as persistent wave-like objects, much like the eddies on a fluid in turbulent flow.

In contrast, the aether before curvature may be likened to a fluid in laminar flow. This state is well known to represent an ideal isoteric and unstable system, which develops turbulence on the slightest disturbance. It is noted that the two contrasting states of flow are distinguished as linear and nonlinear systems respectively.

The most efficient way of describing material motion is in terms of differential equations, which may also be divided into linear and nonlinear equations [7]. This distinction depends on the order and degree of the differential equation. The order of an equation is defined as the order of the highest-ordered derivative in the equation. For instance

$$\frac{d^2y}{dx^2} + 2b\left(\frac{dy}{dx}\right)^3 + y = 0 \tag{7.4}$$

is a second-order equation.

The degree of an ordinary differential equation is the algebraic degree in the highest-order derivative in the equation. The equation

$$\left(\frac{d^2y}{dx^2}\right)^3 + \frac{d^2y}{dx^2}\left(\frac{dy}{dx}\right)^4 - x^4y = \sin x$$

is of degree three, because in as far as the second derivative alone is concerned, the equation is a cubic. Equation (7.4) is of degree one.

An equation is said to be linear if each term of the equation is either linear in all the dependent variables and their various derivatives or does not contain any of them. Otherwise the equation is nonlinear. The term $y\frac{dy}{dx}$ is of degree two in y and its derivative together and is therefore nonlinear. Every linear equation is of degree one.

The equation

$$x^2\frac{d^2y}{dx^2}+x\frac{dy}{dx}+\left(x^2-n^2\right)y=4x^3$$

is linear in y. The manner in which the independent variable enters the equation has nothing to do with the property of nonlinearity.

Mathematically, the essential difference between linear and nonlinear equations exists therein that any two solutions of a linear equation can be added together to form a new solution [1]. In contrast two solutions of a nonlinear equation cannot be added together to form another solution. Superposition fails. For this reason there is no general analytic approach for solving typical nonlinear equations. Applied mathematicians therefore tend to describe physical systems as far as possible with linear differential equations. On dealing with essential nonlinear behaviour this approach is an oversimplification that may obscure the actual characteristics of a system.

The traditional handling of matter waves suffers from precisely this defect. The discussion that follows initially treats the problem linearly, with the constant awareness that the final analysis presents a nonlinear problem.

The more daunting prospect in all of this is to persuade the next generation of chemists not to dismiss nonlinear effects as insignificant second-order perturbations. A spectacularly popular recent textbook [8], aimed at senior undergraduates, introduces quantum theory by way of five postulates, featured as

> …the bedrock on which the theory is built.

The first of these postulates declares:

> Any superposition of state vectors is also a state vector.

Whoever graduates under this paradigm with the added conviction that [9]:

> Quantum theory is the deepest explanation known to science… There is no other.

would, understandably have little patience with arguments about nonlinearity.

De Broglie Waves

The wave model of an electron originated in de Broglie's work which associated a frequency with an electron at rest according to the quantum relation

$$E=mc^2=h\nu$$

that defines the electron as a standing wave

$$\psi=\psi_0e^{-2\pi i\nu t},\quad (x=0).$$

From a relatively moving frame of reference the energy and momentum of the electron is observed as [10]

$$p' = mv\beta, \quad E' = mc^2\beta, \quad \beta = \left(1 - v^2/c^2\right)^{-\frac{1}{2}}$$

to define a running wave

$$\psi' = \psi_0 e^{2\pi i \nu t'} = \psi_0 \exp\left[2\pi i \nu\left(vx/c^2 - t\right)\beta\right],$$

which is of the form

$$\psi = \psi_0 e^{2\pi i (x/\lambda - \nu t)}.$$

It follows that

$$\nu' = \nu\beta = mc^2\beta/h = E'/h,$$
$$\lambda' = c^2/\beta v \nu = h/\beta m v = h/p',$$

the famous de Broglie definition of matter waves. The phase velocity of the de Broglie wave

$$v_\varphi = v'/\beta' = E'/p' = c^2/v > c.$$

The group velocity

$$v_g = \frac{d\nu}{d(1/\lambda)} = \frac{dE}{dp},$$

$$\text{i.e.} \quad v_g = \frac{d}{dp}\left(p^2c^2 + m^2c^4\right)^{\frac{1}{2}},$$
$$= \tfrac{1}{2}E\left(2pc^2\right) = pc^2/E,$$
$$= mvc^2/mc^2 = v,$$

the velocity of the electron. The de Broglie wavelength corresponds to the oscillatory function of Fig. 7.2.

The only remaining inconsistency of the de Broglie wave model of an electron is that linear wave packets change their shape and flow apart in time. That is, with the exception of the harmonic-oscillator wave packet, originally proposed by Schrödinger [11] as a wave-mechanical model of an electron.

In order to avoid the problem of dispersion Louis de Broglie [12] proposed a double-solution formulation of wave mechanics by associating a particle with the singular points of a differential wave equation. As a linear equation cannot have singular solutions [7] the particle was postulated as described, more specifically, by a nonlinear solution. This singular solution, characteristic of the nonlinear region that represents the particle, is not a special case of the general wave equation, but tangent to that in the boundary surface. Despite some sporadic efforts, this proposal has not led to the formulation of a convincing nonlinear wave equation.

Schrödinger Waves

Wave mechanics, by definition, originated in Schrödinger's famous equations, commonly formulated in time-dependent and time-independent forms as:

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m}\left(\nabla^2 + V\right)\Psi, \tag{7.5}$$

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \tag{7.6}$$

with potential energy, V, independent of time. As explained in the previous chapter these equations do not account for spin, which is only defined in four-dimensional space-time. It was however, shown by Dirac [13] how to linearize the time-dependent Hamiltonian of (7.5) by the introduction of Pauli matrices as coefficients and in this way to add the spin as an additional variable.

An incisive quantum-mechanical analysis of electron structure, based on Dirac's equation, was published in a series of papers by Schrödinger [14–16] in 1930–31.

Each coordinate of an electron, which refers to the centre of mass of a charge cloud, was shown to be specified by the sum of two terms. The first of these terms changes continuously with time and describes the linear motion at the group velocity of a wave packet, which in size corresponds to the de Broglie wavelength ($\lambda_{dB} = h/p_x$) of the electron. The second term specifies a smaller high-frequency periodic component that represents a small amplitude trembling motion[1] superimposed on the linear motion of the charge cloud. The average periodic displacement in a given direction amounts to $\lambda_C/4\pi$, where $\lambda_C = h/mc$ is the Compton wavelength of the electron. In this interpretation λ_C clearly specifies the wavelength of a spherical standing wave within the de Broglie profile. Trembling motion at the speed of light about a mean position represents a contribution of $\hbar/(2mc)\cdot mc = \hbar/2$ to the angular momentum, naturally interpreted as electron spin.

In the case of the hydrogen atom trembling motion is shown not to distort the spectroscopic fine structure appreciably. The maximum perturbation without a serious effect, estimated as the ratio between $2\lambda_C/4\pi$ and the Bohr radius a_0, amounts to

$$f = \frac{h}{2\pi mc}\cdot\frac{4\pi^2 me^2}{h^2} = \frac{e^2}{\hbar c} = \alpha,$$

the fine-structure constant. We note that the ratio of λ_C to $\lambda_{dB} = 2\pi a_0$ also yields

$$\frac{\lambda_C}{\lambda_{dB}} = \frac{h}{mc}\cdot\frac{2\pi me^2}{h^2} = \alpha.$$

This conclusion seems to indicate a natural equilibrium condition characteristic of non-dispersive wave packets; a proposition to be discussed later on.

---

[1] Zitterbewegung.

At an early stage Schrödinger identified [16] an essential difference between quantum and relativity theories in that the time variable in the former is not treated on the same footing with the space coordinates, as required by the Lorentz transformation

$$\left(x', y', z', t'\right) = F(x, y, z, t)$$

of special relativity. In our view this problem arises from the formulation of a wave equation in three dimensions by the separation of space and time coordinates. The only obvious remedy lies in the 4D quaternion solution of d'Alembert's equation for matter waves.

On subsequent reconsideration Schrödinger [17] concluded that the concept of position had to be given up in microphysics because there was nothing in reality that corresponded to it. However, as a possible alternative the position of an electron could arguably be considered as specified by the centre-of-mass coordinate of a soliton.

Zitterbewegung Several authors [18–21] have commented on the meaning and interpretation of *Zitterbewegung* (zbw) with respect to the internal structure of an electron, in all cases treating the electron as a point particle.

Hestenes [21] examined the derivation of the zbw by reformulation of Dirac's equation in terms of a Clifford algebra, closely related to standard hypercomplex quaternion formalism. It is shown in particular that

> *…the complex phase factor in the electron wave function can be associated directly with zbw…,*

that

> …the spin was "smuggled" into the Dirac theory…,

that the quaternion tensor $\boldsymbol{J}$

> …expresses the total angular momentum of the electron as the sum of an orbital angular momentum $p \times x$ and a spin angular momentum S…,

that

> …the electron moves with the speed of light, as in Schroedinger's original zbw model…,

and finally, that

> …the spin angular momentum can be regarded as the angular momentum of zbw fluctuations.

Sporadic interest in Zitterbewegung has not managed to provide a simple physical explanation of the phenomenon. Most commentators (*e.g.* [19, 22]) return to the original characterization as arising from the mixing of positive and negative energy states in Dirac theory. Alternatively [20] it is considered "…an unobservable mathematical curiosity…" or [21] "…a physical interpretation for the complex phase factor…".

It is less common for authors to interpret the appearance of Compton and de Broglie wavelengths in a single construct as the attribute of a real matter wave. From a purely mathematical point of view such a wave is readily formulated as the superposition of two complementary waves. The associated physical model is more difficult to describe.

7.2.3 Two-Wave Models

A notable effort to address the problem in terms of de Broglie's double-solution model for elementary matter is due to Elbaz [23]. Using both alternative expressions for the rest energy of a matter wave, $E_0 = h\nu_0 = m_0c^2$, it was demonstrated to be associated with an amplitude function of Compton wavelength ($\lambda_C = h/mc$) and a wave function with de Broglie wavelength ($\lambda_{dB} = h/mv$). The combination $u(x,t) \cdot \psi(x,t)$, where

$$u(x,t) = \exp\bigl[2\pi i(x/\lambda_C - \nu_C t)\bigr],$$
$$\psi(x,t) = \exp\bigl[2\pi i(\nu t - x/\lambda_{dB})\bigr]$$

describes a standing wave packet, characterized by a pair of waves that move in opposite directions [24].

The amplitudes u and ψ are related by the equations

$$\frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} - \nabla^2 u - \left(\frac{m_0c}{\hbar}\right)u = 0, \tag{7.7}$$

$$\frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} - \nabla^2 \psi + \left(\frac{m_0c}{\hbar}\right)\psi = 0, \tag{7.8}$$

$$\frac{1}{c^2}\frac{\partial u}{\partial t} \cdot \frac{\partial \psi}{\partial t} - \nabla u \cdot \nabla \psi = 0. \tag{7.9}$$

Equations (7.7) and (7.8) can be formally regarded as the equations for bradyonic and tachyonic components respectively with the invariant interaction condition (7.9). As stated [25]:

> The u-function planewave solutions have a wavelength equal to the Compton wavelength $\lambda = h/mc$, a phase velocity equal to the particle velocity v, and a group velocity c^2/v, while the quantum mechanical ψ-function planewave solutions have a wavelength equal to the de Broglie wavelength $\lambda_B = h/mv$, a phase velocity c^2/v and a group velocity v.

From another perspective the situation is described [26] as the trapping of a time-like bradyon ($v < c$) and a space-like tachyon ($v > c$) in a relativistic invariant way.

An equivalent standing wave, generated by the superposition of a pair of converging and diverging spherical waves,

$$\begin{aligned}\Phi &= \frac{A}{r}e^{i\omega t}\left\{e^{ikr} - e^{-ikr}\right\}\\ &= \Phi_0 e^{i\omega t}\sin(kr)/r\end{aligned}$$

was proposed by Wolff [27] as an electron model in which the wavelength of the sine function $h/\gamma mc = \lambda_C$ and of the exponential oscillator $h/\gamma mv = \lambda_{dB}$, as perceived from a relatively moving frame of reference, as before. This model is mathematically closely related to the wave packet (7.2) obtained by the integration of linearly superimposed harmonic waves as shown in Fig. 7.2.

The common factor in this variety of presentations is the attempted modification of a Schrödinger wave packet to produce the equivalent of a nonlinear wave packet [28] that involves an internal spectrum of matter waves with the appearance of a stable extended massive particle in motion.

All of these models are mathematically feasible, but none of them describes the origin of the component waves in physically meaningful form.

7.2.4 Fine-Structure Parameter

The appearance of the fine-structure constant as the ratio of Compton and de Broglie wavelengths should be examined more closely in the search for a convincing wave description of an electron. In the context of the Bohr model the relativistic mass of an orbiting electron, seen from the nucleus, with respect to the rest mass, m_0, is given by

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}} = \frac{m_0}{\sqrt{1-\alpha^2}}.$$

Noting that

$$\begin{aligned}\alpha^2 &= \left(\frac{e^2}{\hbar c}\right)^2, \qquad E_1 = -\frac{me^4}{2\hbar^2},\\ \alpha^2 &= -2E_1/\left(mc^2\right).\end{aligned}$$

Hence

$$\begin{aligned}2E_1/\left(mc^2\right) &= (m_0/m)^2 - 1,\\ 2E_1 &= c^2\left(m_0^2/m - m\right),\\ E_1 &\simeq -\frac{1}{2}(\Delta m)c^2.\end{aligned}$$

The increase in relativistic mass represents a proportional decrease in the potential energy that stabilizes the system at $-\frac{1}{2}e^2/r$, in esu. This is the same argument that explains nuclear binding energy as a mass defect. The same explanation holds in the Bohmian interpretation [29, 30] of quantum theory, which argues that an atomic stationary state occurs when the potential energy of an electron at rest, is balanced by the quantum potential [31]:

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

For the hydrogen atom in the ground state, $R(r) = Ne^{-r/a_0}$ and hence,

$$\frac{d^2R}{dr^2} = \frac{N}{a_0^2}e^{-r/a_0},$$

such that $V_q = \hbar^2/2ma_0^2$. In general

$$V_q = \frac{\hbar^2}{2mr^2},$$

and the quantum force on the electron:

$$F_q = \frac{\partial V_q}{\partial r} = -\frac{\hbar^2}{mr^3},$$

whereas the electrostatic force, in electrostatic units ($4\pi\epsilon_0 = 1$), $F = e^2/r^2$. These forces are in balance when

$$\frac{\hbar^2}{mr^3} = \frac{e^2}{r}; \quad r = \frac{\hbar^2}{me^2} = a_0,$$

the Bohr radius. This means that $V = V_q$ at $r = a_0/2$, halfway between proton and electron.

Transition of an electron with $n > 1$ to a lower unoccupied energy level by emission of a photon with energy $h\nu$ and spin $\hbar$, is anticipated. However, in the $1s$ state of minimum action, with quantum number $l = 0$, there is no orbital angular momentum to transfer in stimulating photon emission and the ground state remains stable. The calculation does not imply different velocities for the electron at different energy levels—only a quantized change in de Broglie wavelength. The mass-energy difference amounts to exchange of a (virtual) photon in the form of a standing wave between the charge centres. With the classical radius of the electron defined as $r_0 = e^2/mc^2$ it is noted that

$$\frac{r_0}{a_0} = \frac{me^4}{m\hbar^2c^2} = \left(\frac{e^2}{\hbar c}\right)^2 = \alpha^2$$

where a_0 is the Bohr radius.

In terms of the Compton wavelength $\lambda_C = h/mc$ it follows that:

$$\alpha\lambda_C = \frac{2\pi e^2}{mc^2} = 2\pi r_0,$$

$$\frac{\lambda_C}{\alpha} = \frac{2\pi\hbar^2}{me^2} = 2\pi a_0 = \lambda_{dB}.$$

From this result the parameter $\alpha' = v/c$ for the freely moving electron with $\lambda_{dB} = h/mv$ is defined, more appropriately as $\alpha' = \lambda_C/\lambda_{dB}$.

Now define $\lambda_Z = 2\pi r_0$. Whereas the wavelength $\lambda_{dB} = \lambda_C/\alpha$ represents a wavepacket with group velocity $v_g < c$, the phase velocity $v_\phi > c$ is associated with the Zitterbewegung of wavelength $\lambda_Z = \alpha \cdot \lambda_C$; $v_g v_\phi = c^2$ [32].

The Wave Model Common sense dictates that an electron must have extension and so eliminates the particle model and supports Schrödinger's interpretation [11] of an electron as a wave structure, further developed by Madelung [33] and Takabayasi [34], in hydrodynamic analogy, as an indivisible flexible charge. The internal wave structure of the electron is observed as high-frequency Zitterbewegung, at Compton wavelength, while the macroscopic effects in an electromagnetic field are fixed by the spread of a wave packet, conveniently defined as a de Broglie wavelength. A wave packet is formally described by the superposition of converging and diverging spherical waves. The generation of such waves will have to be examined in more detail. The fine-structure parameter is associated with this wave nature of an electron.

Trapped in the field of a proton the de Broglie wavelength is quantized to avoid self-destruction, such that

$$\frac{\lambda_C}{\lambda_{dB}} = \alpha_n = \frac{e^2}{n\hbar c}.$$

For an effective charge separation of r_n, the ratio α_n may be considered the ratio of two energies:

$$\frac{e^2}{n\hbar c} = \left[\frac{e^2}{r_n} \cdot \frac{1}{h\nu}\right]$$

an electrostatic and a quantum-mechanical factor. The constant $c = \lambda/\tau$ describes the virtual photon that occurs as a standing wave ($n\lambda = 2\pi r_n$) between the charge centres. The balance between the classical coulombic attraction and the quantum-mechanical repulsion (the quantum potential) now defines the fine-structure constant with a value, fixed by the de Broglie wavelength of the virtual photon.

In a strong field the size of an electronic wavepacket may be compressed below the Compton radius to an absolute minimum of λ_Z, which describes the minimum size to which an electron may be compressed, measuring $r_0 = \lambda_Z/2\pi$, for an electron defined as an electric charge $-e$ distributed over a sphere of radius r_0. The classically measured value of $r_0 = e^2/m_0c^2$ is retrieved from this relationship.

Discussion The fine-structure parameter is a dimensionless variable that describes the wave structure of an elementary charge in space. It has been interpreted as the ratio of wavelengths, charges, energies or radial distances:

$$\alpha = \lambda_C/\lambda_{dB} = e^2/\hbar c = e^2/a_0 h\nu = \sqrt{r_0/a_0}.$$

The quantity $q_P = \sqrt{\hbar c} \simeq \sqrt{137}e$ is known as the Planck charge.

Without the benefit of dimensional analysis it is not obvious which of these ratios is the most fundamental. However, the parameter λ_C/λ_{dB} which refers to any electron and assumes special values in special quantum states, provides the simplest definition. We note that the approximate value of $1/\alpha \simeq 137$ is numerically purely accidental and without physical significance. Should the value of α be dictated by a more fundamental consideration, it can only be the general curvature of space-time.

There is nothing mysterious about α. It is the parameter that describes the shape of an electronic wave packet of wavelength λ_{dB}, made up of elementary waves of length λ_C. The dimensionless ratio varies as a function of electric field strength. In the field of a proton, in the H atom, the "constant" value of α is fixed by the quantized ground state.

The mystique that surrounds α derives from the fact that it is a dimensionless number such as π or the golden ratio τ, in both cases the ratio of two lengths. Its intrinsic relationship with the electromagnetic field is even less of a mystery as it depends on the wave properties of the field's source.

7.3 Nonlinear Systems

As described by Dodd *et al.* [4] in a wave system, driven or pumped with energy through some mechanism, for example a rotation, a background flow or a heat gradient, potential energy is made available to the waves.

> ...the system may become unstable under the influence of the background energy flow when some parameter passes through a critical value.

In hydrodynamics turbulence is said to occur.

> At the critical value the initial stationary state becomes unstable—a bifurcation occurs as the unstable state moves to another stable state

This statement precisely describes Schrödinger's proposed resonance mechanism to explain 'quantum jumps' [35]. The way in which nonlinear motion differs from linear wave motion is not because it is non-oscillatory wave motion, but also because its velocity is amplitude dependent. For linear waves the speed is always independent of amplitude.

Coherent nonlinear systems have been identified in nature on scales ranging from 10^8 to 10^{-9} m—seventeen orders of magnitude [1]. The largest example is the famous red spot on Jupiter, with a diameter equal to the distance from the earth to the moon. The structures identified as eddies in globular clusters [36] could measure light years across. At the other extreme are the charge-density waves in a cleaved surface of a tantalum disulphide crystal. We now propose that the structure of an electron with an estimated diameter of 10^{-15} m is of the same type, known as a soliton.

To substantiate this conjecture it will be necessary to demonstrate that nonlinear wave equations can be found to improve on the electronic wave models of Schrödinger and Dirac, which are based on linear equations. The demonstration that elementary particles correspond to classical solitons [37] lends credibility to this proposal. By way of introduction the anomalous stability of the wave-mechanical oscillator, described by Bohm [6, p. 307], is examined in more detail in comparison with shallow-water waves.

7.3.1 Hydrodynamic Analogy

Some insight is gained into the behaviour of harmonic-oscillator wave packets by comparison with the properties of waves on water [38]. By the principle of superposition a general wave on deep water in a narrow channel is formed by adding together many plane-wave solutions. As the elementary components with different wave numbers will propagate at different group velocities the general solution will change its form, or disperse as it moves. In shallow water the long wave components, which travel faster than the short wave components, cannot develop and dispersion effects become negligible. The resulting non-dispersive wave packet is known as a *solitary wave*.

The shallow water wave is no longer described by a linear differential equation and the superposition principle no longer applies. The restricted depth of the channel is seen to introduce a boundary condition that leads to the formation of nonlinear non-dispersive wave packets.

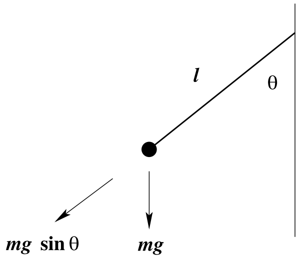
7.3.2 Schrödinger Oscillator

Schrödinger harmonic-oscillator waves differ from the more general solutions for all other systems in a similar way because of the more restrictive boundary condition.

The motion of a simple plane pendulum is described by a nonlinear differential equation [1]:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\sin\theta(t) = 0$$

where θ is the angular displacement of the pendulum from the vertical,



l is the length of the arm and g is the acceleration due to gravity. For small displacement $\sin\theta \sim \theta$ and the resulting linear equation has the familiar solution

$$\theta(t) = \frac{1}{\omega}\left(\frac{d\theta}{dt}\right)_0 \sin\omega t + \theta_0 \cos\omega t$$

where $\omega = \sqrt{g/l}$. Wave-mechanical analysis of the harmonic oscillator, considered within this approximation, also exhibits approximate linear behaviour, but enters the nonlinear regime for large displacement.

Noting that the natural dispersion of all other matter-wave packets arises from the invariable use of the superposition principle, excites the reasonable suspicion that the idealized linearity of Schrödinger's equation does not apply to real physical systems. In fact, it is widely recognized that most systems are inherently nonlinear, but that most nonlinear problems are essentially inaccessible to analytic methods. Without fast computers there hence was the tendency of resorting to linear approximations wherever feasible. At the same time constant efforts were made to simulate expected nonlinear behaviour by other means. Related to this problem it was pointed out [39]:

> ...that physical theory is unduly dominated by the use of point-particle abstractions, yet no physicist truly believes in the reality of a point particle.

We now look for a nonlinear model to provide a more realistic description of electron structure and behaviour at the same time.

The amazing reality is that the correct nonlinear behaviour of the oscillator was described in detail by Schrödinger in 1926 [11], but, to his annoyance, remained unrecognized by his contemporaries and imitators. He demonstrated that a group of proper harmonic vibrations of high quantum number n and relatively small quantum-number differences represents a particle-like object, oscillating with the frequency ν_0. This was achieved by singling out a relatively small group of normalized proper vibrations in the neighbourhood of $n = A^2/2$, $A \gg 1$, finally resulting in

$$\psi = \exp\left[\tfrac{1}{4}A^2 - \tfrac{1}{2}(x - A\cos 2\pi\nu_0 t)^2\right]\cos\left[\pi\nu_0 t + (A\sin 2\pi\nu_0 t)\left(x - \tfrac{1}{2}A\cos 2\pi\nu_0 t\right)\right]. \tag{7.10}$$

The first exponential factor represents a relatively tall and narrow hump, with the form of a Gaussian error curve at position

$$x = A\cos 2\pi\nu_0 t. \tag{7.11}$$

According to (7.11) this narrow hump behaves like a particle of mass m in linear oscillation, and with energy

$$2\pi^2 a^2 \nu_0^2 m = \tfrac{1}{2}A^2 h\nu$$

where n is the average quantum number of the select group.

The second cosine factor in (7.10), which varies rapidly with x and t resembles the central wave packet of Fig. 7.2. The number and breadth of the oscillations vary with time. The wavelets are most numerous and narrowest at the central point $x = \pm A$, where this second factor is independent of x: $\cos, \sin 2\pi\nu_0 t = \pm 1, 0$. However, the entire extension of the wave group remains constant. The variability of the "corrugation" depends on the velocity. The wave group remains compact and does not spread out. This behaviour is ascribed to the use of discrete harmonic components rather than a continuum of such. It will become apparent later on that Schrödinger had discovered the nonlinear soliton structure for an electron in 1926.[2]

In three dimensions the spatial wave group moves round harmonic ellipses, as represented by the wave mechanics of the hydrogen atom, on half-integral quantum levels—the first demonstration of quantum spin.

7.3.3 Korteweg–de Vries Equation

Solitary waves were first observed in a shallow narrow canal by the Scottish engineer John Scott Russell in 1834. He noticed how the wave that was generated by the motion of a horse-drawn barge kept on moving as the boat came to a sudden stop. He followed this unusual wave on horseback for a long distance and subsequently managed to generate and study similar waves on other canals and experimental tanks. One point of interest was the nondispersive nature of the solitary wave as it moved over the surface of the water without disturbance.

A mathematical model to account for Scott Russell's observation was published years later by Korteweg and de Vries, two Dutch scientists [41] who derived a differential equation that governs the propagation of waves along the surface of a narrow canal, generally known as the KdV equation,

$$\frac{\partial u}{\partial t} - 6u\frac{\partial u}{\partial x} + \frac{\partial^3 u}{\partial x^3} = 0.$$

The nonlinear second term and the third dispersion term describe opposing effects. When these terms are in balance the equation describes a solitary wave that moves without change in shape. The effect is illustrated graphically in Fig. 7.3(a). The nonlinear wave, about to break, combines with the dispersive wave, about to dissipate, to generate a persistent solitary wave.

It was shown that the equation has a solution of the form

$$u(x,t) = 2\kappa^2 \operatorname{sech}^2 \kappa(x - ct + \delta)$$

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[2] At an even earlier date Schrödinger was the first to recognize the phase invariance of electronic motion [40] that subsequently developed into modern gauge theory, the basis of elementary-particle physics, but rarely attributed to the seminal source.

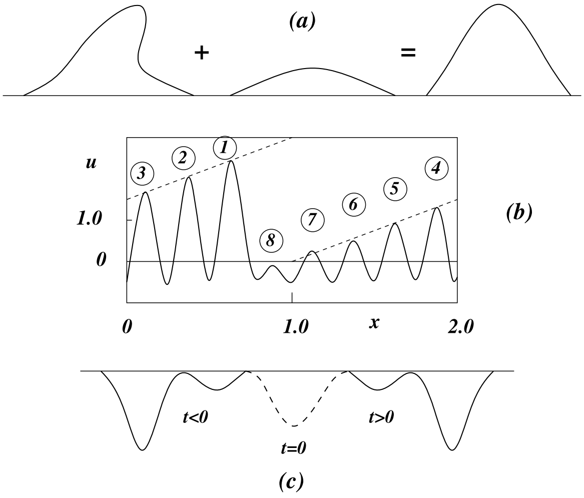

Fig. 7.3 (**a**) Formation of a solitary wave as the balance of nonlinear and dispersive components. (**b**) Generation of solitons by numerical solution of KdV equation. (**c**) Collision of two unequal solitons

with arbitrary δ and $c = 4\kappa^2$, describing a hump-like shape as described by Scott Russell and moving at constant velocity without change in shape. As the velocity is amplitude dependent it follows that a taller wave moves faster than a small one.

7.3.4 Solitons

Numerical solutions of the KdV equation were studied by Zabusky and Kruskal [42]. Starting from a normalized ($u = 1$) periodic initial condition, $u(x, 0) = \cos \pi x$, developing as $\cos \pi(x - ut)$, the first two terms of KdV dominate and u steepens with time, as in Fig. 7.3(a), in regions where it has negative slope. As the third term gains importance and balances the nonlinearity it prevents the formation of a discontinuity. Instead, small wavelength oscillations develop and grow in amplitude, assuming a shape like that of an individual solitary-wave solution. Eventually these *solitons* move apart (Fig. 7.3(b)) and may interact with one another as they follow the cycles forced by the periodic boundary condition. They reappear virtually unaffected in size or shape—they pass through one another without losing their identity (Fig. 7.3(c)). This soliton behaviour does not depend on the boundary condition. Simulations in which $u \to 0$ as $x \to \infty$ show that as a faster taller wave overtakes a smaller one they pass through one another as before.

The linearized version of KdV[3]

$$u_t + u_x + u_{xxx} = 0$$

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[3] It is customary to use the notation $u_t \equiv \partial u/\partial t$, $u_{xx} \equiv \partial^2 u/\partial x^2$, *etc.* in writing nonlinear wave equations.

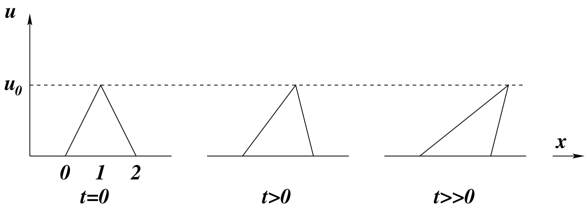

Fig. 7.4 Diagrams to illustrate the nonlinear deformation of a wave form

is dispersive, with $\omega = k - k^3$. It is the u_{xxx} term that introduces dispersive effects into the dispersionless equation: $u_t + u_x = 0$. To model the effect of a nonlinear term we next consider the equation

$$u_t + (u + 1)u_x = 0.$$

It can be solved [4] with the initial condition

$$u(x,0) = f(x) = \begin{cases} u_0 x & 0 < 1, \\ u_0(2-x) & 1 < x < 2, \\ 0 & x < 0; x > 2. \end{cases}$$

The gradient on the left slowly decreases with time while the gradient on the right changes from negative to positive as shown in the series of diagrams in Fig. 7.4. This behaviour is understood intuitively by noting that, since larger values of u travel faster than smaller values, the apex of the triangle overtakes all the lower points. The wave breaks.

Many nonlinear equations have localized solitary wave solutions, but not all of these are solitons, which have the special property of maintaining their identity through numerous interactions. A much smaller number of equations, among them the nonlinear Schrödinger equation (NLS) and the sine-Gordon equation (sG), have soliton solutions of the KdV type and are of special importance in the present context.

7.3.5 Soliton Eigenvalues

It is of special importance for understanding the soliton structure of electrons to note that the KdV equation, usually abbreviated in the form

$$u_t - 6uu_x + u_{xxx} = 0, \tag{7.12}$$

is associated with the eigenvalue Schrödinger equation

$$\psi_{xx} + (\lambda - u)\psi = 0$$

where λ is independent of time and where u changes with time according to the KdV equation. This conclusion was reached by *inverse transformation* solution[4] of

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[4] This procedure is analyzed in detail by Toda [43].

the KdV equation [44]. The eigenvalue equation

$$-\psi_{xx} + u\psi = \lambda\psi$$

is rewritten in the form $u = \lambda + (\psi_{xx}/\psi)$, which is used to calculate u_t, u_x and u_{xxx} and substituted into (7.12). After rearrangement one has

$$\lambda_t\psi^2 + [\psi Q_x - \psi_x Q] = 0$$

where $\lambda_t = d\lambda/dt$ and $Q = \psi_t + \psi_{xxx} - 3(u+\lambda)\psi_x$.

The term in square brackets is a perfect differential with respect to x and in the limit

$$\lim_{x\to\infty} u = 0, \quad \text{the integral} \quad \lambda_t \int \psi^2 dx = 0,$$

which implies $\lambda_t = 0$, *i.e.* $\lambda =$ constant. From this result it can be shown that a soliton has a time-independent eigenvalue that satisfies Schrödinger's equation. Stated differently, if the potential in Schrödinger's equation evolves according to the KdV equation, the eigenvalue parameter λ remains constant. Two solitons have two eigenvalues which remain constant as they approach, collide and separate again.

A more detailed analysis [45], using numerical methods and a large-amplitude initial condition,

$$u(x,0) = -p(p+1)\,\mathrm{sech}^2 x, \quad p > 0,$$

was shown to yield one-dimensional soliton solutions that match the known central-field radial wave-mechanical results. Bound states emerged with eigenvalues, given in ascending order by $\lambda_n = -(p-n)^2$, such that $|\lambda_n|$ is directly proportional to n, as in Fig. 7.3(b) above. Like the wave-mechanical result, the KdV simulation conserves total bound-state momentum and energy and generates an oscillating "tail" related to the continuous Schrödinger spectrum.

We interpret these results as conclusive proof that the wave-mechanical electron is described more appropriately as a soliton, which means that the linear Schrödinger equation gives a good, but incomplete, description of the atomic hydrogen electronic spectrum. Apart from being at variance with 4D space-time geometry it also fails to recognize small, but important, nonlinear effects, related to space-time curvature.

7.3.6 Soliton Models

The KdV is not the only integrable nonlinear equation with soliton solutions. Closely related to it is the modified KdV, (MKdV):

$$u_t \pm 6u^2 u_x + u_{xxx} = 0$$

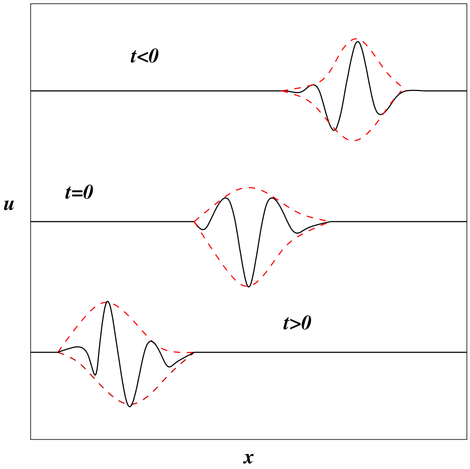

Fig. 7.5 Breather solution of KdV [47]

with the single-soliton solution

$$u(x,t) = \pm 2k\,\mathrm{sech}\big(2kx - 8k^3t\big).$$

The pulse profile is in the form of an oscillatory solution that is modulated by a sech-shaped envelope. The oscillations and the envelope move at different velocities. As a result of the undulations in the profile that take place as the pulse propagates (shown in Fig. 7.5), it is referred to as a breather solution [47]. It is a localized entity with the essential features of a soliton and interacts with other solitons in an elastic fashion.

As a small-amplitude, slowly varying phase term F, for a MKdV soliton, is substituted into the KdV equation the result is readily simplified [47] to read:

$$iF_t + F_{xx} + 2|F|^2F = 0.$$

This equation is of the same form as Schrödinger's equation

$$i\hbar\psi_t + \big(\hbar^2/2m\big)\psi_{xx} - V\psi = 0$$

and is known as either the cubic or nonlinear Schrödinger equation, which arises for a potential $V \sim |\psi|^2$. This condition is immediately recognized as characteristic of the hydrogen electron or a single valence electron that surrounds a monopositive atomic core [48].

In view of this result it is not surprising to learn that by the modification of a linear differential equation such as the non-relativistic Schrödinger equation or the relativistic Klein–Gordon equation, on the addition of a term that generates a nonlinear frequency condition, $\omega(k)$, it is possible to obtain soliton solutions without seriously affecting the original meaning.

The NLS equation [46]

$$i\hbar\frac{\partial\Psi}{\partial t} = -\left(\frac{\hbar^2}{2m}\right)\nabla^2\Psi - \epsilon^2\big(\Psi^*\Psi\big)\Psi, \tag{7.13}$$

commonly abbreviated in one dimension to read:

$$i\frac{\partial\phi}{\partial t}+\frac{\partial^2\phi}{\partial x^2}+\beta|\phi|^2\phi=0$$

has the same form as the quantum Schrödinger equation with $\beta|\phi|^2$ as potential. ϕ is a complex function that implies a travelling wave solution with an oscillatory modulation. Subject to the condition

$$\lim_{|x|\to\infty}\phi=0 \quad \text{it has the travelling wave solution}$$

$$\phi=a\sqrt{2/\beta}\exp\left\{\left[\tfrac{1}{2}bx-\left(\tfrac{1}{4}b^2-a^2\right)\right]\right\}\operatorname{sech}\left[a(x-bt)\right]$$

with a and b arbitrary constants. The sech wave acts as an envelope to the oscillary part, producing a structure that resembles the wave packet of Fig. 7.2.

One form of the NLS equation can be written in terms of the electric field amplitude $E(x,t)$ as [1]:

$$i\frac{\partial E}{\partial t}+\frac{\partial^2 E}{\partial x^2}+|E|^2E=0$$

to describe a soliton that moves through an optical fibre. It should describe a conduction electron equally well.

The linear Klein–Gordon equation

$$\frac{\partial^2 u}{\partial t^2}-c^2\frac{\partial^2 u}{\partial x^2}+m^2u=0, \quad m=m_0c^2/\hbar$$

when turned into the non-linear form

$$\frac{\partial^2\theta}{\partial t^2}-c^2\frac{\partial^2\theta}{\partial x^2}+m^2\sin\theta=0 \tag{7.14}$$

is known as the "sine-Gordon" equation.

In the limit of small θ this equation reduces to

$$\frac{\partial^2\theta}{\partial t^2}-c^2\frac{\partial^2\theta}{\partial x^2}+m^2\theta-\frac{1}{6}\theta^3+\cdots=0$$

which approximates the linear equation.

The sine-Gordon equation has a single solitary-wave solution

$$\theta_k(x,t)=4\tan^{-1}e^{\gamma(\zeta-v\tau)}$$

with $\gamma=1/\sqrt{1-v^2}$, $\zeta=mx/c$, $\tau=mt$, known as a *kink*.

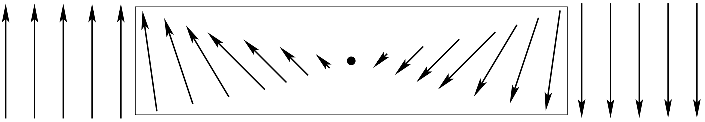

Fig. 7.6 Bloch wall

7.3.7 *Electronic Solitons*

Details of the soliton behaviour of an electron depends on the environment. We contend that an electron in empty Euclidean space behaves as a dispersive linear wave and hence dissipates indefinitely. On propagation through the intrinsic nonlinear curved space of general relativity [49] it encounters modulation on which the final wave form depends.[5] A single non-linear equation that describes the modulation in different situations is not known, but a number of special equations, such as the KdV, MKdV, NLS and sG equations, together give an adequate description of the electron in most chemically important nonlinear environments.

Free Electron

An interesting nonlinear model for an electron, based on the minimization of energy density in space, was proposed by Enz [50], using a variational procedure that considers the electron as the entity of lowest energy with respect to any variation of the parameters which describe its interaction with the space-time vacuum. A Bloch wall [51], which balances magnetic energy against the anisotropy between magnetic domains in a crystal was used as minimization model. The gradual change in magnetization within a Bloch wall is shown schematically in Fig. 7.6.

The magnetic domains are considered in analogy to simulate the spin function that distinguishes between electron and positron in four-dimensional space-time on rotation of the variable θ between $\pm\pi$. Exchange energy is defined as

$$F_A = A\sum_{\mu=1}^{4}\left(\frac{\partial\theta}{\partial x_\mu}\right)^2,$$

with $x_4 = -ict$ and the constant A, an energy per unit length. The anisotropy energy density is given by

$$F_K = K\sin^2\theta, \quad \text{where } K \text{ measures energy per unit volume.}$$

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[5] As pointed out by Goldstein [3, p. 283], the most general transformation in Minkowski space that preserves the velocity of light has the form $\boldsymbol{x}' = \boldsymbol{L}\boldsymbol{x} + \boldsymbol{a}$, where $\boldsymbol{a}$ is an arbitrary translation vector of the origin and $\boldsymbol{L}$ is the orthogonal matrix of the homogeneous Lorentz transformation $\boldsymbol{x}' = \boldsymbol{L}\boldsymbol{x}$ (4.4). The modified inhomogeneous (Poincaré) transformation has ten independent elements compared to the six of (4.4). This condition generates the intrinsic nonlinearity of curved space-time.

In two dimensions the solutions of the energy-minimized nonlinear equation

$$\frac{\partial^2\theta}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2\theta}{\partial t^2} = \frac{K}{2A}\sin 2\theta$$

$$\textit{i.e.} \quad \theta = n\pi \quad (n = 0, 1, 2\ldots),$$

$$\text{and} \quad \sin\theta = \pm[\cosh\sqrt{K/A}\cdot x]^{-1}$$

define a non-zero extent x_0, to which the non-vanishing energy density, $E_s = 2\sqrt{AK}$, and the associated mass, E_s/c^2, are confined.

Minimization of this Bloch-wall equivalent was finally stated to generate either a stable electron or a positron. This interpretation of the energy density as an extended elementary particle is not convincing. More realistically it represents a situation of stable equilibrium between an electron and a positron in space-time, related by an element of CPT symmetry, equivalent to the Bloch wall. The involution shown in Fig. 7.6 was interpreted as ±π rotation of the spin function, in either clock— or anti-clockwise sense and the asymmetry as referring to differences in electric charge and the chiral forms of matter. In the magnetic case rotation of the spin vectors through the Bloch wall *interconverts* magnetic domain fields. We therefore propose as the correct analogy that electron-positron interconversion should be described here by involution across an interface, such as the achiral vacuum interface, proposed before [36, 52], to separate the chiral antipodes in the double cover of projective space-time. This interpretation would account for the fact [50] that three-dimensional spherically symmetrical solutions do not exist.

An equivalent result was obtained by Einstein and Rosen [53] on solving the equations for a directed gravitational field near a singularity at the origin, as the model of a massive particle. In this case the four-dimensional space splits into two congruent parts, or "sheets", on opposite sides of a hypersurface, interpreted as representing

> . . . a gravitational field which ends in a plane covered with mass and forming a boundary of the space.

We consider it more logical to interpret the singular hypersurface as an interface between chiral regions of space-time, populated by matter and antimatter respectively, rather than a "mass bridge". Mutual annihilation is prevented by inverted time flow if the two-sheet structure is assumed to result from involution in elliptically curved space-time.

In another attempt to extend the Enz model into three-dimensional space [54] θ was assumed to be a function of $\boldsymbol{r}$ only—*i.e.* time-independent. The negative result, so obtained is not entirely surprising in view of the fact that the spin function required for the simulation only exists in four-dimensional space-time [55].

Wave Structure As an electron wave propagates through the vacuum nonlinear modulation causes periodic variation in the amplitude of the individual wavelets to generate a wave train as shown in Fig. 7.1. However, this periodic variation is not due to the superposition of different waves as used in the construction of Fig. 7.1. As indicated before, it occurs as the resultant of two opposing forces—natural dis-

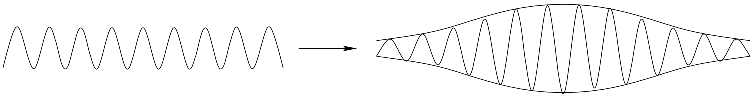

Fig. 7.7 KdV elastic modulation of a sinusoidal wave

persion of the wave and nonlinear cresting and breaking of wave profiles. A hydrodynamic analogy based on restricted flow of an incompressible fluid, correctly described by KdV, is outlined by Lamb [47] as represented graphically in Fig. 7.7.

The effect is velocity dependent and for a given mass, m a wave profile of de Broglie wavelength, which depends on momentum, appears at $\lambda_{dB} = h/p = h/mv$. The wavelength shrinks with increasing velocity and reaches a minimum, called the Compton wavelength, $\lambda_C = h/mc$, at the speed of light. All intermediate forms of the electron is characterized by the fine-structure parameter, $\alpha' = \lambda_C/\lambda_{dB}$. The common factor is Planck's constant h, which evidently is another manifestation of general space-time curvature.

By considering the meaning of continuous matter density in space-time, Eddington [56, p. 147], arrived at a similar conclusion:

> Density multiplied by volume in space gives us *mass* or, what appears to be the same thing, *energy*. But from our space-time point of view, a far more important thing is density multiplied by a four-dimensional volume of space and time; this is *action*. The multiplication by three dimensions gives mass or energy; and the fourth multiplication gives mass or energy multiplied by time. Action is thus mass multiplied by time, or energy multiplied by time, and is more fundamental than either.
>
> Action is the curvature of the world.

The earlier conclusion that the distortion of Euclidean space-time generates elementary units of matter may now be modified to state that elementary units of *action* occur in curved space-time. This means that general relativity implies, not only the appearance of a gravitational field, but also of the quantum-potential field, characterized by $\hbar$.

Electron Diffraction

Diffraction effects are directly explained by the electronic wave structure outlined in the previous paragraph. This includes the notorious two-slit experiment quoted in many textbooks to ponder the mysterious nature of the electron. The crucial factor to appreciate is that the diffraction effects associated with a wave train as in Fig. 7.1, depend on the wavelength of the modulated profile, rather than the Zitterbewegung.

Nonlinear Perturbation

Electrons were first directly observed in radioactive decay as β-rays, behaving in all respects like particle beams, for instance as judged by the tracks left behind in a cloud chamber. In this case the de Broglie wave train of the free electron is perturbed in the more nonlinear medium and converted into single solitons that travel like particles. Increased nonlinearity due to continued interaction with the medium is described by the damped NLS equation

$$iu_t + u_{xx} + 2|u|^2 u = -i\gamma u$$

that leads to the eventual spreading and decay of the soliton [47, p. 276].

It may be inferred from Fig. 7.4 that in collision with a solid object as in a scintillation screen, the breaking waves disappear with transfer of kinetic energy.

Photoelectric and Compton Effects

Electromagnetic radiation obeys the general wave equation (7.1) in three dimensions. In photoelectric interaction it transfers energy in discrete units to electrons in the surface of an active metal. So strong is the conviction that an electron is a point particle that, for more than a century, the only generally accepted explanation of the effect has been based on the assumption of a complementary photon structure for radiation. The situation can hardly be that simple. Equation (7.1) describes a linear monochromatic wave. The creation of discrete photons must clearly require some pronounced nonlinear modification thereof. Examination [54] of the nonlinear form

$$\nabla^2\phi - \left(1/c^2\right)\left(\partial\phi^2\right)\left(\partial t^2\right) = (1/2)\sin 2\phi$$

provided no evidence of time-independent localized solutions. The possibility of time-dependent and four-dimensional solutions could admittedly not be excluded, but the observed constant speed of light militates against the formation of photonic solitons in the vacuum. At this stage it appears very likely that this conclusion would be generally valid for the dispersive system of massless photons [57], with infinite Compton wavelength in the vacuum. However, photons may well occur in media that induce increased nonlinearity.

For the sake of argument we may conjecture that encounter with the metal surface provides sufficient nonlinearity to transform the light wave into solitons. To rationalize the photoelectric interaction it would then be necessary for the electron to occur as a single soliton in the surface. That by itself cannot account for the photoelectric effect as solitons are known to pass through one another without changing their shape. Maybe not if one of these carries an electric charge that interacts with the fluctuating electric vector of the other. This scenario explains the effect and avoids the dilemma of assigning a frequency to a point particle.

During the interaction of radiation with an atom, mutual polarization of the atomic charge cloud as well as the electromagnetic field of the light wave, generates a nonlinear response, reflected in the modified wave equation [47, p. 206]:

$$\nabla^2\boldsymbol{E} - \frac{1}{c^2}\frac{\partial^2\boldsymbol{E}}{\partial t^2} = \frac{4\pi}{c^2}\frac{\partial^2\boldsymbol{P}}{\partial t^2}$$

where $\boldsymbol{P}$ is known as the *polarization* of the medium. An induced atomic dipole essentially interacts nonlinearly with the coherent light wave, giving rise to soliton phenomena. In this sense photons are not present in propagating light waves, but are created during nonlinear transfer of energy to an electron.

An encounter, inverse to the interaction envisaged here, was analyzed by Schrödinger [58] in his reconstruction of the Compton effect as Bragg diffraction (reflection) of a light wave on a de Broglie wavetrain—not appreciating the importance of solitary waves at the time.

Atomic Structure

It is in the interpretation of the extranuclear electron distribution on atoms that the Copenhagen probabilistic model is at its most confusing. Solutions of the linear wave equation give an excellent account of the energy spectrum of the hydrogen electron, but not perfect in detail. Some obvious defects of the model relate to the separation of variables, the intrinsic nonlinearity of space-time and neglect of environmental perturbation. Treated as a radial distribution in one dimension a properly adapted NLS equation could provide an immediate improvement, numerically analyzed. Multi-soliton solutions of the KdV equation could conceivably serve as a model, even for non-hydrogen atoms, inaccessible at present, except by way of unwarranted linear superpositions.

Scattering and Absorption

To envision the scattering of light on an atom [47] the leading edge of a light pulse is assumed to invert and hence attenuate the electronic arrangement, while the trailing edge of the pulse returns the population to its initial state by means of stimulated emission.

Absorption occurs when the frequency of the light matches a separation between electronic energy levels ($\Delta E = h\nu$) to create a resonance pulse that excites the electron to the higher level. The reverse process, in which the photon is re-emitted, completes an event, equivalent to scattering, albeit at a retarded rate.

X-ray and/or electron diffraction is initiated by scattering on atomic electrons, without absorption. The energy of the X-ray photon or fast electron exceeds the possible resonance conditions on the atom. Interference between the scattered waves leads to the familiar diffraction effects.

Lattice Solitons and Diffraction

The detailed process of diffraction is poorly explained as the linear superposition of randomly scattered photons. More precisely, a diffraction pattern is generated by the interaction of a coherent wavefront with a regular lattice such as the rigid grating in optical diffraction. An X-ray beam constitutes such a wavefront and the electron clouds, concentrated on atoms in a crystallographic plane, are traditionally considered to define an equivalent grating, as described in detail elsewhere [48]. However, whereas an optical grating is a static construct, the crystallographic equivalent is not. The atoms are in constant vibration, causing mutual polarization in interaction with immediate neighbours. In one-dimension the interaction within a chain of atoms resembles that in a linear lattice of particles connected by springs, which obey Hooke's law [43].

Denoting the mean distance between adjacent particles when the lattice has no motion, by d, treating the position of the nth particle, $x = nd$, as a continuous variable, the displacement $y = y(x,t) = y_n(t)$ is described for long wavelengths by the wave equation

$$\frac{\partial^2 y}{\partial t^2} = c_0^2 \frac{\partial^2 y}{\partial x^2}$$

where $c_0 = d\sqrt{\kappa/m}$ for particles of mass m and κ is the force constant of the spring.

This dispersive equation is known experimentally not to describe the ergodic behaviour of lattice phonons correctly. An obvious improvement would be by addition of a nonlinear term. The equation

$$\frac{\partial^2 y}{\partial t^2} = c_0^2 \left(1 - \varepsilon \frac{\partial y}{\partial x}\right) \frac{\partial^2 y}{\partial x^2}$$

introduced by Raleigh in 1877 to describe nonlinearity in sound waves [43] also fails to simulate lattice phonons as the numerical solutions become multi-valued and break up after a while. It was found by Zabusky [59] that the wave is stabilized by addition of a fourth derivative:

$$\frac{1}{c_0^2} \frac{\partial^2 y}{\partial t^2} = \left(1 + \varepsilon \frac{\partial y}{\partial x}\right) \frac{\partial^2 y}{\partial x^2} + \frac{d^2}{12} \frac{\partial^4 y}{\partial x^4}.$$

If the KdV equation is modified by analogy, on introducing an interaction with quartic nonlinearity

$$\phi(r) = \tfrac{1}{2}\kappa r^2 + \tfrac{1}{4}\kappa r^4,$$

the resulting equation, simplified by substituting $\varepsilon = 3\alpha d^2$, $\xi = x - c_0 t$, $\tau = \frac{1}{2}\varepsilon c_0 t$, $\mu = 1/36\alpha$, $v = \partial y/\partial\xi$:

$$\frac{\partial v}{\partial \tau} + v^2 \frac{\partial v}{\partial \xi} + \mu \frac{\partial^3 v}{\partial \xi^3} = 0,$$

known as the modified (MKdV) equation, has soliton and multi-soliton solutions corresponding to lattice phonons, with eigenvalues that satisfy the linear Schrödinger equation.

This conclusion is interpreted to confirm that the thermal motion of scattering centres on a crystallographic plane is correlated and therefore unlikely to disrupt the coherent scattering of X-rays. On the other hand, in an ideal harmonic solid, the independent vibration modes are dispersive and the energies stored in them never come into thermal equilibrium.

X-ray diffraction is therefore seen to depend on the interaction between a linear wavefront and a nonlinear soliton lattice, giving rise to coherently scattered secondary waves, in exact analogy with optical diffraction. Linear superposition of the scattered waves define the Fourier transform of the electron density.

Conduction and Superconductivity

An electric current is intuitively described as the flow of electrons through a conductor, typically a metal. Phenomenologically an electron in this context is considered to be a particle, which in terms of the wave model assumed here, should be defined as a single soliton. In terms of the classical Drude model of metallic conduction valence electrons pervade a metal in the form of an electron gas. The highly nonlinear medium must ostensibly promote the formation of propagating solitons.

By contrast, superconductivity is associated with the alignment of high-spin atomic nuclei [60], that creates a uniform aperiodic field and promotes uninhibited flow of linear electron waves.

7.4 Chemical Aspects

The consistent failure to formulate convincing quantum-mechanical models that represent fundamental chemical concepts such as molecular structure and shape, optical activity and chirality, chemical cohesion, electronegativity and many others, is often ascribed to an inadequate understanding of the difference between classical and non-classical systems. A common strategy to address the problem is by searching for an informative definition of the illusive classical limit. A critical review of such efforts was published by Rosen [61] who examined the difference between Schrödinger's equation and its "classical" counterpart.

It is well known that Schrödinger derived a wave equation in analogy with the Hamilton–Jacobi (HJ) equation in the geometrical-optics limit. The inverse operation that relates the Schrödinger wave function to Hamilton's principal function, S, is done by substituting

$$\Psi = Re^{iS/\hbar} \tag{7.15}$$

into (7.5), to yield[6]

$$-\frac{\partial S}{\partial t} = \frac{1}{2m}(\nabla S)^2 + V - \frac{\hbar^2}{2m}\frac{\nabla^2 R}{R}, \tag{7.16}$$

$$\frac{\partial \rho}{\partial t} = -\frac{1}{m}\nabla \cdot (\rho \nabla S) \tag{7.17}$$

where $\rho = R^2 = |\Psi|^2$.

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[6] For details see [31, p. 134].

Equation (7.16) is identical with the HJ equation for a particle moving in a potential-energy field of $P = V + V_q$:

$$-\frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2m} + P \tag{7.18}$$

with $V_q = -\frac{\hbar^2 \nabla^2 R}{2mR}$, known as the quantum potential.

In order to recover the classical HJ equation with $P = V$ it is necessary to define the "classical Schrödinger equation":

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V + \frac{\hbar^2}{2m} \frac{\nabla^2 |\Psi|}{|\Psi|} \right] \Psi \tag{7.19}$$

and its complex conjugate with $|\Psi| = R$. Substitution for Ψ, as in (7.15), produces the classical HJ equations.

Equation (7.19) differs from (7.5) only in the last term on the right, in exactly the same way as the NLS equation (7.13) defined before. The nonlinear term in (7.19) is proportional to the quantum potential, represented by a quadratic term in (7.13). In fact, the two nonlinear equations are identical for $\beta |\phi|^2 = V_q$.

As there is nothing "classical" about (7.19) it is more plausible to simply describe it as a modified NLS equation that transforms gradually into the nonlinear HJ equation for $m > m_P$, the Planck mass, $m_P = \sqrt{\hbar c / G} = 2.17 \times 10^{-8}$ kg. In this case there is no discontinuous change from a linear to a nonlinear regime at some classical limit, as occurs for systems described by (7.5) and (7.18).

This conclusion is in line with the notion that, because of space-time curvature all material systems, including quantum objects, are intrinsically nonlinear, according to (7.19) and (7.18), linked by (7.15). For massive objects, $V_q \rightarrow 0$ and (7.18) provides the more appropriate description. There is a grey area, the analog of geometrical optics for linear systems, where (7.18) and (7.19) apply equally well. In the limit of massless entities ($m \rightarrow 0$) the sine-Gordon equation (7.14) converts into the general linear wave equation (7.1) that governs the propagation of electromagnetic waves.

The grand conclusion is that a linear differential equation cannot give a correct description of electronic structure and behaviour. Although the linear Schrödinger and Dirac equations account for most observations, some features of spectroscopic fine structure, such as the Lamb shift remain unexplained and the concept of electronegativity undefined. Correction factors based on mass renormalization and quantum electrodynamics are of the correct magnitude, but the physical basis, which attempts to smear out a point electron into a finite sphere [62, p. 231], are plagued with serious infinity problems.

The most glaring defect of linear wave mechanics is the failure to account in detail for the observed structure of the periodic table of the elements. It is more than a suspicion that a reformulation based on a nonlinear equation in 4D curved space could eliminate the need of all *ad hoc* correction factors.

7.4.1 Solving the Equation

Solution of the NLS equation (7.13) by means of an "inverse scattering transform" is described by Kaup [46]. The procedure involves mapping of the field into a nonlinear Fourier transform space, defined as the "scattering data". The coupling constant ϵ^2 in (7.13) is assumed to be real. When $\epsilon^2 < 0$, ϵ is purely imaginary and no bound states occur. However, when $\epsilon^2 > 0$ and the integral

$$\int_{-\infty}^{\infty} \left|\Psi(x,t)\right| dx < \infty$$

is sufficiently large the mapping becomes essentially linear and bound states can occur.

The bound-state part of the spectrum is analyzed by assuming the continuous part to be absent. In this case, each bound state corresponds to exactly one soliton. For the simplest case of a one-soliton solution it has the form

$$\Psi(x,t) = F(\eta_1,\epsilon)\cdot \exp\left[f_1(x-\bar{x}_0),\eta_1\right]\cdot \operatorname{sech}\left[f_2(x-x_0),\eta_1\right]$$

where x_0 and $\bar{x}_0$ are arbitrary real constants. The imaginary part of the complex eigenvalue η_1 determines the height and width of the soliton and the real part determines the velocity.

The solution for the continuous part of the spectrum, in the limit of $\epsilon \to 0$, develops in time like the solution for the linear problem ($\epsilon = 0$), in that it slowly disperses and decays away. Because of nonlinear decaying oscillations this continuous part of the spectrum is referred to as "radiation".

Remarkably, the eigenvalues for the continuous part of the spectrum are identically the same as for the linear case ($\epsilon = 0$). It was pointed out [46] that no effects requiring renormalization are found, and the zero-point energy is independent of ϵ. For $\epsilon^2 > 0$ bound states of n_j excitations moving as coherent units, occur with binding energy $\propto (n_j + \frac{1}{2})^3$. These bound-state solutions, even more so than KdV solitons, can be interpreted directly as models for electron structure and motion, both in the free state and in atoms.

7.4.2 Chemical Interaction

All chemical interactions are mediated by electrons and therefore proceed according to (7.19). In principle the behaviour of all chemical systems, from electrons to molecules and crystals, is therefore controlled by the quantum potential of that system.

Equation (7.19) as it stands, is impossible to solve unless one resorts to numerical analysis, using solutions of the linear equation (7.6) as an initial value, $\Psi(x,0)$ at $t = 0$. For the hydrogen atom in its ground state (compare Sect. 7.2.4) the linear solution predicts $V_q = -\hbar^2/2ma_0^2$, as an initial value for iterative solution of (7.19). We predict that such a solution would provide an improved simulation of the hydrogen spectrum, without *ad hoc* corrections. We note in passing that the Feynman sum over histories, the basis of quantum electrodynamics, is essentially a linear superposition and hence of dubious validity for the problem in hand. Formulation of the quantum potential of a many-body system as a linear superposition,

$$V_q = -\sum_i^n \frac{\hbar^2 \nabla_i^2 R_i(x_i, t)}{2m R_i(x_i, t)},$$

also needs nonlinear revision.

For the electron in an atomic valence state V_q, known as a function of the ionization radius [63], defines electronegativity and could be used directly as a parameter in (7.19). As for the hydrogen atom, a strategy of starting with the calculated quantum potential to analyze electron-pair covalent interaction by Heitler–London simulation is envisaged. However, any progress beyond this step must depend on the interaction between electrons in atoms and molecules. Do they behave like solitons that freely interpenetrate one another or as extended interfering standing waves? Judging by the experience with other nonlinear systems we further anticipate the need of additional nonlinearity parameters on dealing with more complex molecular systems for which (7.19) will be of limited use.

The virtue of nonlinear analysis is that it recognizes the complexity of natural systems. Although the algorithms required to address meaningful problems are vastly more complicated, the temptation of linear superposition as a strategy is eliminated by definition. Problems such as the half-dead Schrödinger cat need no longer confuse the quantum philosophers. We call into doubt the entire industry known as quantum chemistry, which is based on the linear combination of atomic orbitals. Alternative strategies are explored in the next chapter.

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Chapter 8
Matter-Wave Mechanics

Abstract The concept of matter waves as a product of four-dimensionally curved space-time is examined. A vital step in the analysis is taking cognisance of the controversial concept of an all-pervading aether. The discrepancy between relativity and quantum theory is traced to the three-dimensional linear equations of wave mechanics, in contrast to Minkowski space-time. The notion of space-like interaction is reexamined and shown to arise from a superficial interpretation of space-time curvature. The more appropriate projective topology is shown to be suitable, in principle, to define four-dimensional matter waves. The transformation from the more general underlying space-time to the familiar three-dimensional affine space is shown to be mediated by the golden ratio, which is further characterized in terms of Fibonacci numbers, Farey sequences and other concepts of number theory. It is demonstrated conclusively that the observed periodic table of the elements and the wave-mechanical approximation are correctly simulated by number theory, with a clear distinction of the respective four- and three-dimensional bases of the two models.

8.1 Introduction

The matter-wave postulate of de Broglie, developed into a wave-mechanical theory by Schrödinger, Madelung and Bohm, has revolutionized chemistry without producing a convincing working model of chemical interaction, molecular structure, or the periodicity of atomic matter. Chemical systems in the laboratory are still manipulated on the hand of the 19th century models of chemical affinity and molecular structure. The Dreiding model remains the most reliable guide in the analysis of chemical change and covalent interaction is described by straight lines that connect atomic symbols as prescribed by the principles laid down by Gilbert Lewis. In writing, chemical bonding is described by hybridization formulae, such as sp^2, with distinction between σ, π and δ types to emphasize the quantum-chemical, or orbital, meaning of the Lewis stripes. Until a convincing definition of a covalent bond can be presented all of this remains meaningless window dressing. The ploy to invoke spin pairing explains nothing while the concept of electron spin remains an empirical postulate.

Although never openly admitted the periodic table of the elements is understood no better than a hundred years ago. Molecular structure is still interpreted in terms

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of van't Hoff's model and the physical grounds of optical activity have not been identified beyond a group-theoretic statement of molecular chirality. A non-classical theory of chemistry simply does not exist.

The amount of confusion and uncertainty about the essential nature of matter is simply too much for a consensual theory of atomic structure and chemical interaction to be feasible. Models that recognize atoms-in-molecules peacefully coexist with molecular-orbital theories, free-electron simulations and sterically dubious molecular rearrangements. At a deeper level the concepts of a physical vacuum and of a void are used interchangeably, while assuming the presence of an electromagnetic field and wave motion in the vacuum. Even Aristotle realized that there would be no upper limit to the speed of an object in a void. On the one hand the same theory of relativity that imposes such a limit is invoked to declare the non-existence of an aether in the vacuum. Or does it?

According to Dirac [1]

> ...the existence of an æther could not be fitted in with Einstein's discovery of the principle of relativity... This argument is unassailable from the 1905 point of view...

Another authority [2] states that:

> [Poincaré's theory of relativity] was based on the full theory of electromagnetism and was restricted to phenomena associated with the concept of a universal ether that functioned as the means of transmitting light, *a concept that Einstein shared.*

Emphasis added.

Einstein himself is quoted [3] to have stated repeatedly that

> ...Ether exists. According to the general theory of relativity, space is inconceivable without ether...
>
> We cannot manage in theoretical physics without ether, *i.e.* a continuum provided with physical properties.

It is rather obvious that the relativity objection was not so much against the medium through which the radiation propagates as against Maxwell's vortex model of the aether, when he declared that:

> We can scarecely avoid the conclusion that light consists in the transverse oscillations of the same medium which is the cause of electric and magnetic phenomena.

In this he referred to his mechanical model of the aether [4] that guided him in the derivation of the electromagnetic equations. To him the aether was composed of subatomic vortices, all rotating in the same direction so as to produce the circulation of the magnetic field. Some details, shown in Fig. 8.1, are explained by Maxwell [4] as follows:

> The contiguous portions of consecutive vortices must be moving in opposite directions... The only conception which has at all aided me in conceiving

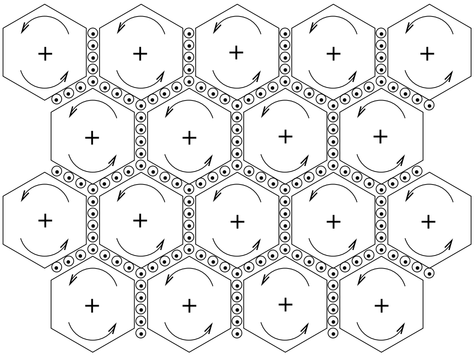

Fig. 8.1 Maxwell's model of the aether, composed of vortices that rotate in the same sense so as to produce circulation of the magnetic field

> of this kind of motion is that of the vortices being separated by a layer of particles, revolving each on its own axis in the opposite direction to that of the vortices, so that the contiguous surfaces of the particles and of the vortices have the same motion
>
> In mechanism, when two wheels are intended to revolve in the same direction, a wheel is placed between them so as to be in gear with both, and this wheel is called the 'idle wheel'. The hypothesis about the vortices which I have to suggest is that a layer of particles, acting as idle wheels, is interposed between each and the next, so that each vortex has a tendency to make the neighbouring vortices revolve in the same direction with itself.

The idle wheels were supposed to be particles of electricity.

Ignoring the 19th century mechanical details Maxwell's aether may, in hindsight, be interpreted as a tenuous medium that resonates in a structured way with electromagnetic disturbances in a process that minimizes four-dimensional action.

8.2 The Aether and Matter

To understand the results of special relativity it is necessary to assume that matter does not move through the aether, but that a four-dimensional æther penetrates through matter.[1] This interpretation would explain why certain forms of matter are transparent to some forms of radiation, but less so than the vacuum. The electromagnetic field of the aether is perturbed by the local electron distribution as it passes through matter. Radiation of different wavelengths responds characteristically to the degree of perturbation and, although the nature of the field is more subtle than Maxwell's aether the result is the same.

We recall that the electromagnetic field is a gauge field that is generated by space-time curvature. The local gauge field affects the phase of electromagnetic waves and

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[1] This is interpreted to mean that there is no *motion* through the aether. The perception of three-dimensional motion reflects a *static* situation in space-time [5].

its influence on ponderable matter in the bulk must therefore be minimal. However, space-time curvature has another manifestation as discovered accidentally in a calculation by Schrödinger [6, 7], which was aimed at the analysis of wave motion in an expanding universe.

8.2.1 Alarming Phenomena

Schrödinger [6] studied the massive scalar field, described by the covariant Klein–Gordon equation

$$-\nabla^2\psi + \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} + \mu^2\psi = 0$$

where $\mu = mc/\hbar$, by separating space and time variables. The temporal part

$$\frac{d^2 f(\tau)}{d\tau^2} + \omega^2(\tau) f(\tau) = 0$$

describes a linear oscillator with circular frequency $\omega(\tau)$, $d\tau = dt/R^3(t)$.

This equation can be solved only for special choices of $R(t)$. For constant R, *i.e.* constant ω, it reduces to the linear oscillator equation which is solved by plane waves $e^{\pm i\omega t}$. After an accelerated change of $R(t)$ the initial solution of $e^{i\omega t}$ (say) need not be the same after the event, and more generally will be a superposition of plane waves with different signs of frequency (and energy):

$$f(\tau) = Ae^{i\omega t} + Be^{-i\omega t}.$$

This unavoidable frequency mixing or mutual adulteration of positive and negative frequency terms gives rise to what Schrödinger called “alarming phenomena”. What it means is that the accelerated change has created a particle–antiparticle pair from the vacuum. In general relativity where acceleration is equivalent to curvature the inference is that equal amounts of matter and antimatter are produced by space-time curvature.[2]

In the present context this observation is anything but alarming. Rüger [7] expressed surprise at the fact that the proponents of continuous creation in a steady-state universe had not seized upon this result in support of their theory. The obvious

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[2] As an interesting side-issue it is of interest to note Schrödinger’s conclusion about universal expansion as the cause of nebular red-shifts. For galaxies of constant diameter and energy output he found that expansion had no effect. He pointed out:

> To speak of a Doppler-effect is rather inappropriate, for the thing has nothing to do with dR/dt in the moment of emission or in the moment of observation, but only with the ratio of the R’s of these two moments.

Clearly an effect of curvature as surmised by Hubble [8].

dilemma must have been to explain away the antimatter that, in good time, would annihilate their equivalent of conjugate matter, with zero net creation of matter.

What is more exciting is the fact that in this instance wave mechanics confirms a conclusion inferred before from the field equations of general relativity. We recognize the possibility of a unified quantum-relativistic approach towards a new theory of matter as a condensation of space-time aether.

8.2.2 *Generation of Mass*

Space-time curvature distorts the geometry of the aether to the point where the stress, so generated, is relieved by the release of elementary quanta. This process may be considered as restoring the plane-wave structure of Euclidean aether by extrusion of distorted regions in the form of elementary solitons, which, by definition, are totally transparent to the primary plane wave.

Elementary solitons occur in a limited variety of forms, observed to emerge with characteristic properties of spin, charge and mass, dependent on internal wave structure. Composite structures result through the combination of complementary entities with increased mass, although spin and charge are typically neutralized in the process.

Standing waves, like gas molecules, exert pressure on the walls of a container. With the container at rest or in uniform motion the force exerted on any wall is balanced by that exerted on the opposite wall. If the container is accelerated radiation reflected off the rear wall gains more momentum than that lost by the radiation which reflects off the front wall. It has been demonstrated [9–12] that radiation exerts a net force, which opposes an applied force on the container, such that

$$\left(m + \frac{E_R}{c^2}\right)a = F.$$

The radiant energy adds an effective inertial mass E_R/c^2 to the mass of the container. In the same way the total mass of an elementary soliton may be interpreted as deriving from internal motion in a phase-locked cavity.

8.2.3 *Space-Time Topology*

Special relativity is formulated in pseudo-Euclidean Minkowski space and Schrödinger wave mechanics in 3D Euclidean space. In order to establish common ground with general relativity both of these need to be recast into four-dimensional non-Euclidean space-time. The immediate purpose of this is to arrive at a model for elementary matter which is consistent with both quantum theory and general relativity. We are constantly aware of the fact that the use of the Klein–Gordon equation in the following does not recognize the intrinsic nonlinearity of curved space-time.

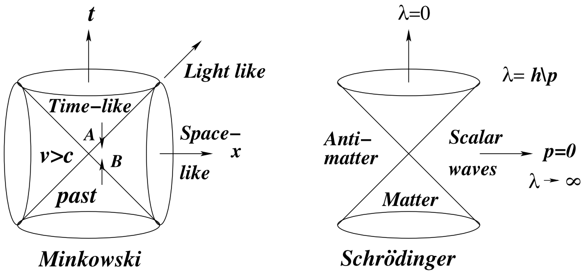


Fig. 8.2 Diagrams to illustrate the correspondence between Minkowski and Schrödinger spaces

Minkowski Space

The theory of special relativity distinguishes between three types of motion, clearly defined by a Minkowski light cone, as in Fig. 8.2.

Electromagnetic interaction is propagated at constant speed of c in the surface of the light cone. Time-like motion of mechanical objects at speeds of $v < c$ occurs within the light cone and superluminal space-like motion, on the outside, is traditionally considered to be non-physical. There are no obvious grounds for this assumption, which actually is at the root of the discord. Space-like motion can clearly be non-local, which means that in the special case, when lacking a time component, displacement happens instantaneously, exactly as in the quantum process denounced by Einstein [13].

Relativistic and quantum theories both depict the world as an entangled whole. Relativity makes no distinction between the space and time coordinates of a four-dimensional reality, meaning that the world-line of a general event is a function of space-time rather than of space and time. There are three special cases:

(i) a stationary object that proceeds along the time axis;
(ii) a non-local event that spreads (instantaneously) along the space axis;
(iii) an electromagnetic disturbance in the isotropic surface of the light cone, which separates time-like and space-like events.

Quantum theory attempts to achieve holistic entanglement in the correlation of distant events.

Schrödinger Space

Quantum theory tells the same story in different words. A wave that mediates electromagnetic interaction, also referred to as a photon, has zero rest mass and does not obey the equation for matter waves, propagates with a speed v that equals its phase velocity $v_\phi = c$, and has an effective momentum related to its wavelength, $p = h/\lambda$. It is the epitome of a quantum object with a quantum potential $V_q \to \infty$, compared to classical objects with $V_q \to 0$. Entities within the light cone, which include all composite waves and wave packets with group velocity $v_g < c$, are known collectively as matter and antimatter. Complementary stuff, known as *tachyons*, occurs

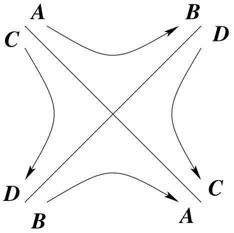


Fig. 8.3 Two-dimensional projection of closed geodesics in Minkowski space-time. The curve *AB(CD)* returns through a point at infinity to continue as the involuted curve *BA(DC)* that meets up with *AB(CD)* in the same way

in the region excluded by the light cone, with $v_g > c$. In all cases $v_g v_\phi = c^2$. The superluminous stuff may also be considered as scalar waves with $\lambda \to \infty$, $p = 0$, *i.e.* completely non-local.

It is instructive to consider non-dispersive wave packets made up of tachyonic and bradyonic ($v < c$) components. Matter wave packets with a structure as shown schematically in Fig. 7.2, may be synthesized from the interaction of two waves moving in opposite direction with speed $v <$ and $> c$. A macroscopic radius is defined by the de Broglie wavelength, $\lambda_{dB} = h/mv$, and the internal structure is characterized by the Compton wavelength $\lambda_C = h/mc$ of the superluminal waves known as *Zitterbewegung* (trembling motion) [14].

We note that the instantaneous response of an electron in interaction used to be considered a violation of special relativity, unless the electron is seen as a point particle. The argument is readily refuted by considering the electron as a holistic unit, but the conviction remains.

The wave description of the electron accounts for the fine-structure parameter $\alpha_e = \lambda_c/\lambda_{dB} = v_g/c$. The related tachyon would have $\alpha_t = c/v_\phi$. The familiar fine-structure constant, $\alpha = e^2/\hbar c$, refers to an electron in the ground level of a proton field (H atom), with $v_1 = e^2/\hbar$, in electrostatic units. Within the light cone velocity refers to the motion of massive objects and matter waves. In the light-cone surface it refers to electromagnetic waves, and in the space domain to long-wavelength scalar waves and tachyons.

Curved Space

Minkowski space in the real world cannot be flat on a large scale. In order to generate a connected surface it is necessary that all of space should be curved appropriately. The curvature should be such that the isotropic lines that appear to diverge in two-dimensional projection should close onto themselves in more dimensions. A useful clue is provided by the pseudocircles in Minkowski space, $\mathbb{M}^2$, $x^2 - c^2t^2 = \pm r^2$, which appear as a pair of hyperbolas [15] that may join up into two Möbius bands as shown in Fig. 8.3. The four-dimensional equivalent defines what is known as a projective plane, an elliptic space, which, like a Möbius band is one-sided and non-orientable. Motion along the double cover of the projective plane (or the Möbius band) goes through an involution which entails an inversion of chirality. It thereby defines an isotropic interface that separates regions of matter and antimatter.

Separation of the four-dimensional equation $\Box^2\phi = 0$, on assuming the product function $\phi(x,t) = u(x) \cdot \psi(t)$, into the temporal and atemporal pair of equations:

$$-\frac{1}{c^2}\frac{d^2\psi}{dt^2} + k_0^2\psi = 0,$$

$$\nabla^2 u + k^2 u = 0,$$

although mathematically feasible, is physically dubious, as the constants k_0 and k are not separable, unless either $k_0 = 0$ or $k = 0$. The equations therefore remain linked and only with appropriate choice of constants (*e.g.* $k = ik_0$) is a physically allowed separation into space-like and time-like wave equations of the form

$$\nabla^2\psi \pm \left(\frac{m_0 c}{\hbar}\right)^2 = \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} \tag{8.1}$$

obtained as a first approximation by setting $\hbar\omega = m_0 c^2$. This is the Klein–Gordon equation in a form used by Elbaz [16] to describe both time-like and space-like matter waves, the latter with rest mast of im_0, as derived for tachyons by Feinberg [17]. Equation (8.1), although a notable improvement on Schrödinger's amplitude equation, still fails to reflect the large-scale structure of curved space-time.

Solution of (8.1), by projection from homogeneous projective coordinates was described by Veblen and Hoffmann [18]. The transformation from the projective manifold into three-dimensional tangent space was noticed [19] to be mediated by the golden ratio and local gauge invariance [20].

Complex Geometry

This simple picture is flawed. Not only is the time axis perpendicular to each of the three cartesian space axes but, with respect to each of the space axes, it is an imaginary axis in the mathematical sense. The four-dimensional differential element of separation

$$ds^2 = \sum_{\mu=0}^{3}(dx_\mu)^2$$

defines $x_0 = ict$. The isotropic line, which represents the light cone, implies $x = it$ in Fig. 8.2 and has some unusual properties. In standard 2D coordinate geometry the distance between two points is defined as

$$d = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}.$$

For $x = iy$ in the complex plane, noting that $i^2 = -1$, it becomes:

$$d = \sqrt{-(y_1 - y_2)^2 + (y_1 - y_2)^2} = 0.$$

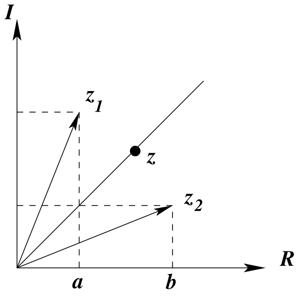


Fig. 8.4 Minkowski perpendiculars

The dot product of two complex vectors, as in Fig. 8.4:

$$z_1 = a + ib \quad \text{and} \quad z_2 = b + ia, \quad i.e.\ z_1 \cdot z_2 \cos\theta$$

is calculated from $z_1 \cdot z_2 = x_1x_2 + y_1y_2$ as $ab - ba = 0$, and hence these vectors are perpendicular to each other (Effectively, $\theta = \pi/2$).

The vectors coincide, on the isotropic line, $z \cdot z = 0$, which means that the line is perpendicular to itself. The two isotropic lines of Fig. 8.2 are therefore one and the same line and must join up geometrically. Any two points on the isotropic line are in contact ($d = 0$) and therefore connected non-locally. Crossing the isotropic line at A, in Fig. 8.2, implies crossing at B, showing that the isotropic light cone constitutes an interface between time-like (matter) and space-like (antimatter) domains.

Antimatter

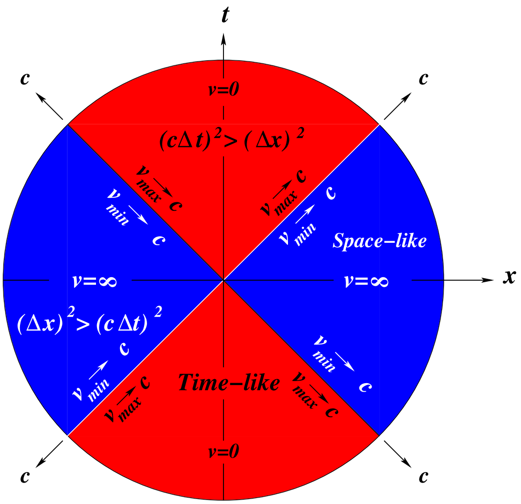
As shown in the previous section, the closure of Minkowski space-time is only possible with involution, which implies projective geometry. Relevant details for chemists were published recently [19] and will not be repeated here. The essential argument recognizes a closed surface of which the double cover is non-orientable, with identity period of 4π. The involuted conjugate arrangement is reached by a 2π rotation along the double cover.

As a model of space-time the closed surface represents the vacuum as an interface between the conjugate forms in the double cover. It makes good sense for weightless achiral bosons to move in the interface which is the same as the aether, with the chiral forms of matter and antimatter on opposite sides in the double cover. The alarming phenomena now become charming phenomena.

The matter and antimatter that result from the curving of space-time are separated directly by the interface. For the conjugate forms to come into contact would require 2π rotation along the double cover, through the involution that inverts chirality. A unit of matter on 4π transplantation along the double cover therefore gradually changes into antimatter and back into matter without catastrophe, in line with the original conjecture [21].

This construction implies complete independence of the gravitational and electromagnetic fields. Both of them have their origin in space-time curvature, with

Fig. 8.5 Minkowski space-time diagram to explain the possibility of superluminal speeds, approaching infinity in the space-like domain



electromagnetism confined to the interfacial aether and gravity in the double cover, pervaded by the vacuum.

The caricature of closed Minkowski space-time as in Fig. 8.3 shows that, like the closed projective plane that represents the vacuum interface, the double cover is closed on all sides by the interface. The isotropic light surfaces all intersect on a line at infinity.

Tachyonic Motion

In a more radical analysis of Minkowski space-time superluminal motion is assumed to occur in the space-like domain.

The idea is based on Feinberg's [17] interpretation of space-like events in terms of tachyonic motion ($v > c$), with a limiting minimum speed of c. Details are summarized in Fig. 8.5. In this model an increase in velocity corresponds to a lowering of kinetic energy.

In line with common usage a theory is developed in the context of quantum-field particle theory, not always in line with the wave theory subscribed to in the present discussion. The statement that "tachyons are fermions, even though they have spin-zero" points at one serious inconsistency. The remark that emission of Čerenkov radiation by tachyons in free space had been known to Sommerfeld in 1904 needs careful attention. In Sommerfeld's analysis [22], communicated by Lorentz, the motion of a charged object with velocity close to or exceeding c is examined. He did indeed calculate the field of a hypothetical charged particle with superluminal speed in the form of a "shadow of motion", as in Fig. 8.6.

It has the same shape as a sonic boom or Čerenkov radiation with $\sin\theta = c/nv$, associated with β-particles of velocity $v > c/n$, emitted by a radioactive source in a

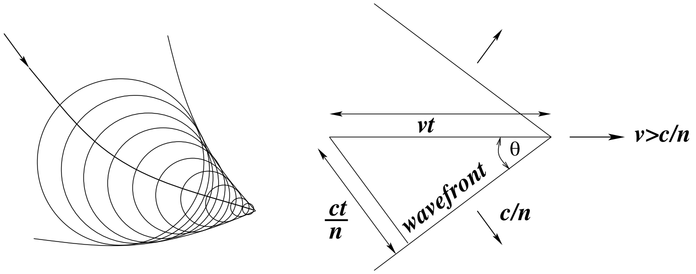


Fig. 8.6 The shadow of motion calculated by Sommerfeld [22] for a superluminal charged particle, compared to the Čerenkov radiation emitted by β-particles in a nuclear reactor

medium of refractive index n. As pointed out [22] "…it is the smaller, the more the velocity of the electron exceeds that of light", as for Čerenkov radiation as $n \to 1$.

The analysis is put into perspective by the following relevant statements [22]:

> …you deduct easily the value of the force, necessary to maintain a motion of a bodily charge with a velocity exceeding that of light. This force is distinctly finite, even in case of infinite velocity…
>
> …in case the charge is concentrated at one point, the force is infinite even in the case of a velocity less than that of light.
>
> *Although the stationary motion with velocity exceeding that of light is no free possible movement of the electron, yet this motion is not impossible from a physical point of view as requiring* (even if the velocity is infinite) *in every moment only a finite expense of force and also for every finite path only a finite expense of work.*
>
> *The stationary motion of an electron, charged uniformly over its surface, with a velocity exceeding that of light is actually impossible; it would require an infinitely great expense of force and energy.*

Of importance in the present context is the description of an electron as an object of finite size that carries bodily charge, rather than having it spread over the surface. The implication is that elements of charge, smaller than the unit electronic charge cannot be identified. However, superluminal electronic motion is considered feasible in an accelerating field, admittedly without taking the effect of radiation into account. Since tachyons lose energy when accelerated the inverse must be equally true. A charged tachyon that emits Čerenkov radiation must therefore accelerate indefinitely, with runaway energy production.

Without the projective involution Feinberg's proposal of tachyonic motion could perhaps be a valid model, but only in infinite space-time. The model has indeed been used successfully to interpret a variety of elementary particle interactions [23], but later analyzed [24] equally well in terms of a nonlinear wave hypothesis. A more plausible interpretation to prevent the infinite energy catastrophe is that only from a time-like perspective does a tachyon appear to move with superluminal speed, away from the interfacial light surface. Within the space-cone the laws of motion are therefore the same as in the light cone.

Feinberg's interpretation of Minkowski space-time contradicts the assumption of projective topology. Displacement of 2π through the projective involution implies inversion of chirality, as in a gauge transformation, without measurable effects on internal kinematics. Superluminal velocity therefore remains undefined and leaves the meaning of space-like displacement unexplained.

Without experimental evidence that tachyons exist the projective interpretation of curved space-time must therefore be preferred and the idea of tachyonic motion considered as another example of the misreading of four-dimensional phenomena in three-dimensional mode.

The relativistic barrier to superluminal motion is to be interpreted to physically coincide with the topological interface that separates the world and antiworld. This could mean that superluminal motion is prevented by the structure of the vacuum because of an effect such as the sound barrier in air and that is why the Lorentz transformation is universally valid.

8.2.4 The Vacuum

The nature of the vacuum clearly holds the key to a proper understanding of matter and energy. The existence of an electromagnetic field can be inferred with a high degree of confidence, but an exact model of this field is difficult to conjecture. Even more speculative is the existence of a quantum-potential field and still harder to imbed is the gravitational field. Precise details of these fields, beyond a mathematical account of their effects, are simply unknown. To populate the vacuum, as a basis for understanding quantum-field theory, by 10^{80} virtual particles, signals desperation on a par with Maxwell's aether or Descartes' aetherial foam.

The only firm evidence about the nature of the vacuum is that it supports the flow of energy. In the case of electromagnetic energy this process is clearly associated with wave oscillations. The remarkable fact is that the rate of energy transmission is independent of the energy and motion of its source. Only the wavelength changes, $\lambda = c/\nu = hc/E$. For no transfer of energy between emitter and absorber, $\lambda = \infty$ $(p = 0)$, in the state of equilibrium.

For matter waves with rest mass of m, $hc/E = hc/mc^2 = h/mc = \lambda_C$, the Compton wavelength. As discussed in Sect. 7.2.2 λ_C is characteristic of a wave packet with de Broglie wavelength $\lambda_{dB} = h/mv_g$, where the group velocity v_g represents the velocity of a soliton, interpreted as the electron.

The displacement of ponderable matter follows a similar pattern, except that the state of motion is subject to external stimuli. In this case the transmission of energy does not depend on interaction with the aether, as a massive object is no longer part of it. Not subject to any interaction such an object maintains its inertial motion along the geodesics of space-time. In local tangent space these are straight lines and on a larger scale they follow the general curvature of space-time with local perturbations in the vicinity of massive objects like planets and stars. This scenario defines the gravitational field. It is an attractive possibility to define this field along the same lines as electromagnetism. However, the gravitons, postulated to mediate such interaction, have never been observed and probably never will.

The substance of the vacuum is undefined in spaces of three or less dimensions. It is noted that one-dimensional motion is proscribed by the potential energy equation $d^2y/dx^2 = 0$, with the geodesic solution $y = mx + b$. In four-dimensions $\Box^2 y = 0$ defines a potential-energy field created by space-time curvature. Separation of the variables denies physical reality and the only acceptable solution of the equation is in terms of hypercomplex quaternions.

The aether which supports quantum fields in the vacuum is subject to the same geometry of space-time that accounts for the geodesic motion of light rays. To distinguish between light and matter the former may be viewed as energy waves that move at the constant velocity that defines the limiting speed of both matter and antimatter waves. This statement comes with the caveat that speed and velocity are strictly three-dimensional concepts with vastly different meaning in four-dimensional space-time.

8.3 The Wave Model

Our quest for the essence of atomic matter that underpins a fundamental understanding of chemistry is drawing to a close. The evidence that matter originates in the vacuum rather than independently existing as point particles in a void, appears conclusive. The crucial decision to decide between the alternatives hinges on an understanding of mass.

One version of the particle model [25] ascribes the acquisition of mass to interaction of virtual particles, modelled as open points, with the Higgs field that resulted from a phase transition of the big-bang vacuum at $0 + 10^{-36}$ seconds, initiating inflationary expansion that lasted until $0 + 10^{-33}$ seconds, increasing the diameter of the universe to 10 cm and transforming the virtual particles into point particles with mass.

The phase transition was supposedly triggered by spontaneous breakdown of the symmetry of the vacuum, with the release of sufficient latent energy to drive the expansion. The hidden assumption is that the big bang started as a stable point universe of high symmetry and energy. The only possibility whereby the temperature could be lowered, was by an increase in size. The creation of space and time to allow this is therefore the real miracle that enabled the transformation of the static point into a dynamic topology. The mathematical description of the procedure is equivalent to a local gauge transformation (Sect. 4.3.3).

Inflation theory is claimed to have solved all cosmological problems, but in the process it created all the problems, related to point electrons, that exist in chemistry today.

In the wave model the attribute of mass is described by the same mathematical model, without the creation miracle. Instead of point symmetry, that spontaneously transforms into extended space-time of lower symmetry, the relevant symmetry states of the argument are the alternative perceptions of tangent Euclidean space and the lower-symmetry non-Euclidean description of the same vacuum. Interaction with a hypothetical Higgs field is obviated. Ponderable matter represents the difference between Euclidean and non-Euclidean forms of a uniform continuous wave field.

The difference between differently curved surfaces is described in terms of their Euler characteristics as derived from *differential topology* [26]. An elementary example concerns the extent to which a hairy surface can be brushed with all hair in the same continuous direction. Failure to achieve complete continuity of direction results in the appearance of *tufts*, *holes* and *crowns* in surfaces of different topology. These are known as *singular points* of the surface and may include *sinks*, *sources*, *vortices*, *crosspoints*, *dipoles*, *foci* and others of higher and higher Euler *index*, depending on the local topological features in the manifold. Some of these, such as sources and sinks would clearly mutually annihilate each other on encounter, in the same way as matter and antimatter, unless they are generated on opposite sides of an interface.

In the wave model of matter these singularities appear as standing waves or solitons, with different characteristics and represent what is commonly known as *elementary particles*. Different combinations of topological qualities manifest as different characteristics of mass, charge and spin.

8.3.1 Projective Solution

The way in which special relativity and quantum theory describe the world from different perspectives is only rarely acknowledged. Relativity describes the motion of particles and quantum theory that of waves. Confusion sets in when the two theories are used carelessly to address the same problem, or inappropriate physical models are forced onto the mathematical results of a theory. Several examples of such confusion have been highlighted and some of these are repeated here by way of illustration.

Most recently we discussed the unwarranted interpretation of the space-like segment of Minkowski space-time to postulate the existence of tachyons, which relates to the presumed non-local nature of quantum theory. In this case the confusion centres around the unphysical separation of the spin function. In one analysis of the problem the components of electron spin is considered to be undefined until the wave function is collapsed by a physical measurement, when they assume probabilistic values. The relationship, observed to persist between previously correlated spins, is then interpreted as non-local interaction. The alternative description of the electron as a wave structure with intrinsic four-dimensional spin immediately resolves the problem.

The confusion spreads even further when electromagnetic radiation is described as particulate photons. It seems to work in accounting for the photoelectric and Compton effects, but have no explanation of elementary optical effects such as diffraction. The postulate of wave-particle duality only clouds the issue even more. The wave model works in all cases.

The honourable way out for all concerned is shown by the theory of general relativity, based on the non-Euclidean geometry of space-time. This way out was recognized early on by Schrödinger's [6] on pointing out that:

> Wave mechanics imposes an a priori reason for assuming space to be closed; for then and only then are its proper nodes discontinuous and provide an adequate description of the observed atomicity of matter and light.

As a working model we accept that energy propagates as wave motion through the electromagnetic field. Linearity of the field is maintained by the extrusion of flexible standing waves to compensate for the intrinsic nonlinearity of curved space-time. These elementary units behave as four-dimensional matter waves. Their motion and interactions can only be adequately described by nonlinear wave equations, the formulation of which depends on the topology of space-time. To outline the procedure that leads to such a wave equation in projective space-time we follow the detailed description as presented by Oswald Veblen and Banesh Hoffmann [18].

Unification of the gravitational and electromagnetic fields by Kaluza and Klein, in terms of a five-dimensional field is shown to reduce to a four-dimensional theory based on projective geometry. Projective tensors have 5^k instead of 4^k components and in each coordinate system they have an infinity of components dependent on a factor x^0, identified as a gauge parameter.

With any point $(x^1x^2x^3x^4) = x$ of space-time there is associated an infinity of differential sets $(dx^1dx^2dx^3dx^4) = dx$. These differentials are arbitrary numbers and may be regarded as coordinates of another four-dimensional space, called a tangent space of the underlying space. The point $dx = 0$ is identified with the point x and is called the point of contact. Thus to each point of space-time there is an associated affine tangent space. The theory of these tangent spaces together with the underlying space becomes a Riemannian geometry if a Euclidean metric is introduced in each tangent space by means of a quadratic differential form[3]

$$g_{ij}dx^idx^j.$$

The tangent spaces can be converted into projective spaces by introducing points at infinity as explained before [19]. The projective spaces are studied analytically by means of homogeneous coordinates (X^α) and projective tensors. The effect of this is that Kaluza–Klein 5-space becomes a projective rather than an affine theory of space-time. The symmetric covariant tensor of second degree, $G_{\alpha\beta}$, determines a metric in each tangent space:

$$G_{\alpha\beta}X^\alpha X^\beta = 0.$$

The point of contact of the tangent space with the underlying space has homogeneous coordinates such that $X^i = 0$. The tangent lines to the quadric from this point meet it in points which all lie in a hyperplane

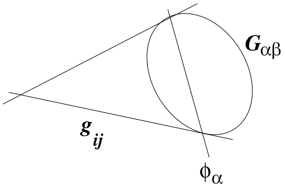
$$G_{\alpha 0} = X^\alpha = 0.$$

---

[3] Latin suffixes take on values from 1 to 4 and Greek suffixes from 0 to 4.

The tangent lines generate a quadric cone with its vertex at the point $X^i = 0$. The equation of this cone may be written in nonhomogeneous coordinates

$$g_{ij}dx^i dx^j = 0.$$



The coefficients g_{ij} represent the gravitational potentials of ordinary relativity. The ϕ_α is a projective vector such that $\phi_0 = 1$. The components ϕ_i represent the potentials of the electromagnetic field.

Under an ordinary transformation the ϕ_i transform like the components of an affine vector

$$\bar{\phi}_i = \phi_j \frac{\partial x^j}{\partial \bar{x}^j}, \qquad \bar{\phi}_0 = \phi_0$$

but with a change of gauge factor

$$\bar{\phi}_i = \phi_i - \frac{\partial \log \psi}{\partial x^i}, \qquad \bar{\phi}_0 = \phi_0$$

ϕ_i changes by the addition of a gradient and so in any coordinate system is determined only to within an additive gradient, which is the property of the vector potential of the relativistic Maxwell field (compare Sect. 4.3.3).

Following the procedure for deriving the field equations of general relativity in terms of projective tensors leads to

$$\Gamma_{\alpha\beta} - \phi_\alpha \phi_\beta \Gamma = 0.$$

These expand into a set of equivalent affine equations that are identical with those of classical relativity. More generally the equations afford a solution of the unification problem by combining the field equations for gravitation and electromagnetism into a single invariant set of equations. Solutions to this set of equations must describe the motion of an electron in curved space-time. Of special interest in the present context is the solution obtained for the general field equations which, in affine form, reduce to:

$$\frac{1}{\sqrt{g}}\frac{\partial}{\partial x^i}\left(g^{ij}\sqrt{g}\frac{\partial \psi}{\partial x^j}\right) - \frac{4\pi ie}{h}g^{ij}V_j\frac{\partial \psi}{\partial x^i} - \frac{2\pi ie}{h}\frac{1}{\sqrt{g}}\psi\frac{\partial}{\partial x^i}\left(g^{ij}V_j\sqrt{g}\right)$$
$$-\frac{4\pi^2e^2}{h^2}g^{ij}V_iV_j\psi\left(\frac{5}{27}R - \frac{4\pi^2mc^2}{h^2}\right)\psi = 0.$$

Nowhere is the equivalence of relativity and quantum theories demonstrated more convincingly than in the transformation of the projective relativistic field equations to affine tangent space. In gravitation-free Minkowski space of signature $\{1\ 1\ 1\ -c^2\}$ the field equations reduce to a form that closely resembles the relativistic Klein–Gordon wave equation in the electromagnetic field. Conversion of the four-potential to tangent space was achieved by setting

$$(\tau + \tfrac{1}{2})\phi_j = \left(\frac{e}{mc^2}\right)V_j,$$

in which the golden ratio, τ appears as a proportionality constant. The quantum condition is introduced by scaling the arbitrary gauge index, N, of the projective curvature tensor as in

$$(\tau + \tfrac{1}{2})N = -\frac{3}{4}\left(\frac{mc}{\hbar i}\right),$$

which is equivalent to the stipulation of gauge invariance, as prescribed by Schrödinger [27]. Noting that $\tau^2 + \tau = 1$, the product of these two expressions reduces to

$$\tfrac{5}{3}\phi_j N = \left(\frac{ie}{\hbar c}\right)V_j \equiv \phi_\alpha$$

as it occurs in the Klein–Gordon equation [28, 29]:

$$\left[\left(\frac{\partial}{\partial x_\alpha} + i\phi_\alpha\right)\left(\frac{\partial}{\partial x_\alpha} + i\phi_\alpha\right) - k^2\right]\psi = 0,$$

$$\phi_i = \left(\frac{e}{hc}\right)A_i, \qquad \phi_4 = \left(\frac{e}{hc}\right)iV, \qquad k^2 = \frac{m_0^2c^2}{\hbar^2}, \qquad x_4 = ict.$$

The quantity in brackets is the same as the phase factor associated with a five-dimensional electronic wave function [30], or equivalently, the four-dimensional function in homogeneous projective coordinates. It was introduced here [18] to define the projective scalar $\Phi = \psi^{3/5}$.

The remarkable resemblance between the two diagrams of Fig. 8.2 reflects the common ground between quantum theory and relativity discovered by Veblen and Hoffmann.

8.4 Matter in Space-Time

Four-dimensional space-time, which is intrinsically nonlinear and chiral, is described by a form of d'Alembert's equation

$$\Box^2\psi = f(m)\psi$$

as a function of matter and energy in homogeneous projective coordinates. The function $f(m)$ derives from fourteen algebraically independent equations that involve the fifteen quantities $G_{\alpha\beta}$ of a projective tensor of arbitrary index N. Direct solution in projective space-time, without separation of the variables, has never been attempted beyond the separation of gravitational and electromagnetic potentials in affine tangent space.

A more detailed solution is not anticipated to be forthcoming any time soon. The only practical alternative is to simplify the formidable projective field equations into a manageable set, with the clear understanding that each simplifying assumption entails a loss of information.

It has been emphasized several times how the separation of space and time variables destroys the four-dimensional spin function, reducing it to an approximation in terms of two-dimensional rotations and vibrations.

It has also been remarked that by adopting a system of linear differential equations the intrinsic nonlinearity of curved space-time is unaccounted for. Sophisticated experiments [31] to explore the subtle effects of linear superpositions may be chasing phantoms. The use of nonlinear wave equations may be a better approximation, but on solution by the separation of variables still ignores hidden effects.

The status of chemistry, the central science that should clarify the condition with respect to the fundamental nature of matter, is of special concern. The chemists of the world seem to be content that the ultimate understanding was achieved in Max Born's interpretation of wave mechanics as a statistical formula to predict the most likely position of a particle that performs random jumps. To elucidate chemical bonding, valence electrons are assumed to "occupy" atomic orbitals that demarcate high-probability vibration directions, identified by a linear superposition of real functions in the complex plane. This model violates each and every condition implied by wave mechanics in, not only four, but also in three-dimensional tangent space.

A few attempts to solve a wave equation in curved spaces [32, 33] relied on separation of the variables and assumed spin matrices, without adding anything to the standard approach.

If the brute-force approach is unlikely to produce a new basis for theoretical chemistry it may be necessary to examine less direct alternatives. An attractive possibility is to explore the way in which non-Euclidean effects could qualitatively augment the approximate results obtained with the three-dimensional Euclidean model, without solving the full four-dimensional problem. The importance of the golden ratio as a conversion factor between projective and affine environments suggests one possible approach.

8.4.1 Fibonacci Numbers

Fibonacci numbers were first (?) discovered to model the population of a rabbit colony, but have a much wider significance. The numbers are generated as an infinite

Table 8.1 Fibonacci numbers as a basis of natural numbers

n	1	2	3	5	8	13	21
0	0						
1	1						
2	0	1					
3	0	0	1				
4	1	0	1				
5	0	0	0	1			
6	1	0	0	1			
7	0	1	0	1			
8	0	0	0	0	1		
9	1	0	0	0	1		
10	0	1	0	0	1		
11	0	0	1	0	1		
12	1	0	1	0	1		
13	0	0	0	0	0	1	
14	1	0	0	0	0	1	
15	0	1	0	0	0	1	
16	0	0	1	0	0	1	
17	1	0	1	0	0	1	
18	0	0	0	1	0	1	
19	1	0	0	1	0	1	
20	0	1	0	1	0	1	
21	0	0	0	0	0	0	1
22	1	0	0	0	0	0	1
23	0	1	0	0	0	0	1
24	0	0	1	0	0	0	1
25	1	0	1	0	0	0	1
26	0	0	0	1	0	0	1
27	1	0	0	1	0	0	1
28	0	1	0	1	0	0	1
29	0	0	0	0	1	0	1
30	1	0	0	0	1	0	1
31	0	1	0	0	1	0	1
32	0	0	1	0	1	0	1

series

$$F_n = F_{n-1} + F_{n-2}$$

with seed values of $F_0 = F_1 = 1$, generating

$$F_{n=2}^{\infty} = 1\ 1\ 2\ 3\ 5\ 8\ 13\ 21\ 34\ldots$$

These numbers can be used in more than one way to code for all the natural numbers. The presentation shown in Table 8.1 has the advantage that two adjacent Fibonacci numbers never contribute to the definition of an integer. The symbols 1 and 0 are used to identify the F_n that contribute to each sum. In Fibonacci notation an integer is represented by the inverse of the strings defined in Table 8.1. For example

$$32 = 1010100.$$

A periodic pattern in the least significant figures of the Fibonacci code for the numbers 1–32 reveals an interesting relationship with four-dimensional Euclidean geometry. In Table 8.2 the truncated codes for pairs of odd and even integers are compared.

Interpreted as unit vectors the pattern corresponds in detail with what is known as the *Hamilton path* [34] of a four-dimensional cube. The Hamilton path through any connected set of edges and vertices is a route through the edges that visits each

Table 8.2 Pairs of integers in Fibonacci code interpreted as four-dimensional unit vectors

1–2	3–4	5–6	7–8	9–10	11–12	13–14	15–16
0001	0100	1000	1010	0001	0100	0000	0010
0010	0101	1001	0000	0010	0101	0001	0100
1	2	1	3	1	2	1	4
→	→	←	←	→	←	←	→

17–18	19–20	21–22	23–24	25–26	27–28	29–30	31–32
0101	1001	0000	0010	0101	1001	0000	0010
1000	1010	0001	0100	1000	1010	0001	0100
1	2	1	3	1	2	1	4
→	→	←	→	→	←	←	←

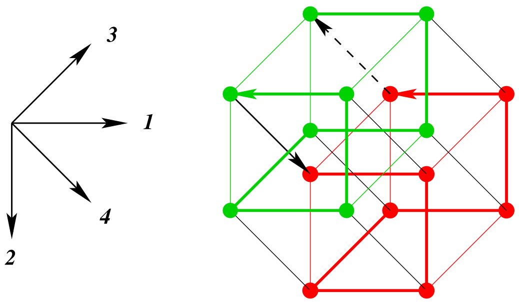


Fig. 8.7 Drawing of a tesseract, or four-dimensional cube, showing the Hamilton path in bold coloured lines, starting at top left. Labelling $x^4 = ict$ the arrows in black may be interpreted as connecting two 3D spaces across a time-inversion interface (Colour figure online)

vertex without revisiting a vertex. The Hamilton path through a tesserack, or four-dimensional cube is shown in Fig. 8.7.

This same pattern had been recognized before [34] by finding the maximum value of p for which 2^p is a factor of each integer. For n odd $p = 0$ and for the even numbers it has the value shown in parentheses

$$2(1),\ 4(2),\ 6(1),\ 8(3),\ 10(1),\ 12(2),\ 14(1),\ 16(4),\ etc.$$

This empirical result also corresponds to the Hamilton path, but without the directional properties and visual appeal in the Fibonacci code.

The Golden Ratio

The major importance of Fibonacci numbers resides in their close relationship with the golden ratio. The most striking feature appears in the formula [36] for powers of τ:

$$\tau^n = \lim_{i\to\infty} \frac{F_i}{F_{i+n}}$$

Table 8.3 Farey sequences, $\mathcal{F}_{1-5}$ and $\mathcal{F}_8$

$\frac{0}{1}$																						$\frac{1}{1}$
$\frac{0}{1}$											$\frac{1}{2}$											$\frac{1}{1}$
$\frac{0}{1}$							$\frac{1}{3}$				$\frac{1}{2}$				$\frac{2}{3}$							$\frac{1}{1}$
$\frac{0}{1}$					$\frac{1}{4}$		$\frac{1}{3}$				$\frac{1}{2}$				$\frac{2}{3}$		$\frac{3}{4}$					$\frac{1}{1}$
$\frac{0}{1}$				$\frac{1}{5}$	$\frac{1}{4}$		$\frac{1}{3}$		$\frac{2}{5}$		$\frac{1}{2}$		$\frac{3}{5}$		$\frac{2}{3}$		$\frac{3}{4}$	$\frac{4}{5}$				$\frac{1}{1}$
$\frac{0}{1}$	$\frac{1}{8}$	$\frac{1}{7}$	$\frac{1}{6}$	$\frac{1}{5}$	$\frac{1}{4}$	$\frac{2}{7}$	$\frac{1}{3}$	$\frac{3}{8}$	$\frac{2}{5}$	$\frac{3}{7}$	$\frac{1}{2}$	$\frac{4}{7}$	$\frac{3}{5}$	$\frac{5}{8}$	$\frac{2}{3}$	$\frac{5}{7}$	$\frac{3}{4}$	$\frac{4}{5}$	$\frac{5}{6}$	$\frac{6}{7}$	$\frac{7}{8}$	$\frac{1}{1}$

as series of modularity

$$m = \begin{vmatrix} n_i & n_{i+1} \\ d_i & d_{i+1} \end{vmatrix} = \pm F_n$$

where n and d denote numerator and denominator respectively. Other forms of the formula are:

$$\tau^n = F_{n-1} - F_n\tau,$$
$$\tau^{n+2} = \tau^n - \tau^{n-1},$$
$$\big(e.g.\ \tau^2 = 1 - \tau\big).$$

The most useful form of the Fibonacci numbers in the present context occurs embedded in the general Farey sequence that specifies all rational fractions as an enumerable array. It is generated by separately adding numerators and denomenators of adjacent fractions in an infinite sequence, starting from $0/1$ and $1/1$. The procedure is illustrated in Table 8.3 for the lower Farey sequences, $\mathcal{F}_n$.

These sequences are all unimodular, *i.e.* $m = 1$. By following a zig-zag path vertically down the table the unimodular sequence $\frac{0}{1}\ \frac{1}{1}\ \frac{1}{2}\ \frac{2}{3}\ \frac{3}{5}\ \frac{5}{8}\dots$ is found converging to the golden ratio. As shown in Table 8.4 all other powers of τ are convergents of k-modular sequences where the k are successive Fibonacci numbers. Only fractions associated with the sequences $\mathcal{F}_n$, with n a Fibonacci number, are involved. Briefly, the power series τ^n occur as Fibonacci sequences with seed values of $0/F_n$ and $1/F_{n+1}$.

By continuing the golden sequence in the opposite sense through fractions less than $\frac{3}{5}$, *i.e.* $\frac{0}{1}\ \frac{1}{2}\ \frac{2}{3}\ \frac{3}{5}\ \frac{4}{7}\ \frac{7}{12}\ \frac{11}{19}\ \frac{18}{31}\ \frac{29}{50}\ \frac{47}{81}\ \frac{76}{131}\ \frac{123}{212}\ \dots$, it converges to 0.5802, a value of special importance in the definition of atomic periodicity [35].

The Periodic Function

A general k-modular set of Farey sequences, defined as

$$\{S_k\} = \frac{n}{n+k}, \quad n = 1, 2, 3\dots$$

Table 8.4 k-modular sequences that converge to powers of τ

$\frac{0}{8}$		$\frac{0}{5}$		$\frac{0}{3}$		$\frac{0}{2}$		$\frac{0}{1}$		$\frac{0}{1}$	
	$\frac{1}{13}$		$\frac{1}{8}$		$\frac{1}{5}$		$\frac{1}{3}$		$\frac{1}{2}$		$\frac{1}{1}$
$\frac{1}{21}$		$\frac{1}{13}$		$\frac{1}{8}$		$\frac{1}{5}$		$\frac{1}{3}$		$\frac{1}{2}$	
	$\frac{2}{34}$		$\frac{2}{21}$		$\frac{2}{13}$		$\frac{2}{8}$		$\frac{2}{5}$		$\frac{2}{3}$
$\frac{3}{55}$		$\frac{3}{34}$		$\frac{3}{21}$		$\frac{3}{13}$		$\frac{3}{8}$		$\frac{3}{5}$	
	$\frac{5}{89}$		$\frac{5}{55}$		$\frac{5}{34}$		$\frac{5}{21}$		$\frac{5}{13}$		$\frac{5}{8}$
$\frac{8}{144}$		$\frac{8}{89}$		$\frac{8}{55}$		$\frac{8}{34}$		$\frac{8}{21}$		$\frac{8}{13}$	
	$\frac{13}{233}$		$\frac{13}{144}$		$\frac{13}{89}$		$\frac{13}{55}$		$\frac{13}{34}$		$\frac{13}{21}$
$\frac{21}{377}$	$\downarrow$	$\frac{21}{233}$	$\downarrow$	$\frac{21}{144}$	$\downarrow$	$\frac{21}{89}$	$\downarrow$	$\frac{21}{55}$	$\downarrow$	$\frac{21}{34}$	$\downarrow$
	τ^6		τ^5		τ^4		τ^3		τ^2		τ
$m = 8$		5		3		2		1		1	

Table 8.5 Special k-modular Farey sequences that simulate the composition of naturally stable isotopes

$$\{S_0\} = \tfrac{1}{1}\ \tfrac{1}{1}\ \tfrac{1}{1}\ \tfrac{1}{1}\ \cdots$$

$$\{S_1\} = \tfrac{0}{1}\ \tfrac{1}{2}\ \tfrac{2}{3}\ \tfrac{3}{4}\ \tfrac{4}{5}\ \tfrac{5}{6}\ \tfrac{6}{7}\ \tfrac{7}{8}\ \cdots$$

$$\{S_2\} = \tfrac{0}{2}\ \left[\tfrac{1}{3}\right]\ \tfrac{1}{2}\ \left[\tfrac{3}{5}\right]\ \tfrac{2}{3}\ \left[\tfrac{5}{7}\right]\ \tfrac{3}{4}\ \left[\tfrac{7}{9}\right]\ \tfrac{4}{5}\ \cdots$$

$$\{S_3\} = \tfrac{0}{3}\ \left[\tfrac{1}{4}\ \tfrac{2}{5}\right]\ \tfrac{1}{2}\ \left[\tfrac{4}{7}\ \tfrac{5}{8}\right]\ \tfrac{2}{3}\ \left[\tfrac{7}{10}\ \tfrac{8}{11}\right]\ \tfrac{3}{4}\ \cdots$$

$$\{S_4\} = \tfrac{0}{4}\ \left[\tfrac{1}{5}\ \tfrac{1}{3}\ \tfrac{3}{7}\right]\ \tfrac{1}{2}\ \left[\tfrac{5}{9}\ \tfrac{3}{5}\ \tfrac{7}{11}\right]\ \tfrac{2}{3}\ \cdots$$

$$\{S_5\} = \tfrac{0}{5}\ \left[\tfrac{1}{6}\ \tfrac{2}{7}\ \tfrac{3}{8}\ \tfrac{4}{9}\right]\ \tfrac{1}{2}\ \left[\tfrac{6}{11}\ \tfrac{7}{12}\ \tfrac{8}{13}\ \tfrac{9}{14}\right]\ \tfrac{2}{3}\ \cdots$$

$$\{S_6\} = \tfrac{0}{6}\ \left[\tfrac{1}{7}\ \tfrac{1}{4}\ \tfrac{1}{3}\ \tfrac{2}{5}\ \tfrac{5}{11}\right]\ \tfrac{1}{2}\ \left[\tfrac{7}{13}\ \tfrac{4}{7}\ \tfrac{3}{5}\ \tfrac{5}{8}\ \tfrac{11}{17}\right]\ \tfrac{2}{3}\ \cdots$$

$$\{S_7\} = \tfrac{0}{7}\ \left[\tfrac{1}{8}\ \tfrac{2}{9}\ \tfrac{3}{10}\ \tfrac{4}{11}\ \tfrac{5}{12}\ \tfrac{6}{13}\right]\ \tfrac{1}{2}\ \left[\tfrac{8}{15}\ \tfrac{9}{16}\ \tfrac{10}{17}\ \tfrac{11}{18}\ \tfrac{12}{19}\ \tfrac{13}{20}\right]\ \tfrac{2}{3}\ \cdots$$

$$\{S_8\} = \tfrac{0}{8}\ \left[\tfrac{1}{9}\ \tfrac{1}{5}\ \tfrac{3}{11}\ \tfrac{1}{3}\ \tfrac{5}{13}\ \tfrac{3}{7}\ \tfrac{7}{15}\right]\ \tfrac{1}{2}\ \left[\tfrac{9}{17}\ \tfrac{5}{9}\ \tfrac{11}{19}\ \tfrac{3}{5}\ \tfrac{13}{21}\ \tfrac{7}{1}\ \tfrac{15}{23}\right]\ \tfrac{2}{3}\ \cdots$$

is summarized in Table 8.5. All of these sequences converge to unity and each fraction represents the composition of a potential nuclide, Z/N for which $N \geq Z$. The relationship between the fractions and the composition of naturally stable isotopes is shown in Fig. 8.8. Only a selection of fractional points to demonstrate the general trend is shown. Open circles represent the fractions that appear within square brackets in Table 8.5. Red dots represent fractions that correspond with the composition (Z/N) of stable nuclides. Arrows show the outline of the triangle of isotope stability that converges to the golden ratio, τ at $Z = 102$.

The stability of nuclides depends on the imbalance between protons and neutrons, measured as either the ratio Z/N, which, with the exception of ^{3}He, is always less than 1.0, or as the relative neutron excess, $(N - Z)/Z \geq 0$. Whereas the ratio Z/N decreases with Z, the excess $N - Z$ increases. The optimum value of

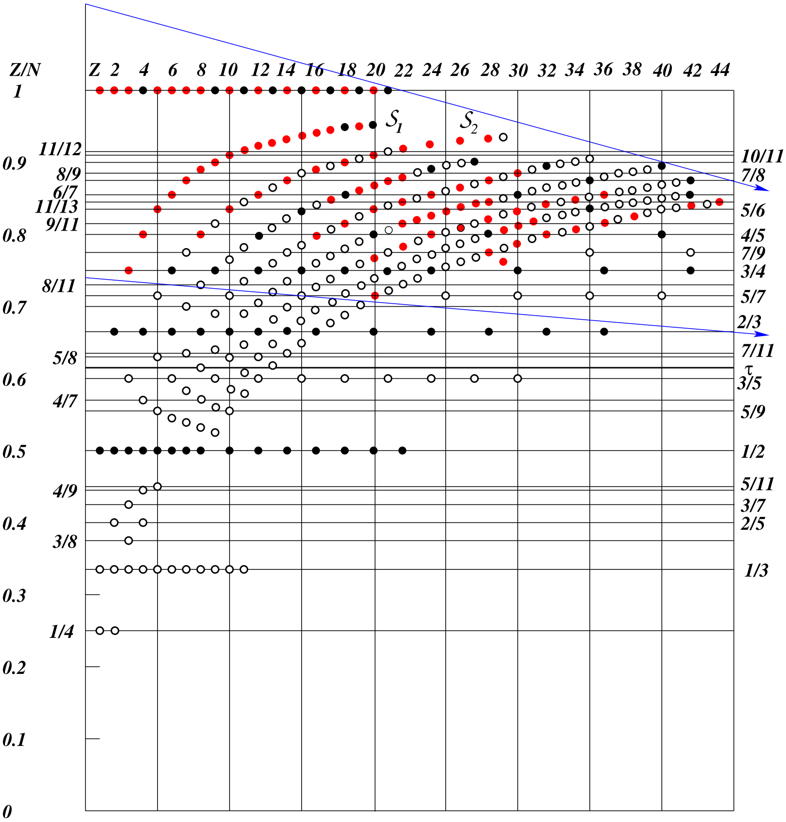


Fig. 8.8 Fractions defined by the k-modular sequences $\mathcal{S}_k$, interpreted as the ratio Z/N, on a plot against natural numbers, Z (Colour figure online)

$0 < Z/N < 1$, is approached as

$$\frac{Z}{N} = \frac{N-Z}{Z},$$

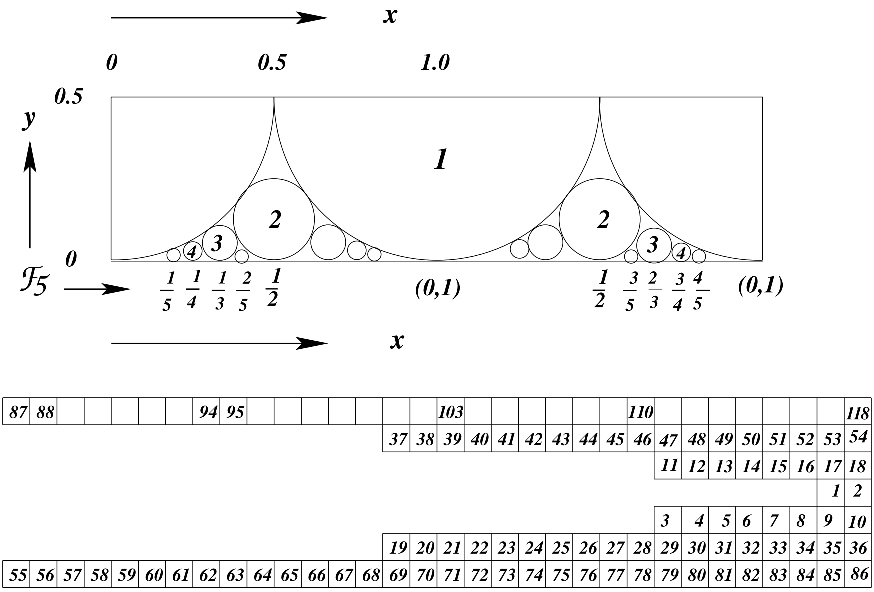
$$i.e. \quad Z^2 + NZ - N^2 = 0$$

to give

$$Z = -\frac{N \pm \sqrt{N^2+4N}}{2},$$

$$\frac{Z}{N} = \frac{-1 \pm \sqrt{5}}{2} = \tau.$$

This is the minimum ratio of Z/N or the maximum of $(N-Z)/Z$ for stable nuclides. Graphical analysis [36] showed that both ratios approach this optimal value



87	88						94	95								103							110								118
														37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
																								11	12	13	14	15	16	17	18
																														1	2
																								3	4	5	6	7	8	9	10
														19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86

Fig. 8.9 The touching Ford circles labeled 1 to 4, which represent the sequence $\mathcal{F}_4$, are centred at coordinates of $x = h/k$ and $y = 1/(2k^2)$. The reciprocals of the y-coordinates are in one-to-one correspondence with the natural numbers, ordered in sets of $2k^2$, *i.e.* 2,8,18,32, *etc.*; a mapping of the periodic table of the elements

as $Z \to 102$, $N \to 165 = Z_{max}/\tau$ and $A \to 267 = Z_{max}/\tau^2$. The extreme values at $Z = 0$ that define the triangle of stability are $2\tau - \frac{1}{2} = 0.74$ and $\tau + \frac{1}{2} = 1.12$.

Although the triangle of stability includes all stable isotopes it does not exclude all radioactive nuclides. However, a number of simple formulae that correctly predict the stability of all potential nuclides within the triangle of stability do exist [37]. The final result identifies a pattern that corresponds in detail with the observed periodic table of the elements and reveals a more comprehensive periodic function of all stable nuclides against mass number, A, atomic number, Z, as well as neutron number, $N = A - Z$ [38].

An intimate relationship between the periodicity of atomic matter and number theory is best demonstrated by the amazing fact that the entire periodic table of the elements is reproduced by the Farey sequence

$$\mathcal{F}_4 : \quad \frac{0}{1}\ \frac{1}{4}\ \frac{1}{3}\ \frac{1}{2}\ \frac{2}{3}\ \frac{3}{4}\ \frac{1}{1}$$

represented by the equivalent set of Ford circles [35]. Each of the Farey fractions h/k, codes for a Ford circle of radius and y-coordinate of $1/(2k^2)$ and x-coordinate of h/k, as in Fig. 8.9.

The resultant geometrical mapping represents the only direct mathematical formulation of the periodic table of the elements, a result that cannot be achieved by standard wave mechanics.

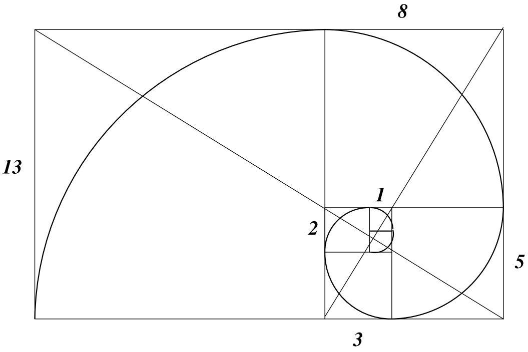


Fig. 8.10 A logarithmic spiral constructed in the rectangle 21 × 13 from circular segments inscribed within a series of squares with side lengths of Fibonacci numbers. It converges to the point where the diagonals of Fibonacci rectangles intersect

To understand the meaning of the wave-mechanically predicted elemental periodicity it is seen to correspond to one half of the $\mathcal{F}_5$ sequence:

$\rightarrow \psi(n,l,m_l)$	$1s^2$	$2(s^2p^6)$	$3(s^2p^6d^{10})$	$4(s^2p^6d^{10}f^{14})$	$5(s^2p^6d^{10}f^{14}g^{18})$
$2k^2$	2	8	18	32	50

Z 0 2 10 28 60 110

It is obvious that the difference between the two schemes cannot be rationalized by invoking interelectronic effects *ad hoc*. We make bold to suggest that the discrepancy is due to the three-dimensional nature of Schrödinger's equation. It disregards the effects of the environment as well as the four-dimensional nature and curvature of space-time. The more correct mathematical model of elemental periodicity, and hence of atomic structure, should be in the form of a nonlinear differential equation, based on a four-dimensional potential in projective space-time. Although such an equation awaits solution, the successful simulation of the observed periodicity in terms of the $\mathcal{F}_4$ sequence is interpreted to be consistent with the envisaged mathematical model.

With good reason the number-theory approach may now be extended, as a reliable coding of four-dimensional wave mechanics, to an analysis of atomic and molecular structure and other chemical effects.

The Fibonacci Spiral

The common procedure of using logarithmic spirals in optimization problems governed by second-order dynamics [39] has its basis in number theory. For the simulation of chemical effects it is convenient to approximate the true logarithmic golden spiral by a Fibonacci spiral, which is constructed by the procedure demonstrated in Fig. 8.10. It follows from the sum of Fibonacci squares

$$\sum_{i=1}^{n} F_i^2 = F_n F_{n+1}$$

that converges to a golden rectangle. As a typical example the placement of botanical leaves on a stalk depends on an optimal divergence angle of $2\pi\tau^2$, measured along a Fibonacci spiral, starting from its focal point. This procedure will be shown to be equally effective in the analysis of chemical systems.

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Chapter 9
Chemical Wave Structures

Abstract The wave structure of the electron lends itself to the formulation of chemical phenomena in terms of number theory. Without a particle concept the behaviour of elementary units of matter, in the form of solitons, is described directly in the wave formalism originally proposed by Schrödinger and Madelung in hydrodynamic analogy. The quantum condition appears naturally as a minimum action principle. All atoms are alike with nuclei bathed in a uniform electronic fluid, the spherical wave structure of which is revealed by optimization on a logarithmic spiral. The density distribution pattern has much in common with the Bohr–de Broglie model of atomic structure and predicts a number of important atomic properties, including atomic size, ionization radius, electronegativity and atomic polarizability. The intimate connection between atomic properties and space-time curvature is convincingly demonstrated by derivation of atomic radii as a periodic function optimized on Fibonacci spirals. Details of covalent interaction are elucidated by the manipulation of ionization radii and the golden ratio as parameters to predict interatomic distance, bond order, dissociation energy, stretching force constant and dipole moments. Extended to molecules the matter-wave approach demonstrates that the concepts of structure and shape of a free molecule are strictly four-dimensional. Molecular structure observed and modelled in three dimensions only applies to condensed phases. Molecules involved in chemical change are essentially in the free state and their mode of interaction is not always obvious as a function of assumed three-dimensional structure. Proposed mechanisms for synthetic processes serve to rationalize the apparent discrepancies.

9.1 Introduction

By now it is well known for many reasons that there is no evidence for the existence of point particles of whatever nature. Although it is widely conceded that chemical atoms have internal structure, the most advanced theories of physics still consider all sub-atomic matter to be made up of elementary point particles. It is therefore instructive to repeat the conclusion reached more than a hundred years ago by Sommerfeld, based on direct calculation [1]:

> ...in case the charge is concentrated at one point, the force [necessary to maintain a motion of a bodily charge] is infinite...

J.C.A. Boeyens, *The Chemistry of Matter Waves*, DOI 10.1007/978-94-007-7578-7_9,

Careful scrutiny of the literature confirms that this simple model, which in the words of Lorentz [2] states that

> . . . electrons which I take to be spheres. . . in the state of rest, have their dimensions [in the direction of motion] changed by the effect of translation,

has never been refuted. In modern terminology this model defines the electron as an indivisible four-dimensional whole, consisting of entangled units of mass, charge and spin, confined to a volume that varies in size and shape in response to its environment.

9.2 Electronic Structures

In a word, the electron is best described as a soliton, with implied standing-wave structure. Despite their variable size solitons are non-dispersive. They interact without losing their identity. They may pass through each other or form a composite from which they reappear virtually unaffected in size and shape.

Interelectronic effects are readily visualized in terms of these criteria. Two electrons of opposite spin may coalesce to form a bosonic pair whereas electrons with equal spins interpenetrate without sticking. In principle a large number of bosonic pairs may flow together under favourable conditions to form a so-called Bose condensate, with all electrons at the same energy level. The phenomena of superfluidity and superconductivity depend on the formation of such condensates. These phenomena are rare because perfect bosonic pairing is readily disturbed by the environment, such as an imperfect crystal lattice. In these cases the restricted electronic mobility gives rise to various degrees of ohmic conduction.

A collective of electronic solitons propagates through the vacuum as a nonlinear plane wave, as described by the sine-Gordon equation:

$$\left(\frac{\partial}{\partial t}+c\frac{\partial}{\partial x}\right)\left(\frac{\partial}{\partial t}-c\frac{\partial}{\partial x}\right)\psi+m^2\sin\psi-0.$$

The terms in brackets define a standing wave by components that move in opposite directions, giving rise to a wave train as shown in Fig. 7.1. The product of group and phase velocities $v_g v_\phi = c^2$.

All sub-atomic entities, even atoms and small molecules, have the same type of wave structure and, concentrated in beams, exhibit familiar wave properties such as diffraction. The wave train envisaged here should not be confused with the photons of traditional quantum theory, which are point particles. However, like photons the energy of a propagating soliton is related to the de Broglie frequency of the wave train, $E = h\nu$.

It is instructive to note how the hydrodynamic interpretation of wave mechanics, proposed by Madelung [3], but rejected with indecent haste at the time, serves as an attractive model for the electronic behaviour considered here. As demonstrated before [4] Madelung's specification of the wave function

$$\Psi = Re^{iS/\hbar}$$

as an action function, separates the wave equation into two equations

$$\begin{aligned} \frac{\partial S}{\partial t} + \frac{1}{2m}(\nabla S)^2 + V - \frac{\hbar^2}{2m} \cdot \frac{\nabla^2 R}{R} = 0, \\ \frac{\partial R^2}{\partial t} + \frac{1}{m}\nabla\left(R^2 \nabla S\right) = 0 \end{aligned} \tag{9.1}$$

that closely resemble Euler's equations of hydrodynamics. This interpretation requires $R^2 = \rho(\boldsymbol{x})$, the density of a continuous fluid with stream velocity $\boldsymbol{v} = \nabla S/m$.

The last term in (9.1) is interpreted hydrodynamically as a function of internal interactions and was later interpreted by Bohm as quantum potential energy. This is the term that appears in the nonlinear wave equation (7.19).

Madelung's distinction between stationary and non-stationary states, where both density and flux vary periodically only in the latter, is of crucial importance. It reflects the results of Sect. 7.3.5 according to which linear eigenvalues appear unchanged, together with the more general nonlinear states. On writing the energy as a volume integral of the form

$$E = \int R^2 \frac{\partial S}{\partial t} dV$$

the same expression is argued to be valid for non-stationary states, that fluctuate with the same periodicity as $\nu_{ik} = (E_i - E_k)/h$. This may now be interpreted as the nonlinear formulation of what became known as a quantum jump. The emission or absorption of radiation therefore happens by slow transition in a non-stationary state.

Commenting on the relationship between wave mechanics and hydrodynamics Madelung concluded that electrons should be interpreted with the ability to interpenetrate without fusing together, correctly anticipating the properties of a soliton.

9.2.1 Numbers and Waves

A modern paraphrase of Madelung's ideas describes an electron or a collective of electrons as a continuous fluid consisting of flexible soliton units, or wave structures. In shape a single electron may vary between an extended plane wave and a point-like object, depending on its environment.

It is of special interest to examine an electron captured in the field of a positive charge, concentrated on a miniscule massive object known as a proton. The symmetry of the field demands the electronic wave structure to be dispersed into a spherical shell around the proton, in an arrangement that minimizes the action of the combined system. To first approximation the implied equilibrium depends on a balance between charge and spin interactions, colloquially referred to as electrostatic and quantum effects. Mathematically this equilibrium is conveniently described as a balance between classical and quantum components of the potential energy, $V = -V_q$.

Should this electron absorb energy from an electromagnetic field, which comes in discrete units, the equilibrium is re-established in a modified arrangement. The allowed energy levels, known from spectroscopic analysis are modelled reliably by the matter-wave equations developed by de Broglie, Schrödinger, Dirac and others.

The increased number of extranuclear electrons on more massive atoms cannot be simulated with the same accuracy as for the hydrogen atom. The standard practice is to describe the electronic configurations of non-hydrogen atoms qualitatively, using arguments based on spectroscopy and the wave-mechanical model for hydrogen.

As more sensitive instrumentation revealed spectroscopic features at variance with theoretical models the response consisted in the addition of secondary assumptions rather than an upgrade of the seminal theory. In particular, no effort was made to eliminate the assumption of elementary point particles, to reformulate the theory as a function of non-Euclidean four-dimensional space-time, or to take cognisance of nonlinear effects. A blind belief in the infallibility of a three-dimensional linear model of the world persists. Even more worrisome is the demonstration [5] that the seminal Rydberg-Ritz equation

$$\Delta E_{mn} = R\left\{\frac{1}{n^2} - \frac{1}{m^2}\right\}$$

that defines a linear graphical relationship with the same slope and intercept, is not identically valid. This equation, based on the original Balmer conjecture is the irreducible assumption on which the entire quantum theory of matter is based.

The deterrent that prevents the exploration of nonlinear four-dimensional alternatives is doubtlessly mathematical complexity. Existing models are of two types—based on matrix algebra and linear differential equations, respectively. This approach commands such respect that it is often overlooked that these quantum models are just that—mathematical models. Wave mechanics reflects the wave nature of matter only in name and matrix mechanics is not based on any recognizable physical model.

The new paradigm advocated here is to recognize that matter exists as wave structures in non-Euclidean space-time and to formulate a mathematical model consistent with this assumption. It is highly unlikely that this could be achieved in the medium of matrix algebra, which becomes unwieldy even in three dimensions. The prospect of solving a four-dimensional nonlinear differential equation without separation of the variables appears equally daunting. Supercomputers could probably do the job.

It appears to be constantly overlooked that physical theory could be supported by any form of mathematical model apart from a differential equation. However, when physical phenomena are correctly described by number theory the tendency is to dismiss the results as mere numerology. It has never been demonstrated in what way the use of differential calculus is any different, or has a deeper physical significance, than numerology.

Inspired by the superior simulation of all forms of atomic periodicity by the methods of number theory, compared to the results obtained by differential calculus, use of the same approach in the analysis of other systems of chemical interest is explored in what follows.

9.3 Atomic Structure

The feasibility of using number theory for the analysis of atomic structure is assessed by comparison with the model that assumes a hydrogen-like wave-mechanical energy spectrum. The corresponding electron configuration dictated by the quantum numbers n, l, m_l and the exclusion principle, implies that a multi-electron atom remains spherical in its ground state. This conclusion depends on the fact that any degenerate set of harmonic eigenfunctions consists of one real (spherical) function with $m_l = 0$ and conjugate pairs of complex functions with $m_l = \pm(0, l)$, which quench into spherical objects. In physical terms this model is interpreted to specify an atomic nucleus spherically surrounded in equilibrium by a uniform electric fluid with a total charge of Ze, rather than so many electrons. The fluid is quantized in the sense that it may be dispersed into Z identical units, but not beyond that. There are no sub-electronic electric charges. The complexity of electronic energy levels increases as a function of atomic number with the addition of a $2n - 1$ degenerate sublevel as compared to the previous lower level.

This arrangement represents an optimization problem of the same type as the gravitational accretion of satellites from a dust cloud in the formation of the solar system, which was solved on a Fibonacci spiral [6]. This two-dimensional problem was solved with a convergence angle of $3\pi/5 = 108^\circ \simeq \pi\tau$.

The electron cloud differs from this in being a three-dimensional distribution that responds to an electromagnetic rather than a gravitational field. The geometrical details of the distribution must depend on the 4π periodicity of the spin function and the variation, limited by a factor of $2n - 1$, of electron density between the $n - 1$ and nth energy levels. Optimization [7] with the variable divergence angle of $4\pi/(2n - 1)$ is shown in Fig. 9.1.

The radial distances that correspond to the convergents increase as n^2, exactly like the Bohr radii of $n^2 a_0$. Unlike the Bohr radii that represent local maxima in electron density, the interpretation [8] in terms of a spherical wave structure correlates n with the closure of the periodic groups of Fig. 8.9, as shown in Fig. 9.2.

From the known number of electrons the density for unitary atoms at the crest of each spherical wave is calculated directly, and found to be in exact agreement with empirical Thomas–Fermi simulations and with Hartree–Fock radial expectation values [8]. More significantly, this predicted nodal structure is observed experimentally in photoionization microscopy [9] and Fourier transform scanning tunneling microscopy [10]. Despite claims [9] to the contrary, these are not the nodal structures of the Schrödinger solution.

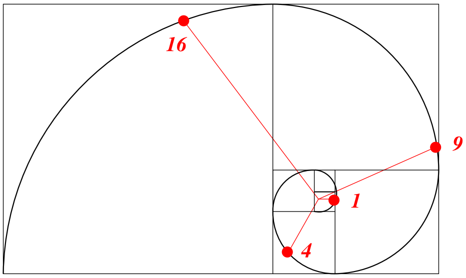


Fig. 9.1 Optimization of atomic electron density on a Fibonacci spiral

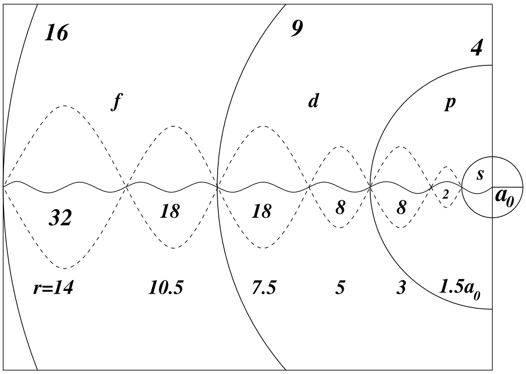


Fig. 9.2 Spherical atomic wave structure with nodal surfaces at n^2a_0. The *stippled curves* indicate electron density as numbered. Spectroscopic sub-levels s, p, d, f follow the fine ripple with $2n-1$ cycles between the nodal surfaces

9.4 Chemical Concepts

The spherical wave structure derived from Fibonacci optimization was shown [8] to predict electron densities as accurately as the computationally intensive Thomas–Fermi and Hartree–Fock calculations that consist of self-consistent optimization of trial functions based on Schrödinger's solution for hydrogen. With as little effort the wave model lends itself to the derivation of several other chemically significant quantities, most of which have never been calculated from first principles before.

9.4.1 Atomic Size

The appearance of spherical nodal surfaces ensures a reliable estimate of atomic size from the radial extent of the outer boundary on the electron density of each atom. As a practical procedure the limiting radii for the alkali metals were calculated directly [8] and by self-consistent interpolation the radii for all other atoms could be derived. The procedure depends on the introduction of empirical parameters, as in

$$r_p = \frac{r(s^1)\cdot\sigma}{\mu^p}$$

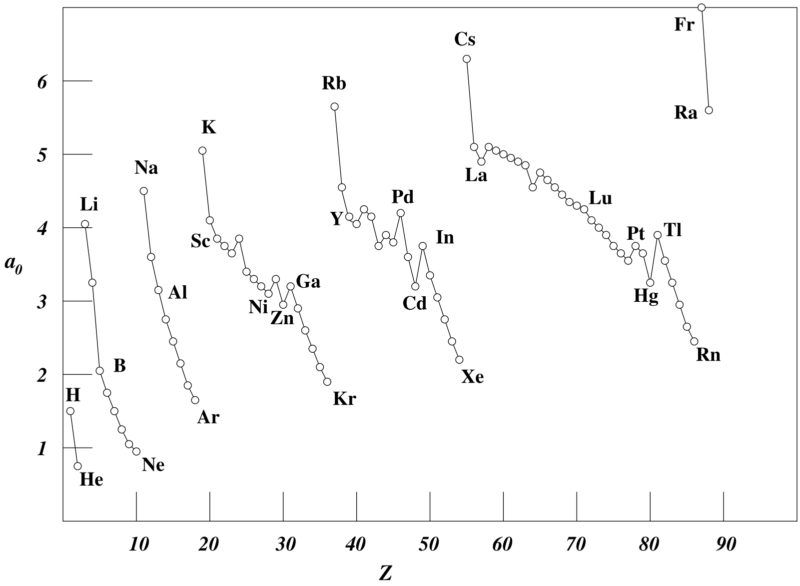


Fig. 9.3 Atomic radii calculated from spherical atomic wave structures, in units of a_0

by which the radii of atoms in a p-block are related to that of the radius, $r(s^1)$ of the alkali metal in the same period. By reference to the mean densities in each period and sub-level the parameters σ and μ converge to self-consistent values.

A remarkable spin-off from this analysis relates to the mean volume occupied by different types of electron. Expressed as $v_i = V_e/100a_0$, electron volumes in period 6 of Fig. 9.2 define a power series in $\phi = 1/\tau$, within rounding-off errors:

$$v_s(\phi^3),\ v_d(\phi^{\frac{8}{3}}),\ v_p(\phi^{\frac{7}{3}}),\ v_f(\phi^2)$$

with an overall mean of $\phi^{\frac{7}{3}}$.

The final results are presented graphically in Fig. 9.3. It is immediately obvious how the distribution reflects a periodic relationship exactly as in Fig. 8.9, and not in line with the hydrogen energy spectrum.

The irregularities in the curves of Fig. 9.3 are due to the use of irregular electron configurations adopted on the basis of spectroscopic results. There are nine irregularities in total, five of which occur in the second transition series, *i.e.*:

Cr, Nb, Mo, Ru, Rh, Pd, La, Gd, Pt.

The textbook explanation [11] of the irregularities is that

> …competition between… two states develops, and the process of filling is not so regular…

More specifically, the s^1d^5 configuration of Cr and Mo and the d^1f^7 of Gd may be rationalized [12, p. 632] as a preference for the maximum spin state of the half-filled arrangement. It probably has some validity although it fails to account for the regular configuration of W or the severe fluctuations in the second transition series. Here is a situation that clearly cannot be dealt with by any qualitative theory as the ultimate explanation should be sought in a full four-dimensional analysis.

Except for these anomalies the pattern that emerges from Figs. 9.2 and 9.3 derives purely from the optimization formula of Fig. 9.1, without further reference to chemical systems. Like the matching periodic structure of Fig. 8.9 it is an independent numerical result, based on the properties of Fibonacci and Farey sequences, and the calculations that are involved require only modest mathematical skills. It matches, and in several ways surpasses, all of the comparable quantum-mechanical results. It is tempting to claim that, given Nagaoka's conjecture [13] and the names of the elements, the number model provides an adequate introduction to chemical theory, without quantum mechanics.

9.4.2 The Bohr–de Broglie Model

Bohr's conjecture that the electron on a hydrogen atom is restricted to exist only in discrete stationary states is given physical content by de Broglie's model of a matter wave of wavelength $\lambda = h/p$, which, for a standing wave in a spherical stationary state, is restricted to values that satisfy $n\lambda = 2\pi r$ for radial distances of r and integer n. This condition implies that a quantity, equivalent to an angular momentum, is quantized in units of action:

$$n\hbar = \frac{nh}{2\pi} = pr.$$

From Bohr's condition of balanced electrostatic and mechanical forces the radii of allowed spherical stationary states follow from

$$\frac{e^2}{r^2} = \frac{p^2}{mr} \quad \text{as} \quad r = \frac{(pr)^2}{me^2} = \frac{(n\hbar)^2}{me^2}.$$

The total energy of the electron as the sum of potential and kinetic energy

$$V = -\frac{e^2}{r}, \qquad T = \frac{p^2}{2m} = \frac{e^2}{2r}$$

reduces to

$$E = V + T = -\frac{e^2}{2r} = \frac{me^4}{2(n\hbar)^2},$$

in electrostatic units. The principal quantum number $n = 1, 2, \ldots$ identifies the spherical standing waves in the stippled outlines of Fig. 9.2.

The quantization of action would follow the pulsation of a three-dimensional fluid sphere in a central field, which is described by Laplace's equation

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

This differential equation may be solved [4] by separation of the variables under the assumption that the potential may be defined as the product of three one-dimensional potentials, or cartesian components of $V = X(x) \cdot Y(y) \cdot Z(z)$. This solution is substituted into the equation and after differentiation, divided by V, to give

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

Each term is a function of one variable only and hence independent of the two other variables, which implies that each term is independently equal to some constant, *e.g.* $d^2X/dx^2 = KX$. By defining the constant as a squared quantity each equation is a one-dimensional Helmholtz equation, which is solved by an exponential function. For $K = k_1^2$, $X(x) = c\exp(\pm k_1 x)$. Noting that $e^a.e^b = e^{(a+b)}$, the overall solution follows as

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

with

$$k_1^2 + k_2^2 + k_3^2 = 0. \tag{9.2}$$

This condition requires at least one of the constants to be a complex quantity, such that $(ik)^2 = -k^2$ and $i = \sqrt{-1}$, unless

$$k_1 = k_2 = k_3 = 0. \tag{9.3}$$

An interesting situation arises as one of the constants is equal to zero. The solution that involves the two remaining terms then requires $k_1^2 + k_2^2 = 0$, *e.g.* $k_1 = k$, $k_2 = ik$. Hence

$$X = c_1 e^{\pm kx}, \qquad Y = c_2 e^{\pm iky}$$

or

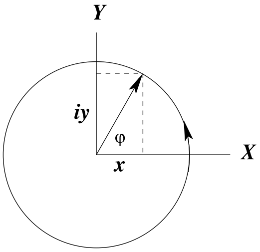
$$V_k = c_1 e^{\pm k(x+iy)}, \tag{9.4}$$

$$V_z = c_2 z + c_3. \tag{9.5}$$

This solution occurs in Fig. 9.2 as the ripple with $2l + 1$ cycles in each region, labeled s, p, d, f, with the so-called angular momentum quantum number $l = 0, 1, 2, 3$ respectively.

It is emphasized that the variables in (9.4) are not separable because of condition (9.2). This means that the complex functions cannot be reduced to real functions

Fig. 9.4 Diagram to define rotation in the complex plane



unless (9.3) applies. The definition of real surface harmonics that feature in chemical orbital theories is thus ruled out as mathematically impossible by this condition.

In polar coordinates the complex exponential $\exp[\pm k(x+iy)]$ defines a rotation of φ about the z-direction, as shown in Fig. 9.4, and noting that $e^{i\varphi}=\cos\varphi+i\sin\varphi$, *i.e.*

$$f(\varphi)=\Phi=e^{ik\varphi}\quad\text{or}\quad\frac{d\Phi}{d\varphi}=ik\Phi.$$

Rearranged into the form

$$-i\frac{\partial}{\partial\varphi}(\Phi)=k\Phi$$

it is known as an eigenvalue equation in which the parameter k specifies the allowed values of the angular momentum, which according to the Bohr model occurs as discrete values $m_l\hbar$.

The quantum number $m_l=0$ generates the vibration (9.5) along z. The $2l+1$ eigenvalues of L_z are generated by an eigenvalue equation for the total angular momentum of the form

$$L^2Y=l(l+1)\hbar^2Y.$$

The important quantized electronic energy and angular momentum eigenvalues in a central field are therefore seen to derive from the simple spherical wave model, without solving the associated differential equation. Although detailed expressions for the radial wave functions are therefore not available, the general exponential action function $\Psi=R\exp(-iS/\hbar)$, known from elementary wave theory, is sufficient for the simulation of most chemically important systems by number theory.

9.4.3 Ionization Radii

Chemical change is controlled by the interaction between the electrons that constitute the outermost maxima of atomic and molecular wave structures. In virtual all cases interaction is initiated by a suitable process of promotion that activates the reactants into a *valence state*. In practice promotion depends on an increase in electronic energy due to heating or photochemical activation, resulting in more violent collisions between interacting atoms and molecules. The desired result is the release of a valence electron from its parent atomic core, suitably activated for interaction with other activated entities.

A controlled process of atomic activation by hydrostatic pressure is particularly well suited for computer simulation. Such a simulation [14], starting from Hartree–Fock wave functions showed that sub-levels of lower angular-momentum quantum number, l, are energized preferentially, leading to an inversion of levels with increased pressure and the invariable ionization of a spherically symmetric s-type electron. For any atom a state of compression to a critical radius is reached where an electron becomes effectively decoupled from the atomic core. These, so-called ionization radii, r_0, are characteristic of individual atoms.

In order to perform an equivalent simulation in the spherical-wave protocol it is argued that the hydrostatically decoupled electron becomes confined at uniform density to a sphere of radius r_0. This radius is calculated by the simple procedure of spreading the concentrated one-electron valence density of an electron at the radial maximum of the outer shell into a sphere at uniform density. The results [8], not only match the Hartree–Fock values, but are more reliable for the smaller important first-period atoms.

The significance of this result lies therein that ionization radii are indispensible in the simulation of chemical abstractions such as electronegativity and the parameters that feature in covalent interactions.

9.4.4 Electronegativity

In reviewing the origin and current status of the electronegativity concept [15] serious confusion around the theoretical basis and appropriate units of the measure is exposed. To unify the disparate models atomic electronegativity is redefined as the chemical potential of the valence state as derived from ionization radius.

As both the classical potential energy and kinetic energy of a decoupled valence electron tend to zero, the energy of the electron confined to the ionization sphere,

$$E_g = \frac{h^2}{8mr_0^2}$$

is interpreted as quantum potential energy, V_q. This is the same parameter that occurs in the nonlinear Schrödinger equation (7.19) which explains why electronegativity is undefined in traditional quantum chemistry.

Correspondence with electronegativities in common use is achieved by setting $\chi = \sqrt{E_g}$. With E_g in eV and r_0 in Å units, it reduces numerically to $\chi = 6.133/r_0$. As remarked before [15]:

> It is indeed the tendency of an atom to interact with electrons and the fundamental parameter that quantifies chemical affinity and bond polarity.

The periodic table of the elements, reprinted here as Table 9.1 from [16], summarizes the values of both r_0 and χ as derived from the spherical-wave model of the

Table 9.1 Periodic table of the elements

2	**1 H** *0.98* *6.25*	🟩 **2 He**	*Z Sym* r_0 *(Å)* χ	🟩 *Closed s shell*	🟦 *Closed p shell*	🟪 *Closed d shell*	🟨 *Cl.osed f shell*	🟥 *Radio–active*
8	**3 Li** *2.36* *2.60*	🟩 **4 Be** *2.20* *2.79*	**5 B** *1.88* *3.26*	**6 C** *1.78* *3.45*	**7 N** *1.69* *3.63*	**8 O** *1.60* *3.83*	**9 F** *1.52* *4.03*	🟦 **10 Ne** *1.44* *4.26*
8	**11 Na** *3.09* *1.98*	🟩 **12 Mg** *2.87* *2.14*	**13 Al** *2.74* *2.24*	**14 Si** *2.62* *2.34*	**15 P** *2.51* *2.44*	**16 S** *2.47* *2.48*	**17 Cl** *2.30* *2.67*	🟦 **18 Ar** *2.21* *2.78*
18	**19 K** *3.50* *1.75*	🟩 **20 Ca** *3.08* *1.99*						
	21 Sc *3.02* *2.03*	**22 Ti** *2.99* *2.05*	**23 V** *2.96* *2.07*	**24 Cr** *3.02* *2.03*	**25 Mn** *2.90* *2.11*	**26 Fe** *2.87* *2.14*	**27 Co** *2.85* *2.15*	🟪 **28 Ni** *2.81* *2.18*
	29 Cu *2.88* *2.13*	🟩 **30 Zn** *2.76* *2.22*	**31 Ga** *3.00* *2.04*	**32 Ge** *2.89* *2.12*	**33 As** *2.80* *2.19*	**34 Se** *2.71* *2.26*	**35 Br** *2.61* *2.35*	🟦 **36 Kr** *2.52* *2.43*
18	**37 Rb** *3.81* *1.61*	🟩 **38 Sr** *3.54* *1.73*						
	39 Y *3.27* *1.88*	**40 Zr** *3.24* *1.89*	**41 Nb** *3.30* *1.86*	**42 Mo** *3.26* *1.88*	🟥 **43 Tc** *3.14* *1.95*	**44 Ru** *3.20* *1.92*	**45 Rh** *3.16* *1.94*	🟪 **46 Pd** *2.29* *2.68*
	47 Ag *3.11* *1.97*	🟩 **48 Cd** *3.00* *2.04*	**49 In** *3.31* *1.85*	**50 Sn** *3.19* *1.92*	**51 Sb** *3.09* *1.98*	**52 Te** *2.98* *2.06*	**53 I** *2.88* *2.13*	🟦 **54 Xe** *2.75* *2.23*
32	**55 Cs** *4.03* *1.52*	🟩 **56 Ba** *3.75* *1.64*	**57 La** *4.62* *1.33*	**58 Ce** *4.69* *1.31*	**59 Pr** *4.68* *1.31*	**60 Nd** *4.66* *1.32*	🟥 **61 Pm** *4.64* *1.32*	**62 Sm** *4.63* *1.32*
	63 Eu *4.61* *1.33*	**64 Gd** *4.51* *1.36*	**65 Tb** *4.58* *1.34*	**66 Dy** *4.57* *1.34*	**67 Ho** *4.55* *1.35*	**68 Er** *4.54* *1.35*	**69 Tm** *4.52* *1.36*	🟨 **70 Yb** *4.50* *1.36*
	71 Lu *3.54* *1.73*	**72 Hf** *3.50* *1.75*	**73 Ta** *3.47* *1.77*	**74 W** *3.44* *1.78*	**75 Re** *3.40* *1.80*	**76 Os** *3.37* *1.82*	**77 Ir** *3.34* *1.84*	🟪 **78 Pt** *3.41* *1.80*
	79 Au *3.38* *1.81*	🟩 **80 Hg** *3.24* *1.89*	**81 Tl** *3.43* *1.79*	**82 Pb** *3.32* *1.85*	**83 Bi** *3.22* *1.90*	🟥 **84 Po** *3.12* *1.97*	🟥 **85 At** *3.03* *2.02*	🟥🟦 **86 Rn** *2.93* *2.09*

atom. As demonstrated in the following sections many characteristics of covalency derive in a simple way from these tabulated values and Fibonacci numbers.

9.4.5 Covalent Interaction

A major objective of theoretical chemistry is to understand and predict the interaction between atoms to form molecules. The hardest to predict is interatomic distance in the resulting molecule. The reasonable suspicion that ionization radius should be a measure of homonuclear interatomic distance [17] is readily confirmed for diatomic interactions traditionally considered to be of first order. A sampling of

Table 9.2 Calculated interatomic distances (Å) for first-order homonuclear interaction

	C	N	Cl	As	Se	Br
$d(X-X)$	1.545	1.467	1.996	2.43	2.35	2.27
Expt.	1.54	1.47	1.99	2.44	2.32	2.28

Table 9.3 Interatomic distance, Å

	C	Cl	S	Br
H–X	1.14	1.30	1.34	1.38
Expt	1.12	1.27	1.34	1.41

calculated results, using the linear equation, $d_c = 0.868r_0$, that relates interatomic distance to ionization radius is shown in Table 9.2. Heteronuclear first-order interactions have been characterized less well experimentally, except for some H–X interactions, shown in Table 9.3, using $R_0 = \sqrt{r_0(1) \cdot r_0(2)}$.

Exceptions to these rules include the homonuclear interactions, traditionally interpreted as first order, O–O, F_2, and I_2 that require a proportionality constant of 0.932 in order to match the experimental distances. This observation prompted a more detailed analysis of the relationship $d' = d/r_0$, where the characteristic dimensionless interatomic distance, d' is a function of bond order [17].

9.4.6 Bond Order

An empirical relationship between d' and bond order is readily established on examination of a large number of well-documented diatomic interactions. The well-defined relationship

$$d' = j_b \tau^n$$

that converges with increasing powers of τ, as a function of Fibonacci numbers, was found [17] to generate definitive values of j_b, and hence of d', for integer and half-integer bond orders, b. The powers, n, for lowest-order homonuclear interactions are in Fig. 9.5.

Within a given period interactions with common n have equal bond orders. Calculated n, for first-order interactions, increases, on average, stepwise from $n = 5, 6$ for second-period elements, to $n = 10$ for period 6. The parameter $n = 6$ for N, O, F defines bond order $\frac{1}{2}$. For second- and third-order interactions the appropriate exponents within a given period are $n_2 = n_1 - 1$ and $n_3 = n_1 - 2$.

The converged values of d' for bond orders from 0 to 4, in half-integer steps, increase from $d' = 1$ to τ. On a Fibonacci spiral the values of

$$d' = 1, 0.935, 0.869, 0.804, 0.764, 0.724, 0.683, 0.658, \tau,$$

are reproduced by a divergence angle of $\pi/16$, as shown in Fig. 9.6.

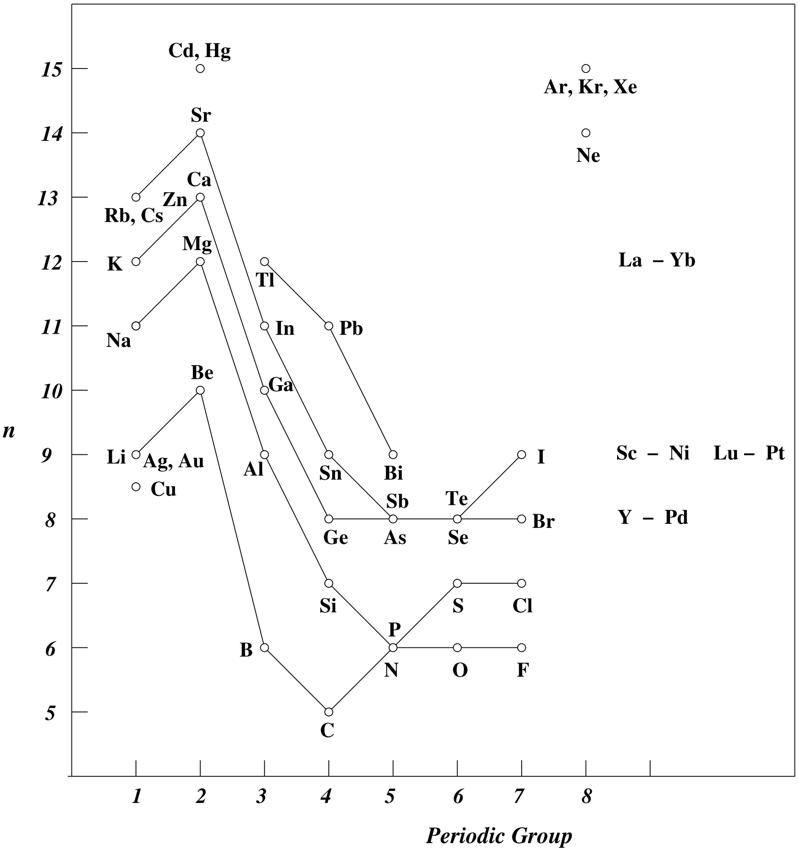
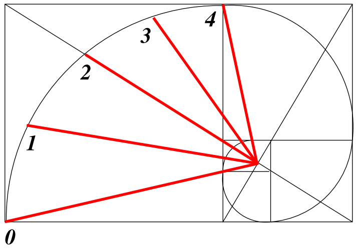


Fig. 9.5 Periodic variation of the bond-order exponents, τ^n

Fig. 9.6 Simulation of integer bond orders on a Fibonacci spiral



9.4.7 General Covalence

A well-defined scheme to calculate the details of pairwise covalent interaction by either point-charge or Heitler–London simulation resulted in the definition of a set of atomic interaction radii, r_a, somewhat different from, but closely related to the more soundly defined ionization radii, r_0 [4].

Table 9.4 Anomalous interaction radii of N, O and F

	C	N	O	F
r_1/a_0	1.75	1.49	1.27	1.09
r_a/Å	1.85	1.69	1.51	1.37
r_{emp}/Å	1.85	1.62	1.51	1.37
r_0/Å	1.78	1.69	1.60	1.52

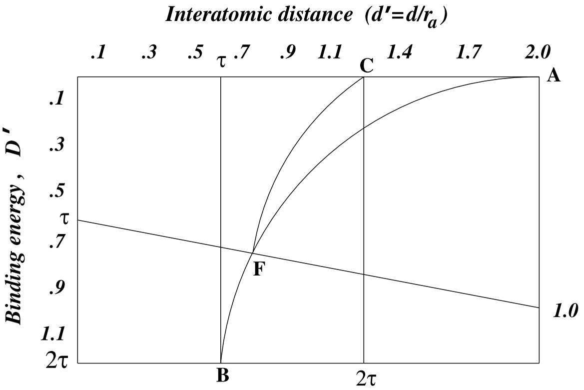


Fig. 9.7 Diagram to define the interdependence of dimensionless interatomic distance and dissociation energy in covalent interaction

The difference between the two sets of radii are readily identified by the ratio $r_a/r_0 < 1$ for electropositive elements (metals) and $r_a/r_0 \geq 1$ for non-metals. In all cases $r_a/r_0 \rightarrow 1$ with increasing atomic number. The only exception to this general rule occurs in the second period for Li and the elements N, O, F, with a progressive tendency for r_0 to exceed r_a.

The reason for this discrepancy traces back to the assumption of uniform electron density in the valence state, which not necessarily holds in a chemical interacting environment. Polarization of the ionization sphere of electropositives depletes the valence density near the radial limit, with the opposite effect for non-metals, which explains the general variation of the r_a/r_0 ratio. The small Li atom is highly polarizable.

The p-shell anomaly occurs because the inner shell of two electrons provides minimal screening of the nuclear attraction that increases with atomic number. The observed one-electron densities in the $2p$-shell [8] are found empirically to increase by a factor $(1.06)^p$ with the number of p-electrons. Noting that $2a_0 = 1.06$ interaction radii in Å are predicted from r_1/a_0 (Fig. 9.3) as $r_a = (1.06)^{p-1}r_1$.

The discrepancy between calculated and empirical r_a for N in Table 9.4 is most likely due to an unreliable empirical estimate. The revised estimate is $r_{emp} = r_0 = 1.69$ Å.

Taking advantage of these observations, and assuming strict linearity with atomic ionization energies [18], some minor adjustments to the empirical radii served to establish a final set of values.

Although the simulation of covalent interaction by point-charge interaction is now superseded by the number-theory approach it is of interest to note the precise way in which it graphically limits the mapping of D' against dimensionless interatomic distance defined as $d' = d/r_a$ to a narrow crescent that depends on the golden ratio, as shown in Fig. 9.7.

The diagram is constructed within a golden rectangle. Homonuclear diatomic interactions, irrespective of bond order, map to the curve CF, centred at the point (2, 1), and continue along FB of the arc BFA for higher order interaction. Interactions with substantial transfer of charge, including the oxides and chalconides of group 4, do not follow the covalence curves—a good diagnostic for ionic contributions to an interaction.

9.4.8 Atomic Polarizability

Atomic polarizabilities are notoriously difficult to either measure or calculate. The most reliable measured polarizabilities are those of the monatomic noble gases, obtained by low-frequency measurement of dielectric constant [19]. These values provide a useful guide for scaling other measurements and theoretical simulations.

The polarizabilities of only the smallest atoms have been calculated in detail, based on a perturbation method [20, 21]. A variational calculation for Be, for example, required a 105 × 53-term perturbed wave function [22]. Various approximations are necessary for both experimental and theoretical estimates to arrive at "recommended" polarizabilities for all other atoms. Empirical estimates are often based on covalent radii or single-bond lengths [23].

The polarizability of atoms and molecules is one of those useful chemical properties which is not only difficult to calculate but even to define in non-classical terms. It is succinctly defined as the electric moment induced by a field of unit strength, *i.e.* as:

$$\begin{aligned}\alpha &= m/F\\ &= \frac{qr}{q/r^2} = r^3\end{aligned}$$

on a charged conducting sphere of radius r, with the dimensions of a volume. Atomic volume as derived from the set of atomic radii [8], calculated from the wave model, is therefore recognized as a potential measure of atomic polarizability.

Atomic volumes calculated as $V = 4\pi r_1^3/3$, in units of $\text{Å}^3 \equiv 10^{-24}\ \text{cm}^3$ exhibit the same periodicity as the recommended values of atomic polarizability [18] and by simple scaling reproduce these in detail. The recommended values are obtained by scaling from SCF calculations and forcing agreement with better values where available [18, 19]. These recommended values are compared with $\alpha' = \sigma V \mu^x$ in

Table 9.5 Calculated polarizabilities of representative elements in units of Å^3

	Li	Be	B	C	N	O	F	Ne
α	24.3	5.60	3.03	1.76	1.10	0.80	0.56	0.40
α'	21.7	**11.3**	**2.74**	1.75	1.07	0.81	0.56	0.40
	Na	Mg	Al	Si	P	S	Cl	Ar
α	24.11	11.0	6.8	5.38	3.63	2.90	2.18	1.64
α'	22.88	11.86	**7.8**	5.32	3.60	2.78	2.14	1.67
	K	Ca	Ga	Ge	As	Se	Br	Kr
α	43.4	22.8	8.12	6.07	4.31	3.77	3.05	2.48
α'	**32.**6	20.5	8.23	6.00	4.31	3.68	3.10	2.60
	Rb	Sr	In	Sn	Sb	Te	I	Xe
α	47.3	27.6	10.2	7.7	6.6	5.5	4.7	4.04
α'	45.7	28.5	13.0	9.45	6.99	5.88	4.86	4.07
	Cs	Ba	Tl	Pb	Bi			
α	59.42	39.7	7.6	6.8	7.4			
α'	62.44	39.6	**14.9**	**11.1**	8.4			

Table 9.5. For the elements Li–Ne, $\sigma = 0.52$, $\mu = 1.15$, $x = p - 3, x > 0$. For higher periods the parameters are the same, except that $\sigma = 0.4$. In addition $\mu = 1.2$, $x = s - 1$ apply for the s-block of periods 4–6. The calculated values that differ from the recommended by more than the stated uncertainties are printed in bold type. General periodic trends suggest that in all of these cases the recommended values are in error.

Essentially equivalent results are obtained for the three transition series as shown in Table 9.6. The scaling parameters for the first two series are $\sigma = 0.36$, $\mu = 1.08$, $x = 5 - d$, $x \geq 0$. All discrepancies in this case relate to the electronic configurations assumed in the calculations. The present calculation is based on spectroscopic results, whereas the recommended values clearly reflect an assumed regular increase according to $s^2d^{1\rightarrow 10}$. Despite some variation in the expected periodicity the polarizabilities for the lanthanides, calculated as $\alpha' = 0.37V$ agreed with the recommended values [18] well within the rather generous estimated accuracy of 25 %.

Judging by the scaling parameters needed to bring calculated atomic volumes [8] into register with polarizabilities the electronic response to an electric field ap-

Table 9.6 Atomic polarizabilities (Å^3) for the transition and lanthanide series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
α	17.8	14.6	12.4	**11.6**	9.4	8.4	7.5	6.8	**6.2**	5.75
α'	17.2	14.5	12.3	13.7	9.5	8.1	7.4	6.8	8.2	5.72

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
α	22.7	17.9	**15.7**	**12.8**	11.4	**9.6**	**8.6**	**4.8**	**7.2**	7.36
α'	22.4	18.9	19.1	16.1	11.5	13.6	12.2	16.7	10.3	7.4

	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
α	21.9	16.2	13.1	11.1	9.7	8.5	7.6	**6.5**	**5.8**	5.7
α'	21.4	17.2	13.8	11.1	8.9	8.1	7.5	9.1	8.3	5.7

	La	Ce	Pr	Nd	Pm	Sm	Eu
α	31.1	29.6	28.2	31.4	30.1	28.8	27.7
α'	26.9	30.5	29.8	28.9	27.8	27.2	26.6

	Gd	Tb	Dy	Ho	Er	Tm	Yb
α	23.5	25.5	24.5	23.6	22.7	21.8	21.0
α'	22.0	24.8	24.2	23.6	22.8	22.0	21.4

pears to be different for the usual s, p, d, f classes of electron. Spin pairing has an additional, more minor effect.

9.4.9 Atomic Radii

Because there is no technique for the direct observation of free atoms the concept of atomic size has remained vaguely defined. Based on a suggestion by Pauling, covalent radii, derived from observed interatomic distances in covalent diatomic interactions, have been used as such a measure for a long time. These radii, from an early compilation [24] are shown in Table 9.7. There is a clear resemblance to the free-atom radii [8] from Fig. 9.3 and the corresponding Hartree–Fock values [8, 25]. The radii for atoms in a polarizing field (r_α), calculated from α' of Tables 9.5 and 9.6 are shown for comparison.

The way in which covalent interatomic distances and all of these different radii are closely related to ionization radii and number theory suggests the possibility of deriving atomic size directly as a function of only the golden ratio.

Table 9.7 Atomic radii (Å)

	Li	Be	B	C	N	O	F	Ne
r_{cov}	1.33	0.89	0.80	0.77	0.74	0.74	0.72	
r_{at}	2.12	1.72	1.06	0.90	0.77	0.66	0.56	0.48
r_{α}	1.80	1.39	0.89	0.75	0.64	0.58	0.51	0.46

	Na	Mg	Al	Si	P	S	Cl	Ar
r_{cov}	1.57	1.36	1.25	1.17	1.10	1.04	0.99	
r_{at}	2.36	1.90	1.66	1.46	1.27	1.12	0.98	0.86
r_{α}	1.76	1.41	1.23	1.08	0.95	0.87	0.80	0.74

	K	Ca	Ga	Ge	As	Se	Br	Kr
r_{cov}	2.03	1.74	1.25	1.22	1.21	1.17	1.14	
r_{at}	2.62	2.12	1.71	1.53	1.38	1.24	1.12	1.00
r_{α}	1.98	1.76	1.25	1.13	1.01	0.96	0.90	0.85

	Rb	Sr	In	Sn	Sb	Te	I	Xe
r_{cov}	2.16	1.91	1.50	1.41	1.41	1.37	1.33	
r_{at}	2.92	2.36	2.00	1.80	1.62	1.46	1.31	1.18
r_{α}	2.22	1.89	1.46	1.31	1.19	1.12	1.05	0.99

	Cs	Ba	Tl	Pb	Bi
r_{cov}	2.35	1.98	1.55	1.54	1.52
r_{at}	3.24	2.62	2.11	1.90	1.71
r_{α}	2.46	2.11	1.53	1.38	1.26

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
r_{cov}	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17	1.25
r_{at}	2.04	1.98	1.90	1.98	1.77	1.71	1.65	1.60	1.77	1.49
r_{α}	1.60	1.51	1.43	1.48	1.31	1.25	1.21	1.18	1.25	1.11

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
r_{cov}	1.61	1.45	1.34	1.29		1.24	1.25	1.28	1.34	1.41
r_{at}	2.28	2.19	2.28	2.20	1.97	2.05	1.98	0.82	1.84	1.65
r_{α}	1.75	1.65	1.66	1.57	1.40	1.48	1.43	1.59	1.35	1.21

Table 9.7 (Continued)

	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
r_{cov}	1.56	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44
r_{at}	2.27	2.20	2.12	2.05	1.97	1.91	1.84	2.05	1.97	1.65
r_{α}	1.72	1.60	1.49	1.38	1.29	1.25	1.21	1.30	1.26	1.11

	La	Ce	Pr	Nd	Pm	Sm	Eu
r_{at}	2.58	2.68	2.65	2.63	2.61	2.58	2.56

	Gd	Tb	Dy	Ho	Er	Tm	Yb
r_{at}	2.40	2.51	2.49	2.47	2.45	2.43	2.40

Table 9.8 Parameters that produce atomic radii for *p*-block elements

n	μ	σ
2	$\phi^2/4$	$\varepsilon^{3/2}$
3	ε^{-1}	$\varepsilon^{5/4}$
4	$\varepsilon^{-3/2}$	ε
5	ε^{-1}	ε
6	$\varepsilon^{-3/2}$	ε

The consilience between the golden ratio, Fibonacci spirals, the curvature of space-time, cosmic self-similarity and the mysterious parameters, $\varepsilon \simeq 1.111$ and 1.0345 [26, 27], prompted a revisit to atomic size. Added impetus was provided by the observation that $\varepsilon = \sqrt{2\tau} = 1.11178\ldots = 1.036^3$, for convenience defined in the following as $\varepsilon = 1.112$.

A set of formulae to reproduce our free-atom radii and the HF equivalents, only based on golden-ratio parameters, has been found:

For s-block atoms in period n: $r(s) = \frac{1}{2}\phi^3\varepsilon^{(n-2s)}$.

For the p-block: $r(p) = \mu\phi\sigma^{(n-p-1)}$, where the parameters μ and σ vary with n as shown in Table 9.8.

For the d-block:

$$n = 4, 5\colon r(s^2d) = r(ns^2)/\varepsilon^{d/3},\ r(sd) = r(ns^2)/\varepsilon^{(d-3)/3},$$
$$n = 6\colon r(s^2d) = r(6s^2)/\varepsilon^{(d+3)/3},\ r(sd) = r(6s^2)/\varepsilon^{(d-2)/3},\ r(\mathrm{Pd}) = r(\mathrm{Xe})/\varepsilon^{d/3}.$$

The lanthanide radii are defined in terms of the parameters τ and ε, noting that $\varepsilon^{1/12} = 1.009$ and $4\tau\varepsilon^{1/3} = 2.56$, as:

$$r(f) = 2.56(1.009)^{7-f}, \qquad r(\mathrm{La}) = 2.56 \times 1.009, \qquad r(\mathrm{Gd}) = 2.56/(1.009)^7.$$

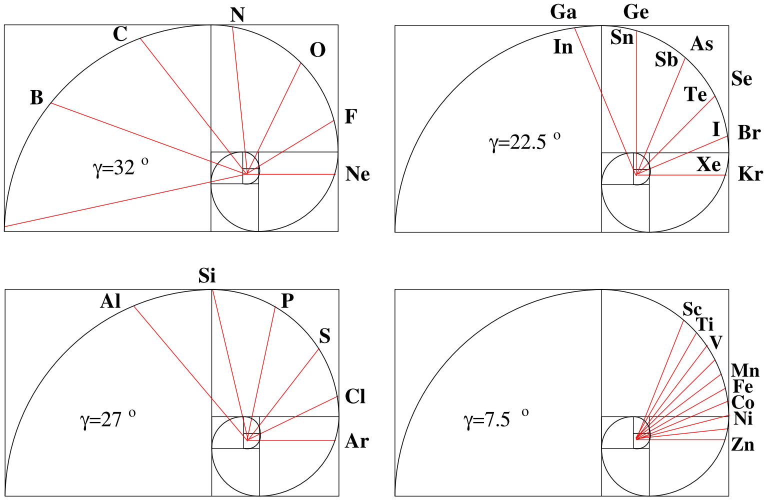


Fig. 9.8 Derivation of atomic radii on Fibonacci spirals

The radii calculated by these formulae are shown in Table 9.7 as r_{at}. The correspondence between the number-based and Hartree–Fock radii is calculated as

$$\frac{\sum |r_{HF} - r_{at}|}{\sum r_{HF}} = 0.023.$$

The correspondence with the free-atom radii calculated directly from the spherical wave model (Fig. 9.3) is even better. The largest single difference of 0.03 occurs here for the Cs atom.

The Golden Number Basis

It becomes increasingly obvious that the various sets of atomic radii have a common basis related to the golden ratio. This being the case the likelihood of deriving atomic radii through Fibonacci spirals needs to be explored. As shown in Fig. 9.8 the optimized set of free-atom radii, r_{at}, is reproduced in detail by assuming divergence angles of $\gamma = 32°$, $27°$, $22.5°$ and $7.5°$ for the atoms of the p-block and the first d-series. Equally convincing results, not shown, are demonstrable for all remaining elements.

By an interesting exercise it can be shown that all of the other radii listed in Tables 9.7 and 9.1 can be simulated in the same way by choosing appropriate divergence angles. A readily testable proposition is to show that the ionization radii of the first p-series are correctly specified by $\gamma = 10°$.

Without any effort to fine-tune divergence angles the observed ratio between γ's in the p-series of ~ 1.2, again points at the involvement of the ε-parameter.

The simple demonstration that the general curvature of a Fibonacci spiral is a function of $\varepsilon = \sqrt{2\tau}$ [26] defines a Gaussian radius of curvature $R^2 = 2\tau$, which, on the strength of the well-documented cosmic self-similarity, confirms that the golden ratio is a measure of space-time curvature.

9.4.10 *Final Results*

In the same way that interatomic covalent approach is a function of ionization radii and bond order, dissociation energy for any homonuclear covalent interaction is simulated as [17]:

$$D_c = Kr_0^2\tau^n$$

where the dimensional constant $K = 1.389$ or 14.35 converts calculated values into either eV or kJ mol^{-1}, for r_0 in Å.

For heteronuclear interaction

$$D_c = Kr_0^3(1)\tau^n/r_0(2) \quad \text{with } r_0(1) > r_0(2).$$

The general validity of the extensively documented results [17] resolves into a self-consistent scheme that fully characterizes all aspects of covalent interaction.

Harmonic stretching force constants are predicted by formulae of the type

$$k_r = \frac{4.615\tau^{n+2s}}{(\Delta d')^2 r_0(1) r_0(2)}\ \mathrm{N\,cm^{-1}},$$

in which s describes the variation of dimensionless interatomic distance, d', with bond order.

Diatomic dipole moments are calculated [17] by a novel method that does not take the difference in nuclear charge directly into account. It is argued that covalent interaction occurs between electrically neutral atoms in their respective valence states. It is only the polarization of the valence shells during heteronuclear interaction that results in a diatomic dipole. The degree of polarization depends on electronegativity differences and polarizabilities, that both derive directly from ionization radii.

9.5 Molecular Structure

The biggest challenge that faces theoretical chemists is the prediction of molecular structure and shape, given a connectivity pattern. The popular quantum-chemical procedure consists of the optimization of a three-dimensional trial structure constructed according to classical valency rules. It differs from an all-classical optimization by molecular mechanics only in the use of unnecessarily complicated algorithms based on a limited real basis set. It is quantum-mechanical only in name.

On reducing atomic wave functions into real form the vectorial properties of the Schrödinger spherical harmonics are lost. The only prospect of deriving the geometrical shape of a molecule quantum-mechanically is by solution of the relevant four-dimensional wave equation without separating the variables. This hopeless operation would in principle reveal the interference pattern between the spherical atomic waves that corresponds to minimum action in the equilibrium arrangement. To first approximation the action consists of electron spin and the three-dimensional Schrödinger harmonics, traditionally interpreted as orbital angular momentum. Three-dimensional molecular structure could hence be simulated mechanically as the arrangement of minimum angular momentum.

This approach has been used to good effect [4] in the simulation of the three-dimensional structures of small molecules and to account for geometrical and optical isomerism. The simulation depends in all cases on the criterion of minimum orbital angular momentum that depends on the mutual orientation of interacting radicals such as $-CH_3$, –OH, *etc*. It needs to be emphasized that this is no more than a convenient model. Rather than angular momentum, which implies rotational motion, the action function, associated with standing waves, unfolds as a distortion of the spherical symmetry that induces a magnetic moment. These moments line up anti-symmetrically and any residual moment, that only survives in chiral systems, is responsible for optical activity.

As pointed out elsewhere [7, 28] absolute three-dimensional chirality and the sense of optical rotation are not reciprocally related. Optical activity is four-dimensional in both cause and effect. Only the three-dimensional projection of molecular structure is observed in diffraction analyses.

In a detailed discussion [29] of four-dimensional molecular structure it is argued that

> [a]part from its structure, a classical molecule has no other properties and a free molecule, which exhibits the full range of chemical properties, has no structure.
>
> Molecules, small enough to persist in free space, are too small to develop a characteristic shape and macromolecules, large enough to exhibit three-dimensional structure, adopt their characteristic shape in response to interaction in condensed phases.

Free biological macromolecules simply fall apart in intergalactic space [30].

In general, molecules only acquire structure in interaction with their environment as in the process of crystallization or dissolution, where they assume a structure dictated by the condensed phase.

9.5.1 Molecular Modelling

Chemical practice is guided in general by the details of molecular structure as derived from crystallographic and spectroscopic analyses. This procedure is well-known to have produced excellent results for close to a hundred years and destined to do so into the foreseeable future. However, the persistent notion that an isolated molecule should have a robust three-dimensional structure almost identical with the crystal molecule, has no validity and is a constant source of confusion. Not to mention frustration.

It is still widely believed that by solving a molecular wave equation a quantal molecular structure can be derived from first principles. In fact, quantum chemists appear to be convinced that they are succeeding. The mere fact that no wave equation, more complicated than that for the one-particle central-field problem, has ever been solved, should advise that this is not the way to go.

The empirical approach [31] is still the only viable option, with the proviso that it is restricted to yield no more than a three-dimensional condensed-phase caricature of four-dimensionally shaped molecules. Problems such as the reversible folding of proteins, the unwinding of DNA and the mechanism of sterically[1] forbidden phase transitions, must inevitably remain unexplored.

There is no obvious alternative for modelling molecular shape, except in self-similar analogy with some astronomical structure. Recall that the three-dimensional atomic wave structure is the analogue of a two-dimensional solar system. The next higher level of a spiral galaxy could be considered as a self-similar molecular model. Optimization of such a structure in three dimensions would result in a radial distribution function.

The molecule emerges from this as a spherical atomic cluster held together by constructive interference between the electron waves that surround the nuclei. There is no fixed connectivity pattern in four dimensions. It only appears in three-dimensional confinement and varies with thermodynamic state. Molecules in the gas phase or in solution are more fluxional compared to the solid state. The situation is conspicuously reflected in the crystallographic structure of a perchlorate ion clathrated in a crystal cavity [7]. Depending on the size of the cavity its shape varies from being entirely structureless to a well-defined tetrahedron in close confinement.

9.6 Reaction Mechanism

Molecular structure is of vital importance in the design and execution of chemical syntheses. It is more than connectivity, but also the stereochemistry that could decide the outcome of a chemical reaction. Although it is a useful guide, the large number of exceptional situations associated with name reactions, special inversions, migrations and rearrangements that occur in the course of chemical change, suggest that reactions which follow the obvious route are the exception rather than the rule.

The study of reaction mechanisms could be seen as an elaborate scheme to find plausible explanations of why chemical reactions, more often than not, do not proceed in the obvious way consistent with the classical rules of chemical affinity. The

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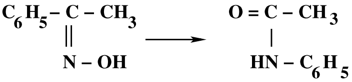
[1] As understood in three-dimensional Euclidean space.

obvious explanation behind the myriad of special mechanisms is that the conformation of fluxional four-dimensional molecules in the reaction medium is not necessarily the same as the assumed three-dimensional solid-state structures.

In formulating reaction mechanisms organic chemists concede as much by resorting to the concepts of mesomerism and resonance, which amount to the transfer of fractional charges, glibly explained as quantum-mechanical effects.

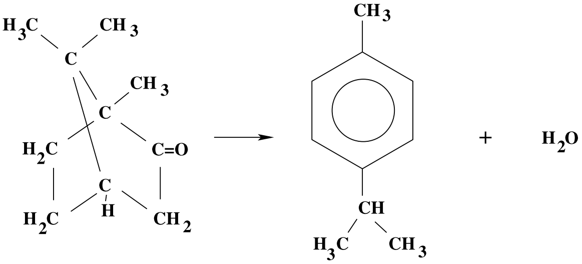
A convincing mechanism remains to be formulated for the famous Beckmann rearrangement that invariably involves the concerted migration of trans substituents as in



$$\underset{\text{N}-\text{OH}}{\text{C}_6\text{H}_5-\overset{}{\underset{\|}{\text{C}}}-\text{CH}_3} \longrightarrow \underset{\text{HN}-\text{C}_6\text{H}_5}{\text{O}=\underset{|}{\text{C}}-\text{CH}_3}$$

irrespective of the electron-releasing ability of the R groups [32].

The rearrangement of camphor into p-cymene



is equally baffling.

All cases point at alternative structures in the valence state.

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Chapter 10
A Fresh Start

Abstract The quantum theory as formulated almost a hundred years ago appears outdated in view of new developments. The firm belief in quantum magic persists and chemical practice appears irrevocably committed to it, despite many failures. By way of re-assessment the assumptions behind the Copenhagen interpretation of the theory are shown to be indefensible on closer scrutiny. It offers no reasonable atomic model nor an explanation of stationary states. The belief in a quantum theory of chemistry appears baseless, and a more useful theory is needed. The extension of chemical modelling by number theory into a general physically meaningful theory is explored through the simulation of the unexplained phenomena of high-temperature superconductivity and low-temperature nuclear activity. The prospect of number-theory analysis in nanoscience is explored.

10.1 Introduction

Quantum theory has become the all-embracing catchword of science and pseudo-science. The version in vogue is still understood in the formulation of the early 20th century. Without trying to belittle the founding pioneers it is fair to note that their interpretation was formulated insensitive to the importance of nonlinear effects, unaware of solitons and without the benefit of supercomputers. Many phenomena that defied comprehension at the time no longer appear mysterious and a reassessment of quantum events from a modern perspective could be of general benefit.

Quantum theory is freely invoked in the modern world by philosophers, cosmologists, organic chemists and psychologists to sidestep awkward situations. Once an intractable problem is labeled as a quantum effect there is no further argument. Quantum effects are agreed to be acausal, unpredictable, illogical and uncertain, but infallible. Pressed for clarification any number of different expositions of quantum theory can be expected. At one level it is a measure of the disturbance effected by an observation or the collapse of a wave function by conscious interference. If needed it eliminates reality or enables action at a distance. Quantum theory supersedes classical mechanics. It solves the many-body problem and invests a point particle with wave properties and intrinsic spin. There is no end to the magic. Quantum theory explains the inexplicable. Everybody seems to know it, but nobody is supposed to understand it [1, p. 129].

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The situation would be comical had it not been that serious. While the bureaucrats who control the funds remain convinced that only quantum-based research merits support the scientists of the world are trapped in a state of paralysis. Too many of them, despite their unease with the reigning paradigm survive by continued lip service to protect their prospects of promotion. Retired sages who dare to speak up are conveniently ignored.

There is a deeper problem. Academic scientists barely have the time to keep up with current literature in their own narrow fields and certainly not to probe beyond the facts recorded in their favourite textbooks or to consider the views of some maverick who pretends to know better. In the case of the quantum theory there is the comforting certainty that it reflects the unanimous views of a hundred Nobel laureates.

David Bohm, who tried to develop a causal interpretation of the quantum theory, died half a century later branded as a heretic [2]. Bohm developed his alternative interpretation of quantum phenomena in terms of hidden variables, without critically analyzing the orthodox views. Maybe that was a tactical error, creating the impression that he was trying to add something, without rejecting the Copenhagen interpretation.

It is fair to say that most modern science writers and commentators, who guide public opinion, are poorly informed about the origins of quantum theory and its interpretational problems. It is generally agreed that such details had been thrashed out in a series of debates between the titans, including Einstein and Bohr, and that the final consensus was confirmed mathematically by von Neumann. By now this perception is entrenched virtually indisputably.

In order to make a fresh start it is probably best to ignore the documented history and examine, without prejudice, the original arguments of Bohr, Heisenberg and Born, the gentlemen responsible for formulating the orthodox Copenhagen formulation, still universally accepted.

10.2 The Copenhagen Interpretation

Although the Copenhagen orthodoxy is accepted and respected worldwide it only exists as folklore without formal documentation. The closest to a statement of the assumptions and considerations that were taken into account leading to the final version is to be found in a collection of early reviews by Bohr [3]. As formulated in this, the theory stands on three pillars:

(1) Complementarity
(2) The Correspondence Principle
(3) The Quantum Postulate.

The aimless repetition and tedious elaboration of these concepts throughout the book of 119 pages provide a hint at Schrödinger's exasperation with Bohr's incessant insistence on quantum jumps during his ill-considered visit to Copenhagen in 1926, *e.g.* [4, p. 261]. The rambling discussion never really comes to a point and part of the reconstruction that follows had to be read between the lines.

10.2.1 Quantum Mechanics

It is clear that Bohr was totally enchanted with Heisenberg's coding of the hydrogen spectrum as a multiplicative scheme, later recognized as the matrix formulation of an eigenvalue problem. It is repeatedly emphasized that

> ...the new quantum mechanics does not deal with a space-time description of the motion of atomic particles.

The entire quantum philosophy that later developed into the Copenhagen orthodoxy is based on this statement, which is by no means beyond dispute.

Although Bohr–Sommerfeld orbits do not feature, the quantum condition, $E = h\nu$, is introduced *via* a modification of Hamilton's canonical equations by defining generalized coordinates and momenta, guided by the correspondence principle, in terms of two-dimensional arrays:

$$q_k = \left\{q(nm)e^{2\pi i\nu(nm)t}\right\}, \qquad p_k = \left\{p(nm)e^{2\pi i\nu(nm)t}\right\}$$

based on classical Fourier sums for multiply-periodic systems. On forming the product

$$(pq)_k = \left\{pq(nm)e^{2\pi i\nu(nm)t}\right\} \tag{10.1}$$

another square array is obtained, providing all elements of the same frequency are added together, *i.e.* those specified by the combination principle

$$\nu(nk) + \nu(km) = \nu(nm)$$

to generate the elements of array (10.1).

In practice observed frequencies are interpreted as the energy difference between stationary states,

$$h\nu_{nm} = (H_n - H_m),$$

which is equivalent to the matrix equation of motion [5]

$$\hbar\dot{q}_{nm} = i(Eq - qE)_{nm}.$$

In terms of general matrices P and Q

$$i(PQ - QP) = \hbar(I)$$

where (I) is the unit matrix.

This is the celebrated procedure that Bohr associates with the *quantum postulate*, stating:

> This postulate implies a renunciation as regards the causal space-time coordination of atomic processes.

Presumably this renunciation is in contrast to the old procedure which is superseded by the new quantum mechanics.

The "old" procedure starts from a classical equation of motion to calculate the energy difference between stationary states, fortuitously[1] ending up with the same condition that links spectroscopic terms to energy differences:

$$\nu_{nm} = \nu_{nk} + \nu_{km} = (H_n - H_m)/h.$$

The novel achievement of the Heisenberg procedure is relating the Ritz combination principle to a matrix operation and highlighting the commutation properties of dynamic variables. The momentum-position commutator is the best-known example, in the form $(pq - qp) = \hbar I/i$, abbreviated to $[p, x] = i\hbar$.

The appearance of non-commuting quantum variables in complex formalism is featured by Bohr as the fundamental departure from classical theory and causality. It is therefore sobering to note that the same features are present, though hidden, in the "fortuitous" Bohr model of the atom.

As shown in Sect. 9.4.2 the two-dimensional rotation of the Bohr electron is described by the complex function (9.4), which in polar coordinates rearranges into the eigenvalue equation

$$-i\frac{\partial}{\partial\varphi}\Phi = k\Phi.$$

Assuming the quantum condition of the Bohr model, $k = m\hbar$, $m = 0, \pm 1$, *etc.* it defines the angular-momentum commutator by

$$L_z = i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

The primary assumption of the Copenhagen argument that "mechanical models in space and time" are rigorously excluded by the "quantum postulate" is based on the presumed difference between the "old" and "new" approaches, now seen to be non-existent.

10.2.2 The Quantum Postulate

Bohr's "search for a more precise formulation of the concepts of quantum theory" led to the following postulates:

(1) An atomic system possesses a certain manifold of states, the "stationary states", to which corresponds in general a discrete sequence of energy values and which

---

[1] Heisenberg [6] explains:

> . . . the partial agreement of the (old) quantum rules with experience is more or less fortuitous. Instead it seems more reasonable to try to establish a theoretical quantum mechanics, analogous to classical mechanics, but in which *only relations between observable quantities appear*.

Emphasis added.

have a peculiar stability. This latter shows itself in that every change in the energy of the atom must be due to a "transition" of the atom from one stationary state to another.

(2) The possibility of emission and absorption of radiation by the atom is conditioned by the possibility of energy changes of the atom, in such a way that the frequency of the radiation is connected with the energy difference between the initial and final states by the relation

$$h\nu = E_1 - E_2.$$

It is presumed in the following that Bohr's frequent reference to *the quantum postulate* refers to these postulates.

As a secondary assumption, in order to renounce any effect related to space and time it is stated that the new "mechanics takes no account of the coupling of transition processes in pairs which show itself in those interactions". To achieve this

> ... only those quantities which depend on the existence of the stationary states and the possibilities of transitions between them occur in the new theory...

The following statements, quoted *verbatim* from Bohr [3] give some idea of the Copenhagen handling of the quantum postulate in the development of their theory:

> ... we have reached a complete understanding of the intimate connection between the renunciation of causality in the quantum-mechanical description and the limitation with regard to the possibility of distinguishing between phenomena and their observation, which is conditioned by the indivisibility of the quantum of action.
>
> ... all changes of state of an atom are [...] in agreement with the requirement of indivisibility of the quantum of action, as *individual* processes by which the atom goes over from one so-called stationary state into another stationary state and for the occurrence of which only probability considerations can be made...
>
> ... the fundamental postulate of the indivisibility of the quantum of action is itself, from the classical point of view, an irrational element which inevitably requires us to forego a causal mode of description and which, because of the coupling between phenomena and their observation, forces us to adopt a new mode of description designated as *complementary*...
>
> ... any measurement which aims at tracing the motions of the elementary particles introduces an unavoidable interference with the course of the phenomena and so includes an element of uncertainty which is determined by the magnitude of the quantum of action.
>
> ... any observation takes place at the cost of the connection between the past and the future course of phenomena.
>
> *... the finite magnitude of the quantum of action prevents altogether a sharp distinction being made between a phenomenon and the agency by which it is observed...*

. . . we can visualize the lack of causality by considering our lack of simultaneous knowledge of the quantities entering into the classical mechanical description. . .

. . . the description of the state of a single atom contains absolutely no element referring to the occurrence of transition processes, so that in this case we can scarely avoid speaking of a choice between various possibilities on the part of the atom.

The impossibility of distinguishing in our customary way between physical phenomena and their observation places us, indeed, in a position quite similar to that which is so familiar in psychology where we are continually reminded of the *difficulty of distinguishing between subject and object.*

. . . in the general problem of the quantum theory, one is faced [. . .] with an essential failure of the pictures in space and time on which the description of natural phenomena has hitherto been based.

. . . the essence [of quantum theory] may be expressed in the so-called quantum postulate, which attributes to any atomic process an essential discontinuity, or rather individuality, completely foreign to the classical theories and symbolized by Planck's quantum of action.

. . . the definition of the state of a physical system, as ordinarily understood, claims the elimination of all external disturbances. But in that case, according to the quantum postulate, any observation will be impossible, and, above all, the concepts of space and time lose their immediate sense.

. . . in the description of atomic phenomena, the quantum postulate presents us with the task of developing a "complementary" theory the consistency of which can be judged only by weighing the possibilities of definition and observation.

[Of] the essence [. . .] is the inevitability of the quantum postulate in the estimation of the possibilities of measurement.

. . . the idea of observation belongs to the causal space-time way of description [. . .] this idea can be consistently utilized also in the quantum theory, if only the uncertainty [. . .] is taken into account.

The matrix theory [. . .] is limited just to those problems, in which in applying the quantum postulate the space-time description may largely be disregarded, and the question of observation in the proper sense therefore placed in the background.

According to the quantum postulate any observation regarding the behaviour of the electron in the atom will be accompanied by a change in the state of the atom.

. . . wave-mechanical solutions can be visualized only in so far as they can be described with the aid of the concept of free particles.

In the conception of stationary states we are concerned with a characteristic application of the quantum postulate. By its very nature this conception means a complete renunciation as regards a time description.

. . . the concepts of stationary states and individual transition processes within their proper field of application possess just as much or as little "reality" as the very idea of individual particles.

Comment

The only aspect of Bohr's "quantum postulate" which is supported by observation is the Planck condition,

$$E = nh\nu.$$

This relationship is considered to arise from the uncertainty associated with any observation, which in this instance is fixed by the "indivisibility of the quantum of action". Apart from this assumption, it is difficult to understand how this condition, by itself, entails acausality and the separation between quantum and space-time events, but that is clearly implied.

As already demonstrated the results of the matrix method are entirely equivalent to that of the atomic model, based on classical mechanics, including commutation properties and complex formalism. The independence from space and time, which is claimed, can therefore only arise from the postulated nature of stationary states, which however, also occur in the mechanical model.

Maybe what makes the difference is the special new feature of stationary states, said not to be subject to any observational probe and hence to exist timelessly without uncertainty. Nothing is more irrational in all of Heisenberg–Bohr mechanics than this very notion. Without the bizarre assumption that there is no interrelation between stationary states, they are in no way different from normal thermodynamic equilibrium states.

In hindsight it is clear that the motivation behind the frantic efforts [7] in Copenhagen to develop an interpretation based entirely on the particle concept was to refute the results of wave mechanics. Popper's remorseless exposé [8] of the sordid attack on Schrödinger reached the same conclusion. Failure to simulate wave characteristics by a particle model necessitated the introduction of probability as a physical agent. It is not too difficult to see how this assumption led on to the notions of uncertainty, unreality and acausality. The impossibility of measuring quantum effects and the equivalence of subject and object are just wild speculation.

The Copenhagen formulation is reminiscent of Kelvin's proof that heavier-than-air flight was theoretically impossible, shortly before the Wright brothers took off. Had they been better informed and suitably aware of Kelvin's authority the aviation industry might not have developed. It is not too difficult to demonstrate that in terms of four-dimensional matter-wave mechanics the quantum mystery disappears. (See Sect. 6.7.)

10.2.3 Atomic Model

It is instructive to consider the Copenhagen atomic model, again as described in Bohr's own words [3]:

> Negatively charged particles, the so-called electrons, which are held within the atom by the attraction of a much heavier positively charged atomic nucleus, enter as common building stones in all atoms. The mass of the nucleus

determines the atomic weight of the element but has otherwise only a slight influence on the properties of the substance, these depending primarily on the electric charge of the nucleus which, apart from the sign, is always an integral multiple of the charge of the electron. Now, this whole number, which determines how many electrons are present in the neutral atom, has turned out to be just the atomic number that gives the place of the element in the so-called natural system, in which the peculiar relationships of the elements as regards their physical and chemical properties are so appropriately expressed. This interpretation of the atomic number may be said to signify an important step towards the solution of a problem which for a long time has been one of the boldest dreams of natural science, namely to build up an understanding of the regularities of nature upon the consideration of pure numbers.

The picture of the atom with which we are dealing is that of a small mechanical system which even resembles in certain main features our own solar system...

One might believe perhaps that the properties of the elements do not inform us directly of the behaviour of individual atoms but, rather, that we are always concerned only with statistical regularities holding for the average conditions of a large number of atoms.

Above all, we must assume that the quality of the light which the elements in certain circumstances emit and which is characteristic of each element is essentially determined by what occurs in a single atom. [...] we expect, on the basis of the electromagnetic theory of light, that the frequencies of the individual lines in the characteristic spectra of the atoms should give us a sufficient basis for interpreting this information; indeed, owing to the possibility of a continuous variation of the mechanical states of motion mentioned above, it is not possible even to understand the occurrence of sharp spectral lines.

The missing element in our description of nature, evidently required to account for the behaviour of the atoms, has been supplied, however, by Planck's discovery of the so-called quantum of action. [...] in contrast with the demand of continuity which characterizes the customary description of nature, the indivisibility of the quantum of action requires an essential element of discontinuity in the description of atomic phenomena.

Taking the indivisibility of the quantum of action as a starting point [...] every change in the state of an atom should be regarded as an individual process incapable of more detailed description, by which the atom goes over from one so-called stationary state into another. According to this view, the spectra of the elements do not give us immediate information about the motions of the atomic parts, but each spectral line is associated with a transition process between two stationary states, the product of the frequency and the quantum of action giving the energy change of the atom in the process.

On the whole, this point of view offers a consistent way of ordering the experimental data, but the consistency is admittedly only achieved by the renunciation of all attempts to obtain a detailed description of the individual transition processes. We are here so far removed from a causal description

> that an atom in a stationary state may in general even be said to possess a free choice between various possible transitions to other stationary states. From the very nature of the matter, we can only employ probability considerations to predict the occurrence of the individual processes…
>
> A peculiar feature of this attack on the problem of atomic structure is the extensive use of whole numbers which also play an important rôle in the empirical spectroscopic laws. Thus, the classification of stationary states, besides depending upon the atomic number, also depends on the so-called quantum numbers…
>
> …referring to the ideas of matter waves, […] in connection with the conception of stationary states, the quantum numbers of which are interpreted as the number of nodes of the standing waves symbolizing these states. […] in wave mechanics, we are not dealing with a self-contained conceptual scheme but, rather, as especially emphasized by Born, with an expedient to formulate the statistical laws which govern atomic phenomena.

Comment

This contrived description represents a brave effort on Bohr's part to dissociate himself from his own elegant planetary model of two decades earlier, in favour of Heisenberg's fanciful proposal of a system, said to be exclusively based on observational data. However, one looks in vain for the specification of how spectroscopic measurement distorts the timeless stationary states.

There is not much method in the madness that invokes atomic free will in order to avoid any mention of the essential mechanical aspects of the structure for an atom, admittedly made up of material particles.

Despite his obsession with whole numbers Bohr only reluctantly admits that in this case they derive from a matter-wave model, but cannot resist the sting in the tail, in the form of a sideswipe that subordinates Schrödinger's wave mechanics to Born's probabilities.

To summarize, there is no Copenhagen model of the atom. Electrons are either particles or waves. An appropriate atomic model must hence be formulated in terms of either particle mechanics or wave mechanics. There is no middle ground and no room for probability mechanics. Particles do not jump around at random and wave structures are not defined at point positions. The final conclusion must be dictated by the "quantum postulate". Only waves can satisfy the equation $p\lambda = h$, and variations thereof. A particle has no wavelength.

The momentum and wavelength variables are both associated with the wave structure and the "quantum of action" is a property of space-time. No measurement is required to account for quantum events. The characteristic mass, charge and spin of an electron imply that it occurs as a non-dispersive solitary wave, known as a soliton. The only uncertainty is associated with the variable size of the soliton, which only depends on the environment, with no dependence on measurement or human intervention. Nothing is unreal, irrational or acausal. A well-defined resonance process mediates the transition between “stationary states” and any development is predictable by the wave equation.

The spherical atomic wave structure, atomic number and the “natural system” of elements are all simulated correctly by “the consideration of pure numbers” as shown in the preceding chapters, presumably in realization of Bohr’s “boldest dream”.

10.2.4 Quantum Chemistry

Traditional wave mechanics is most valuable to the chemist as the interpretational tool of molecular spectroscopy. However, its impact in the elucidation of fundamental chemical concepts and interactions has been minimal. Paradoxically, although not a single problem of chemical significance has been obtained by rigorous solution of the total wave function, or its matrix equivalent, there is an apocryphal belief that the course and outcome of any chemical reaction as well as the structure of all products are predicted quantum-mechanically so well as to render the need of laboratory study redundant [9].

The whole discipline of quantum chemistry is aimed at achieving this same impossible goal. It centres around the prediction of the three-dimensional structure of free molecules, which is undefined, using a methodology which is inadequate for this purpose. Some qualitative results, such as the Heitler–London simulation of molecular hydrogen show that, in principle, molecular properties are wave-mechanical in nature. However, quantitative modelling requires four-dimensional nonlinear methods, based on the non-Euclidean space-time geometry of general relativity. While these remain inaccessible one possible strategy that exploits the notion of self-similarity in number-theory formalism has produced promising preliminary results. Development of this approach to its full potential depends on the willingness of the academic community to abandon quantum chemistry in its present form.

10.3 Two New Models

The phenomena of high-temperature superconductivity and cold fusion represent two notable failures of quantum theory. Although by no means fully substantiated, the superconduction model based on number theory [10], provides a much clearer picture of the phenomenon and a rational elucidation of cold fusion by the same approach will be demonstrated.

10.3.1 Superconductivity

With the discovery of superconductivity of ceramic materials more than a quarter of a century ago it became clear that an entirely new theory was required to account for superconductivity in all its forms and at all temperatures. Because of reluctance to

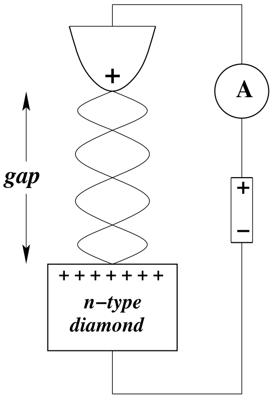

Fig. 10.1 Superconductive standing electron wave in vacuum on the surface of an n-type diamond

abandon the BCS theory that assumes the effect to be mediated by lattice phonons, alternative theories are not received sympathetically at all. The reported observation [11] of a room-temperature superconducting phase in the vacuum between a diamond cathode and a gold anode (Fig. 10.1) was not only coolly accepted [12, 13] at first, but later treated with such hostility that further reports of experimental progress are now denied reasonable access into mainstream media [14].

Creation of this superconducting phase depends on heavy doping of the diamond surface by bombardment with low-energy oxygen ions extracted from an oxygen plasma. On applying a high voltage as shown in Fig. 10.1 electrons, emitted from the diamond surface, are attracted to the anode, leaving behind a positively charged depletion zone. On first contact the accelerated electrons emit visible Bremsstrahlung at the anode, but this disappears as the voltage increases and a constant current flows, conducted by a standing electron wave across the gap, typically $\sim$5 micron wide.

Once this phase in the vacuum has been established it remains intact even when all power is switched off. It stays in place for months and as soon as it is reconnected, even to a source of picovolts, the same current flow as before is resumed immediately. The current across the gap flows in zero field, which is characteristic of, and explained as superconductivity [11]. Although this explanation is widely rejected it is consistent with the number-theory model of superconductivity.

The Number-Theory Model

The ratio of protons to neutrons, Z/N, for stable nuclides is known to converge to the golden ratio as a function of mass number, A. This is interpreted to show that, in order to ensure optimal stability, the same ratio should prevail at the core of each nucleus, which implies a proton excess of $x = Z - \tau N$ at the surface. Noting that a plot of $x/Z \; vs \; A$ reveals the known periodicity of the stable nuclides [10] it is interpreted to confirm that the golden excess, which converges to zero, is a meaningful measure of nuclear properties. It correlates remarkably well, not only with the appearance of anomalously high nuclear spin, but also with the tendency of

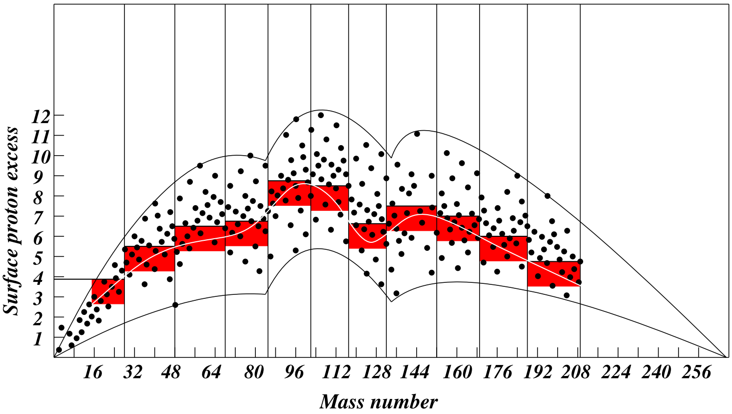

Fig. 10.2 The *red bands* identify the nuclides most likely to cause superconductivity (Colour figure online)

an element to go superconducting on cooling [10]. This relationship is demonstrated in Fig. 10.2.

Superconductivity is empirically found to be associated with nuclides of proton excess not exceeding the limiting lines drawn for each of the 11 × 24 periodic groups. The blocks in red therefore identify the most likely superconducting nuclides with an odd mass number and spin. The correlation is equally valid for the traditional low-temperature as well as the ceramic and organic superconductors.

The rationale behind this observation is that for a critical separation of operative nuclei within and between layers in the solid, the excess positive charges line up to define a featureless background, as in the simple Drude model, that promotes the formation of standing electron waves between the layers.[2] This situation is equivalent to the configuration, as in Fig. 10.1, that creates a standing wave on a diamond surface. Such standing waves define the superconducting phase. This model has been shown [10] to correlate with normal-state properties such as the Hall effect and to account for the Meisner effect and the benefit of isotope enrichment.

10.3.2 Cold Fusion

The hotly disputed phenomenon that became known as *cold fusion* was first reported almost a quarter of a century ago [15] and the argument still remains to be settled [16]. However, this author [16] claims that

> …hundreds of replications […] show consistent patterns of energy production and various nuclear products being produced using four different methods…
>
> Ignorance is no longer an excuse for rejecting the claims.

---

[2] A periodic potential leads to the formation of band structure and scattering at the Brillioun surface.

The seminal observation that inaugurated the cold-fusion saga was the production of unexpected excess heat during the electrolysis of heavy water (D_2O containing LiOD) on a palladium cathode. It was argued that the deuterium produced at the cathode[3] and driven into the metal caused some nuclear fusion reaction.

Convincing evidence exists that cold fusion, with the release of 5 MeV tritons (^3H) occurs on passing an electric current through thin deuterium-loaded titanium foil, from $-196°$ C to room temperature [17, p. 252]. In this case the energy of the bombarding deuterium ions does not exceed 350 eV.

Despite overwhelming evidence that some form of cold fusion happens the actual process remains a mystery. Persistent efforts to formulate a convincing model have by now established a number of criteria to be met for the process to occur and necessary characteristics to serve as guidelines for theoretical simulation. The following characteristics are frequently in evidence:

1. Ability of the metal to absorb large volumes of H_2 or D_2.
2. An induction period related to the texture of the cathode material.
3. Appearance of surface cracks before the onset of heat production, with the creation of a nuclear-active environment (NAE).
4. Sporadic release of tritium $= {}^3H$, ^3He and ^4He, none of which appears to be essential byproducts of the fusion processes, although none can be discounted either.
5. Violent events may occur unexpectedly and irreproducibly, often associated with neutron bursts.
6. Fusion hotspots that persist after electrolysis show up on autoradiographs.

The two metals traditionally found to be most active in cold-fusion processes are palladium and titanium. Palladium occurs in the form of six stable isotopes of mass number 102, 104, 105, 106, 108 and 110. Titanium has five stable isotopes with $A = 46-50$.

Apart from palladium and titanium the only other metal often implicated in cold-fusion processes is nickel. Following the criteria outlined above there may well be other equally effective cathode materials. The various criteria are now examined in turn.

Hydrogen Uptake

Palladium and platinum are known to absorb H_2 up to levels corresponding to $PdH_{0.7}$ [18]. The uptake of both hydrogen and deuterium by Pd is described in detail by Sidgwick [19]. To quote:

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[3] The process consists of:

$$\begin{array}{l} 4D^+ + 4e \rightarrow 2D_2 \\ 4OD^- \rightarrow 2D_2O{+}O_2 + 4e \\ \hline 2D_2O \rightarrow 2D_2 + O_2 \end{array}$$

> Palladium in the colloidal, powdered or compact state will absorb anything up to 900 times its own volume of hydrogen at any temperature from zero to a red heat and beyond.
>
> …The absorption is accompanied by an expansion of the solid, and the lattice constant may increase by as much as 5 %…

Of particular interest in the present context is the analysis of hydrogen diffusion through a palladium plate. It is stated

> …that the process of diffusion consists in the atomization of the hydrogen on one surface, the passage of hydrogen atoms through the foil, and their recombination to hydrogen molecules on the other surface. This explains why the penetration is so rapid when the hydrogen is produced electrolytically; it is then already in the atomic state when it reaches the palladium, and so the heat of activation required by the molecules in order to break the H–H bond is no longer needed.

Based on this analysis it can be assumed that in the cold-fusion electrolysis deuterium reaches the nuclear-active-environment [16] (NAE) in the atomic state.

It is generally agreed [18–20] that the elements Ti, Zr, Hf, Th, V, Nb, Ta and Pt, but not Mo or W, have the same ability, although less pronounced, as Pd to absorb considerable quantities of hydrogen, always with a marked decrease in overall density [21]. Both Ru and Os in finely powdered form absorb large amounts of hydrogen, which cannot be removed under vacuum [19].

The NAE

Modification of the palladium structure on the uptake of increasing amounts of deuterium must eventually cause cracks to develop in the metal surface. Such cracks are routinely implicated to account for the induction period and considered characteristic of the NAE. It is suggested that, rather than directly initiating the nuclear reaction, the cracks are symptomatic of critically increased deuterium pressure at the nuclear-active site.

The Nuclear Reaction

In a related study of nuclear structures [10] convincing evidence was found that superconductivity invariably occurs associated with nuclides that carry excess nuclear spin due to aspherical distortion of the nucleus. In both Pd and Ti the presence of such high-spin isotopes prompted the consideration of possible fusions involving these nuclides.

An attractive feature of an interaction between the high-spin ($\sigma = 5\hbar/2$) nuclide ${}^{105}_{46}\mathrm{Pd}$ of 22 % relative abundance, and deuterium, is the non-appearance of detectable reaction products other than tritium:

$$ {}^{105}_{46}\mathrm{Pd} + {}^{2}\mathrm{H} \rightarrow {}^{104}_{46}\mathrm{Pd} + {}^{3}\mathrm{H}. $$

The change in isotopic composition of Pd would be virtually impossible to observe.

Rather than a standard fusion procedure, the proposed reaction amounts to the capture of a neutron by deuterium from the active Pd isotope. The only measurable effect would be a decrease of 7.1 MeV in the relative nuclear binding energies [22], appearing as excess heat. Simultaneous dissipation of the excess spin into the lattice contributes to the heating. The feasibility of this proposal depends on the existence of the stable ^{104}Pd isotope, the formation of which entails no high-energy radiation.

The same reaction is possible for the two high-spin $^{49}\mathrm{Ti}(\sigma = 7\hbar/2)$ and $^{47}\mathrm{Ti}(\sigma = 5\hbar/2)$ isotopes with respective $\Delta E = 8.1$ MeV and 8.8 MeV and abundances of 5.4 % and 7.4 %, converting to the stable isotopes ^{48}Ti and ^{46}Ti.

Although the production of free neutrons is not required by the proposed reaction, their appearance at highly active hotspots, with melting of the metal, is not rigorously excluded as a secondary reaction. The production of neutrinos to disperse the excess spin is not excluded either.

The Coulomb Barrier

The effective NAE of the proposed model is a distorted aspherical high-spin isotope at 20 % of the nuclear sites in solid palladium. Under deuterium pressure the transfer of a single neutron from palladium restores the spherical symmetry of the distorted nucleus at a lower energy level, releasing excess energy to the lattice. If neutrons can be transferred directly between nuclei [17, p. 254] the Coulomb barrier against the proposed neutron–deuteron interaction cannot be serious.

Discussion

The proposed mechanism lends itself to a number of testable predictions. Isotopic enrichment of the active nuclides would be an obvious improvement.

The search for other active metals is limited by the requirement of a high-spin isotope together with a stable isotope of the same element of mass number $A - 1$. Single-isotope metals such as $^{93}\mathrm{Nb}(\sigma = 9\hbar/2)$ are therefore excluded in a process without radioactivity. The almost-single-isotope $^{181}\mathrm{Ta}(\sigma = 7\hbar/2)$ could transmute into radioactive ^{180}Ta. More promising candidates include:

$^{91}\mathrm{Zr}(\sigma = 5\hbar/2,\ \Delta E = 7.2$ MeV, abundance 11 %)
$^{99}\mathrm{Ru}(\sigma = 5\hbar/2,\ \Delta E = 7.4$ MeV, abundance 13 %)
$^{101}\mathrm{Ru}(\sigma = 5\hbar/2,\ \Delta E = 6.8$ MeV, abundance 17 %)
$^{177}\mathrm{Hf}(\sigma = 9\hbar/2,\ \Delta E = 6.3$ MeV, abundance 13 %)
$^{179}\mathrm{Hf}(\sigma = 7\hbar/2,\ \Delta E = 6.0$ MeV, abundance 18 %).

Mo and W, being inert to hydrogen may perhaps be discounted. Metals with high-spin metastable isomers could however, become active under suitable conditions, *e.g.*:

$^{189m}\mathrm{Os}(\sigma = 9\hbar/2,\ \Delta E = 5.9$ MeV, abundance 16 %)
$^{195m}\mathrm{Pt}(\sigma = 13\hbar/2,\ \Delta E = 6.1$ MeV, abundance 34 %).

Nickel has been mentioned as an active metal, but with a ^{61}Ni abundance of only 1 % not likely by the mechanism proposed here.

Hundreds of experiments to substantiate electrolytic cold fusion under a variety of conditions [17] have identified additional reaction products produced in variable quantities. In many cases unlikely products could be ascribed to careless experimentation and unnoticed impurities. On balance, possible secondary reactions consistent with the proposed model could be formulated with confidence to account for most observations. Possible secondary products in low yield are predicted to result from the reactions

$$^3\mathrm{H} \rightarrow {}^3\mathrm{He} + e^-,$$

$$^2\mathrm{H} + {}^3\mathrm{H} \rightarrow {}^4\mathrm{He} + n.$$

The observation [17, p. 130] that palladium when saturated with deuterium turns superconducting at low temperature implies another possible source of low-level β^--radiation during cold-fusion electrolysis. The most likely reaction responsible for the appearance of superconductivity,

$$^{105}_{46}\mathrm{Pd} + \left({}^2\mathrm{H} + e\right) \rightarrow {}^{107}_{46}\mathrm{Pd} \rightarrow {}^{107}_{47}\mathrm{Ag} + \beta^-$$

could be triggered electrolytically, to produce the radioactive high-spin ^{107}Pd isotope that decays by β^- emission with a half-life of 6.5×10^6 y [23]. It is recognized as the hypothetical intermediate nuclide produced by low-energy He$^+$ irradiation to yield superconducting Pd [10, p. 328].

Research strategies based on the scheme outlined here would be free from the burden of constantly dodging the dictates of nuclear physics. The perennial debate over numbers of neutrons, neutrinos and γ-rays produced in the process, becomes irrelevant. There is no point in further comparison with hot fusion processes. With agreement on the principles involved it should become feasible to standardize control conditions for the comparison and optimization of experimental procedures and results. Falsification of the theory could be attempted by replicating the electrolytic results using a cathode material without a high-spin isotope.

10.4 The Common Wave Model

The common factor between quantum theory, wave motion, self-similarity and the golden parameter is their shared dependence on integers. Barring the unreasonable suspicion with which most scientists treat everything that smacks of numerology, the development of physical models through number theory could well be an attractive pursuit. The problem is that numerical regularities are everywhere in evidence and need no special expertise to observe and exploit—a temptation which is hard to resist by mystics, missionaries and charlatans. The Oxford compact dictionary defines numerology as “the study of the supposed magical power of numbers”. The same stigma adheres to the application of number theory to scientific problems. Exactly the opposite is true for differential calculus, another form of mathematics.

Modern theories in physics and chemistry are ranked according to their mathematical substructure. Conclusions based on solutions of a differential equation are considered superior to empirical observation. A mere numerical regularity, howsoever convincing, remains a coincidence. A wave-mechanical simulation of the periodicity of twenty elements is considered scientifically more meaningful than the demonstration of a general numerical function that predicts the periodicity of all stable isotopes as a function of either Z, A or $N = A - Z$. A differential equation that solves for this function is not known.

For such an equation to exist it must be some generalization of (7.19)—not only nonlinear, but four-dimensional as well. Even computerized solution of such an equation is a daunting prospect. Adapted for the analysis of many-body problems as presented by atoms and molecules turns it into an even more distant dream. Given the encouraging results obtained number theory appears as a more viable interim measure.

At the heart of the number-theory approach is the reality of cosmic self-similarity. Relevant examples in support of this notion are just too numerous to ignore. The golden ratio, often embedded in a logarithmic spiral, features prominently in all applications. To address chemical problems the state of an electron is assumed completely fixed by its environment. As a working model it is assumed that the Compton wavelength, $\lambda_C = h/mc$, describes a free electron in empty space as an infinite plane wave of momentum $p = mc$. Restricted in any way the wave is modulated into a wave packet of de Broglie wavelength $\lambda_{dB} = h/p$ with $p < mc$, as in Fig. 7.7. The modulation is quantified by a fine-structure parameter, $\alpha' = \lambda_C/\lambda_{dB} = p/mc$. An electron in the ground state on a hydrogen atom, with $\lambda_{dB} = 2\pi a_0$, $a_0 = (\hbar/e)^2 m$, has $\alpha' = e^2/\hbar c = \alpha$, the well-known fine-structure constant.

Action, in elementary units of h is generated by space-time curvature and space-time is curved to an extent that depends on the golden ratio. All non-dispersive units of elementary matter and energy which occur as solitons are of the same type, with characteristic properties of mass, charge and spin conditioned by the golden parameter τ.

The same parameter features in the shape of a golden logarithmic spiral, characteristic of self-similar growth structures in four-dimensional space-time and useful as an optimization instrument. The most conspicuous applications are in the optimization of solar and planetary systems [24] and the electronic structure of atoms [25].

10.4.1 The Periodic Function

The periodic table of the elements that reflects the comparative electronic configuration of different atoms is modelled in detail by Farey sequences that converge to the golden ratio and which represent nuclear composition in terms of the rational fractions Z/N. Convergence as a function of A, Z or N defines three equivalent versions of an 11×24 periodicity of stable nuclides. The periodicity as a function of Z, when sampled at fixed values of the Z/N ratio, varies in a predictable way, commensurate with the response of electron configuration under applied pressure.

By interpreting the state of pressure to reflect space-time curvature the periodic function correlates with the dictates of an assumed projective space-time topology. The hypothetical Euclidean state correlates with a periodic function based on the Schrödinger solution for hydrogen in an essentially empty universe. Golden-ratio curvature ($Z/N = \tau$) corresponds to the observed periodic function and for a curvature that approaches infinity ($Z/N = 1$), that could be reached in a black hole, inversion between matter and antimatter and nucleogenesis by α-particle fusion can be inferred. Observed convergences are consistent with an involuted closed function that allows a maximum of 100 natural elements with 300 isotopes. In interplanetary space ($Z/N = \tau$) the maxima are reduced to $Z_m = 81$ and $A_m = 264 = 11 \times 24$.

10.5 New Horizons

At the next level of aggregation it has been shown that the wave structure of covalent interactions is strictly controlled by the geometry of a golden rectangle and the exclusion principle that limits maximum bond order as a function of τ. Bond order derives directly from a Fibonacci spiral. The covalent parameters of interatomic distance, stretching force constant and dissociation energy are all simple functions of bond order and powers of τ.

Optimization procedures for higher-level aggregates like molecules and crystals may not be feasible without computer assistance, but are understood well enough as the interference patterns between standing waves. There is no lack of challenging prospects and plenty of scope for innovative endeavours.

Golden-ratio phyllotaxis imposed on nuclear structure results in the notion of a surface excess of protons as a possible basis of superconductivity and cold fusion, both of which are poorly understood as quantum phenomena.

10.5.1 Nanostructures

The blossoming field of nanoscience is increasingly confronted with phenomena which are hard to explain by the traditional concepts of quantum chemistry [26]. A number of attempts to rationalize the electronic structure [27, 28], conformation [29, 30] and topology [31] of nanomaterials in terms of hybrid orbitals are noted for their misleading content. It is generally agreed that [27]:

> Carbon nanotubes… consist of either one… or multiple… shells of carbon in sp^2 bonding configuration.

This is clearly intended as a precise quantum description of carbon nanotubes, although it strictly applies only to a rigid planar system.

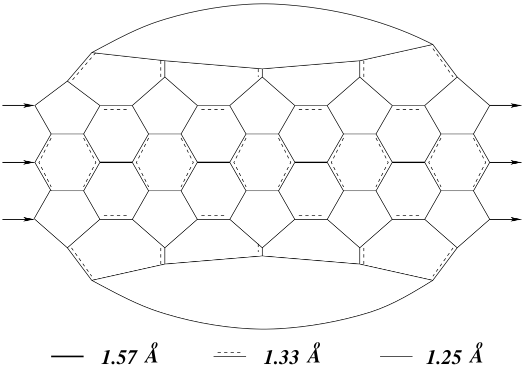

Fig. 10.3 The C_{70} molecule unrolled. The interatomic distances of 1.57, 1.33 and 1.25 Å are of bond order 1, 1.25 and 1.5 respectively

A more precise formulation is attempted elsewhere [31]:

> The angle $\theta_{\sigma\pi}$ between the [π orbital axis vector] and a σ direction (i.e., a bond) indicates the degree of "pyramidalization" and the hybridization. For $\theta_{\sigma\pi} = 90°$ (planar system), the σ orbitals are in a sp^2 hybridization and the π orbital is a pure p_z orbital. For a folded graphene sheet, $\theta_{\sigma\pi}$ has an intermediate value which decreases as the inverse of the radius of curvature of the folding, and reaches 90° at the limit $R \to \infty$.

This is quantum chemistry gone berserk, but perhaps not as wild as the ingeneous affirmation of the quantum-mechanical nature of nanomaterials [30] that follows:

> From a theoretical point of view, the Dirac equation—which replaces the Schrödinger equation for electrons in graphene—has to be modified when defects are in the lattice. … The overlap of p_z-orbitals determines the electronic properties but is altered in the vicinity of structural defects. … defects lead to a local rehybridization of sigma and pi-orbitals which… changes the electronic structure.

The different bonding models proposed for nanocarbon compounds are all based on the assumption that the in-plane interactions in graphite are of sp^2 type. According to the theory, right or wrong, all bond lengths must be the same, $d(\mathrm{C{-}C}) = 1.42$ Å, with each atom trigonally surrounded by three others in the plane. According to hybridization theory such a graphite sheet, like extended aromatic systems, is stabilized by a delocalized grid of π-electrons that ensures sterically rigid planarity as a function of the combined barriers to rotation for each bond. The interplanar spacing of 3.35 Å is ascribed to van der Waals forces [32].

The hybridization model for graphite breaks down completely when applied to graphene and its derivatives. The rigid graphene sheet predicted by the theory has never been observed.

The structure of the smallest nanotube, C_{70}, as derived crystallographically [33] is projected in Fig. 10.3. The first-neighbour interatomic distances observed here are of three types, $d(\mathrm{C{-}C}) = 1.57(3)$, 1.33(3) and 1.25(3) Å, representing proposed bond orders of 1, 1.25 and 1.5 respectively. Note how the bond orders add up to the classical tetravalency of four at each atom. It is also of interest to note that the pentagons have strict five-fold symmetry, whereas the six-membered rings have no chemically meaningful symmetry.

This result is in satisfying accord with the definition of bond order as a fundamental characteristic of wave-like covalent interactions [34]. Hybridization and resonance are powerless in this situation. Not that molecular-orbital methods, also based on linear combination of real atomic orbitals, can perform any better. The only useful results, pertaining to the folding and distortion of graphene sheets, obtained until now, are based on empirical analysis of curved surfaces. Even the nearly-free-electron study of semiconductor band structures of nanomaterials are of limited value, especially those that start from hybridization levels.

Electronic Properties

The quantum-chemical models for nanosized semiconductor crystals are also based on hybridization and resonance, according to the general prescription of Coulson [35] for general intermetallic compounds.

All interactions are modelled by overlapping sp^3 orbitals, augmented by a host of empirical quantities, including effective nuclear charge, Madelung constant, net atomic charge, effective charge per bond, bond length for first neighbours and distance between second neighbours—all of these variationally and empirically adjusted.

An ambitious analysis of semiconductor clusters by this procedure [28] is concluded with remarks, such as:

> The calculated discrete electronic spectra may need modification. . .
>
> Quantitative calculations will require improvement. . .
>
> The atomic nature and structure of intrinsic surface states, and the general question of possible surface electronic bands and reconstruction, remain largely unexplored.
>
> Experiments on CdSe crystallites clearly demonstrate the reality of the electronic quantum size effect.

It is fair to infer that the methods of quantum chemistry have not contributed in a meaningful way to an improved understanding of size effects in nanosized semiconductors, apart from the *assumption* that it is a quantum effect.

Nonlinear Effects

The behaviour of nanomaterials is essentially nonlinear. Any effort to describe the behaviour of colloids and nanoparticles by linear equations is therefore an exercise in futility. The non-classical nonlinear properties of nanomaterials can only be described properly by a nonlinear wave equation. In particular, the simulation of their band structure by linear superposition of sp^3 orbitals [28] is no more informative than the general statement [36]:

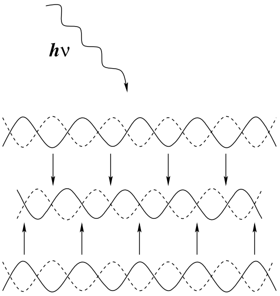

Fig. 10.4 Creation of surface plasmons as electronic charge couples with the fluctuating field of electromagnetic radiation. The *arrows* indicate electronic displacement

> In semiconductor particles of nanometer size, a gradual transition from solid-state to molecular structure occurs as the particle size decreases. Consequently, a splitting of the energy bands into discrete, quantized levels occurs.

It goes without saying that computational quantum chemistry, exclusively based on linear superpositions in all of its forms, holds no promise of contributing any insight into the nature of nonlinear nanostructures.

The rapid progress with computer experiments in the analysis of nonlinear lattices [37] points at an alternative approach that could be of considerable benefit in the development of nanotechnology.

Plasmonics

The optical properties of metallic nanoparticles remain one of the most actively studied aspects of nanotechnology. It is generally referred to as plasmonics, a description that derives from the similarity between metallic films and plasmas. A plasma is a medium with equal concentrations of positive and negative charges, of which at least one charge type is mobile. In a solid the negative charges of the conduction electrons are balanced by an equal number of positively charged ion cores.

A plasma oscillation results from the displacement of electrons as shown in Fig. 10.4 [38]. A *plasmon* is a quantum of plasma oscillation, which may be excited by passing an electron through a thin metallic film or by reflecting an electron or a photon from a film.

Plasmon excitations have been observed in surfaces, interfaces and spherical metallic colloids. The deep red colour of gold nanoparticle sols in water and glasses reflects a surface plasmon band; a broad absorption band in the visible region around 520 nm [39]. The phenomenon is interpreted in Mie's theory, first formulated in 1908 [40]. The resonances of electric and magnetic oscillations in the surface were described by solving Maxwell's equations for spherical particles with the appropriate boundary conditions. The plasmon band may therefore be ascribed to the dipole oscillations of free electrons in the conduction band at energy levels immediately above the Fermi level [41].

An intriguing characteristic of the surface plasmon band is its disappearance from particles with core diameter less than 2 nm, as well as from gold in bulk. This be-

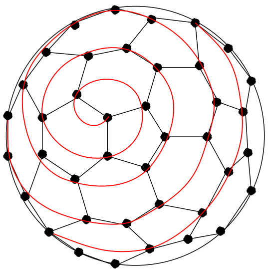

Fig. 10.5 Schematic drawing to show the atomic positions of fullerene connected by a single spiral

haviour becomes hard to rationalize as a simple quantum effect. Phenomenologically there is no mystery. With increased clustering beyond the molecular level the $6s$ conduction electrons accumulate in the surface. On reaching a critical size Mie-type resonance occurs and persists until the particle has grown to a size where normal metallic conduction sets in. This happens when the particle size has increased to match the de Broglie wavelength of the valence electrons, which now propagate as matter waves through the periodic lattice [39].

Fibonacci Patterns

The stress pattern in the surface of $\mathrm{Ag}/\mathrm{SiO}_x$ core/shell microstructures [42] appears as arrays of triangles and pentagons. In addition, the spherules line up along Fibonacci spirals. This observation highlights the similarity between nanoparticles, the growth of biological structures and the conjectured mechanism that controls the shape of polymers and macromolecules in terms of space-time curvature [25]. To explore the likelihood that all nanostructures are shaped in the same style, the atomic positions in the spherical fullerene are shown schematically in Fig. 10.5 to be consistent with the Fibonacci phyllotaxis of spherical growing cacti.

It is concluded that nanostructures are the natural intermediates in the growth of macroscopic bodies from the atomic and molecular building blocks that assemble in a fashion dictated by space-time curvature, which is quantified by τ. From this point of view the C_{60} fullerene molecule consists of twelve interconnected pentagons in a three-dimensional arrangement with six five-fold alternating $\bar{5}$ symmetry axes, that intersect at a centre of symmetry.

Non-classical Structure

The sixty carbon atoms that make up the fullerene molecule, shown in Fig. 10.6, are equivalent in all respects and together they define a holistic unit. Even the appearance of twelve equivalent pentagons is less important compared to the arrangement of all atoms on a closed spiral as shown in Fig. 10.5. Starting with any atom as pole, a spiral connects the 30 atoms in its hemisphere and continues to spiral in towards the opposite pole.

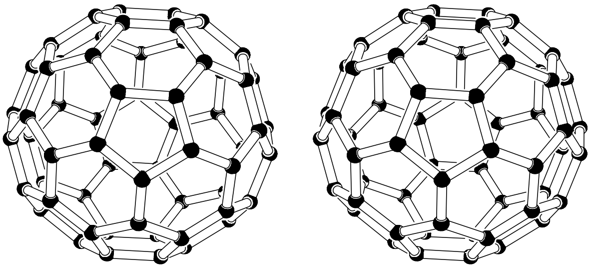

Fig. 10.6 Stereoscopic view of the C_{60} fullerene structure as found crystallographically [43]

By considering the two poles as a single point the double spiral becomes topologically equivalent to a closed single spiral in elliptic, or projective, space, embedded in four dimensions. This is the same structure that was proposed for the periodic table of the elements [10] and for universal space-time [44].

There is no other known molecule that reflects the three-dimensional projection of space-time structure as well as C_{60}. The simple reason is that five-fold symmetry is incommensurate with three-dimensional translational symmetry. Since traditional structural chemistry is based almost exclusively on three-dimensional crystallography the analysis of incommensurate structures and "quasi-crystals" that depends on four-dimensional translational symmetry has largely been neglected until fairly recently.

An interesting variety of structures, including those of viruses and quasicrystals such as icosahedral $Al_{70}Pd_2Mn_9$, of this type, are reviewed in two recently published chapters [45–47]. A central feature of this work is the prominence of the golden ratio in the metrics that characterize these structures. The theoretical implications are discussed in the same volume [48] and elsewhere [25]. The implied self-similarity, ranging from atoms, molecules, through nanostructures, to astronomical systems, strongly suggests an intimate relationship of nanomaterials with botanical growth structures and biological composite materials, as widely recognized empirically [49, 50]. A convenient approach towards the understanding and modelling of the non-classical properties of such nanomaterials is *via* number theory and self-similarity—the recommended new approach to nanoscience and technology.

10.5.2 Quasicrystals

Four-dimensional and nonlinear effects are largely responsible for the occurrence of incommensurate structures and aperiodic, or quasicrystals. In terms of standard crystallography there is no understanding of these materials, of which hundreds of different examples have been crystallized. The well-defined diffraction patterns cannot be indexed in terms of any of the 230 possible three-dimensional space groups, because of the apparent five- and ten-fold symmetry which is incommensurate with three-dimensional translational symmetry. It is impossible to tile a two-dimensional surface with identical pentagons or decagons.

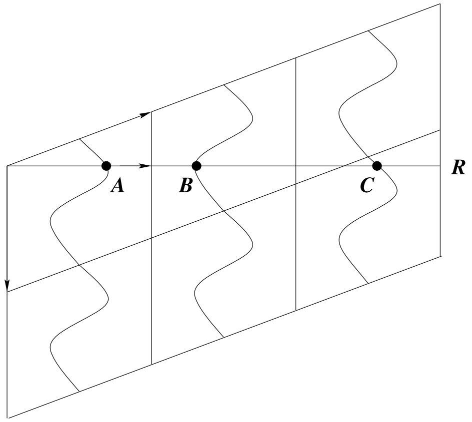

Fig. 10.7 Four-dimensional extension of a crystal in direct space

Several ingeneous models to explain the observed diffraction patterns of such crystals mathematically have been proposed, but a definitive characterization of the symmetry patterns in real physical space is not known; for the simple reason that a Euclidean specification of the atomic arrangement in such phases is impossible. The successful indexing of the observed diffraction patterns (in reciprocal space) in terms of higher-dimensional lattices demonstrates the aperiodic nature of quasicrystals, as shown in Fig. 10.7. In this diagram [51] each atom is represented by a one-dimensional modulation curve which is periodically repeated along the four dimensions of superspace. The observed crystal structure corresponds to the three-dimensional intersection with the four-dimensional object along R. Atoms A, B, and C are not equally spaced in three dimensions ($AB \neq BC$) and the structure is aperiodic. The quasicrystal represents a tiling of the line R in short (S) and long (L) intervals.

It can be shown [52, 53] that the ratio between the long and short intervals is fixed by the generators of a Fibonacci chain, $(-1+\sqrt{5})/2 = \tau$, and $1/\tau$. A self-similarity that leaves these parameters invariant is a crystallographic Lorentz transformation. It is inferred that the aperiodic long-range order of quasicrystals follows a Fibonacci sequence. It starts from S and L and grows by adding the previous (shorter) chain to the current one to produce the next [54]:

$$S \quad L \quad LS \quad LSL \quad LSLLS \quad LSLLSLSLLS \quad LSLLSLSLLSLSLLS \quad \dots$$

This is the same algorithm that creates the numerical Fibonacci sequence in which the ratio of adjacent terms

$$1/1 \quad 1/2 \quad 2/3 \quad 3/5 \quad 5/8 \quad \dots$$

converges to the golden ratio.

The only known naturally occurring quasicrystal was found in a $CV3$ carbonaceous chondrite meteorite [55]. It is inferred that this material was formed in interstellar space, only subject to a gravitational field due to the general curvature of space-time, which is known to relate to the golden ratio.

10.6 Future Prospects

When the final word is spoken on the nature of matter it must surely mention the complex phase that relates it to the curvature of space-time. This relationship was first discovered in Schrödinger's re-interpretation [56] of Weyl's gauge theory and has grown since then into the unspoken assumption of all elementary-particle theories. Unspoken, because it must surely be evident that associating a phase with a point particle makes no physical sense. Still, it's a rare chemist that would be prepared to dispute the models of particle physics on the basis of this argument alone.

The particle model has come a long way without serious dissent, from classical times, and survived the careful scrutiny of twentieth-century acuity. It is perceived as the only true and self-evident basis of atomic theory, without which all of chemistry must collapse. Moreover, only by extension of the particle model, in the hands of Einstein, to electromagnetic radiation, could Planck's quantum conjecture be reconciled directly with real physical systems. The model has become synonymous with sensible science, despite many serious infinity problems. Most obvious is the infinite gravitational field associated with a zero-dimensional massive point particle:

$$\lim_{r\to 0}\frac{m}{r}=\infty.$$

In four-dimensional space-time the point particle not only has no spacial extent, but its lifetime is also limited to zero. It never exists. Dodging the dilemma by defining the particle as a space-time singularity only exacerbates the problem by the introduction of a more serious mathematical anomaly.

Although there is no immediate prospect of changing the chemists' perception of elementary matter a slow paradigm shift could benefit from keeping the wave model alive. It is seen as the only reasonable alternative without the defects of probabilistic point-particle theories.

10.6.1 The Space-Time Vacuum

Sufficient grounds exist to posit that space-time fills the vacuum as a closed positively curved involuted plenum. Curved space, which is intrinsically nonlinear, compared to the Euclidean alternative, is of lower symmetry than continuous, empty flat space. Distortions that appear in curved space-time are recognized as a dynamic mass-energy field that fluctuates between regions of high and low concentration.

The mathematical model which describes the potential field that regulates the vacuum distortions consists of a four-dimensional second-order differential equation with harmonic solutions, characteristic of wave structure. Elementary waves combine in a mode that depends on invariant phase relationships in the formation of elementary forms of matter, interconnected by standing energy waves. Accumulation of matter modifies local space-time curvature with feedback that stimulates further accumulation, responsible for the dynamic cosmic equilibrium.

The reciprocity between mass and curvature that defines the gravitational field is mirrored by a reciprocity between charge and phase invariance. In flat Euclidean space mass is undefined and waves propagate without phase change. In curved space vacuum distortion manifests as mass and phase invariance requires a compensating electromagnetic field for the conservation of charge. The phase, or gauge, factor associated with both mass and charge is an intrinsic property of projective space-time and does not appear in affine space. The third attribute of elementary matter, known as spin, occurs as the solution of the four-dimensional differential equation that defines the potential-energy function in curved space. All attributes of matter are essential wave properties.

10.6.2 Perceptions in Linear Tangent Space

Curvature of the planetary surface, which is now rarely disputed, did go unnoticed for centuries and flat-earth Euclidean geometry remains in general use. It works well, except in navigational applications, and is considered entirely adequate for modelling in the physical sciences.

Twentieth-century quantum mechanics developed as a three-dimensional linear theory in tangent Euclidean space. In this form it is totally inadequate to deal with four-dimensional and nonlinear effects, in particular in its complete reliance on linear superpositions and separation of space-time variables. As a result the matter-wave solutions obtained in this way are dispersive and unsuitable for the simulation of material motion. It has to rely perforce on probabilistic schemes that lead to unnatural situations of acausality, intrinsic uncertainty and non-local interaction. It provides fertile soil for mystics and philosophers.

10.6.3 Four-Dimensional Reality

All is not lost. An awareness of nonlinear phenomena is spreading fast. Once a soliton is accepted as a possible structure for an electron the way is clear to abandon the point particle as a model for elementary matter. The price to pay is finding a mathematical model that does not rely on the separation of variables. A soliton is a holistic unit with an invariant phase relationship between its geometrical components, like the mechanical Scotch yoke that links one-dimensional oscillations into two-dimensional rotation. The electronic soliton does not have spacially directed orbitals that can be hybridized at random and it provides an equally convincing account of the photoelectric effect as an interaction between waves. An acceptable wave function for an electron must be, not only nonlinear, but also four-dimensional to account for spin and flexible enough to allow diffraction.

It is clear that the required equation does not have analytic solutions and the challenge for the future is a computerized analysis. In the interim semi-empirical number-theory methods promise intriguing results beyond traditional wave mechanics.

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