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.

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 $\pm$ 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

$$\phi(x,t) = a(k)\exp\big[i(kx - \omega t)\big].$$

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.
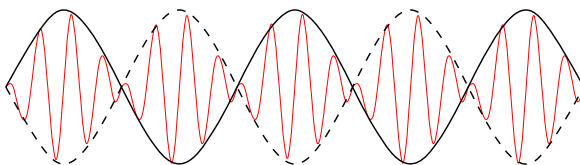
Given some initial data $\phi(x,0) = f(x)$ it is possible to calculate $\phi(x,t)$ for all t [4]. Even though the initial data may not have harmonic form, it may be represented by a Fourier integral

$$\phi(x,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} a(k)e^{ikx}\,dk$$

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

$$\varphi = ae^{2\pi i(kx-vt)}$$

in terms of an amplitude a, wave number $k = 1/\lambda$ and frequency v. The real part of a complex wave is represented by

$$\varphi = a\cos 2\pi(kx - vt)$$

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

$$\begin{aligned}
\Phi &= a\cos 2\pi(k_1x - v_1t) + a\cos 2\pi(k_2x - v_2t) \\
&= 2a\cos 2\pi\big[(k_1 + k_2)x/2 - (v_1 + v_2)t/2\big] \\
&\quad \times \cos 2\pi\big[(k_1 - k_2)x/2 - (v_1 - v_2)t/2\big].
\end{aligned} \tag{7.2}$$

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 $(v_1 + v_2)/(k_1 + k_2)$. For electromagnetic waves this is the same as the velocity of the initial waves, $c = v_1/k_1 = v_2/k_2$. 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, $v_1/k_1 \neq v_2/k_2$, the profiles move with a speed $(v_1 - v_2)/(k_1 - k_2)$, which is different from that of the more rapidly moving oscillating part, whose speed is $(v_1 + v_2)/(k_1 + k_2)$. 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, $v_\varphi = v/k$, and $v_g = (v_1 - v_2)/(k_1 - k_2) = \frac{dv}{dk}$. In terms of the wavelength

$$v_g = \frac{dv}{d(1/\lambda)} = -\lambda^2 \frac{dv}{d\lambda} \quad \text{or}$$

$$v_g = \frac{dv}{dk} = \frac{d(kv_\varphi)}{dk} = v_\varphi + k\frac{dv_\varphi}{dk} = v_\varphi - \lambda\frac{dv_\varphi}{d\lambda}.$$

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

$$\int_{k_0-\Delta k}^{k_0+\Delta k} a \exp\left[i(kx - \omega t)\right]dk = \Phi(x,t)$$

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]:

$$\Phi = \int_{k_0-\Delta k}^{k_0+\Delta k} e^{ik(x-x_0)}dk = 2\sin\frac{\Delta k(x - x_0)}{(x - x_0)}e^{ik_0(x-x_0)}. \qquad (7.3)$$

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
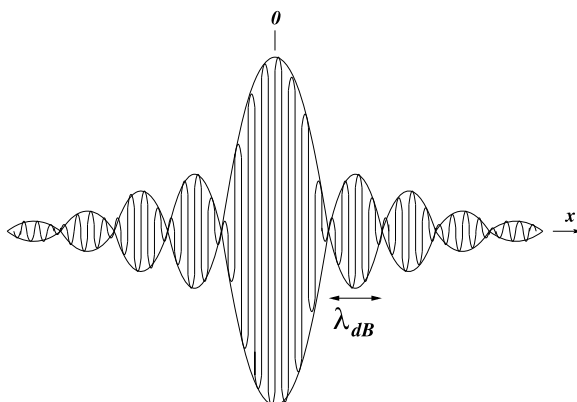
7.2.2 Matter Waves

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 mani-
festation 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 geometri-
cal 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

$$x^2\frac{d^2y}{dx^2} + x\frac{dy}{dx} + (x^2 - n^2)y = 4x^3$$

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

$$\psi = \psi_0 e^{-2\pi i\nu t}, \quad (x = 0).$$

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

$$\psi' = \psi_0 e^{2\pi i v t'} = \psi_0 \exp\left[2\pi i v\left(vx/c^2 - t\right)\beta\right],$$

which is of the form

$$\psi = \psi_0 e^{2\pi i (x/\lambda - vt)}.$$

It follows that

$$v' = v\beta = mc^2\beta/h = E'/h,$$
$$\lambda' = c^2/\beta vv = h/\beta mv = h/p',$$

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

$$v_g = \frac{dv}{d(1/\lambda)} = \frac{dE}{dp},$$

$$i.e. \quad v_g = \frac{d}{dp}\left(p^2c^2 + m^2c^4\right)^{\frac{1}{2}},$$

$$= \tfrac{1}{2}E\left(2pc^2\right) = pc^2/E,$$

$$= mvc^2/mc^2 = v,$$

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:

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m}(\nabla^2 + V)\Psi, \tag{7.5}$$

$$\nabla^2 \psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \tag{7.6}$$

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.

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[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 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, $E_0 = h\nu_0 = m_0 c^2$, 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

$$u(x,t) = \exp\left[2\pi i (x/\lambda_C - \nu_C t)\right],$$
$$\psi(x,t) = \exp\left[2\pi i (\nu t - x/\lambda_{dB})\right]$$

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

$$\frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} - \nabla^2 u - \left(\frac{m_0 c}{\hbar}\right) u = 0, \tag{7.7}$$

$$\frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} - \nabla^2 \psi + \left(\frac{m_0 c}{\hbar}\right) \psi = 0, \tag{7.8}$$

$$\frac{1}{c^2}\frac{\partial u}{\partial t} \cdot \frac{\partial \psi}{\partial t} - \nabla u \cdot \nabla \psi = 0. \tag{7.9}$$

Equations (7.7) and (7.8) can be formally regarded as the equations for brady-onic 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,

$$\Phi = \frac{A}{r}e^{i\omega t}\left\{e^{ikr} - e^{-ikr}\right\}$$

$$= \Phi_0 e^{i\omega t} \sin(kr)/r$$

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

$$\alpha^2 = \left(\frac{e^2}{\hbar c}\right)^2, \qquad E_1 = -\frac{me^4}{2\hbar^2},$$

$$\alpha^2 = -2E_1/(mc^2).$$

Hence

$$2E_1/(mc^2) = (m_0/m)^2 - 1,$$

$$2E_1 = c^2(m_0^2/m - m),$$

$$E_1 \simeq -\frac{1}{2}(\Delta m)c^2.$$

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,

$$\frac{d^2 R}{dr^2} = \frac{N}{a_0^2} e^{-r/a_0},$$

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

$$\frac{r_0}{a_0} = \frac{me^4}{m\hbar^2 c^2} = \left(\frac{e^2}{\hbar c}\right)^2 = \alpha^2$$

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,
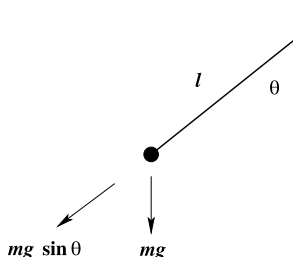
l is the length of the arm and g is the acceleration due to gravity. For small displacement $\sin\theta \sim \theta$ and the resulting linear equation has the familiar solution

$$\theta(t) = \frac{1}{\omega}\left(\frac{d\theta}{dt}\right)_0 \sin\omega t + \theta_0 \cos\omega t$$

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 v_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

$$\psi = \exp\left[\tfrac{1}{4}A^2 - \tfrac{1}{2}(x - A\cos 2\pi v_0 t)^2\right]\cos\left[\pi v_0 t + (A\sin 2\pi v_0 t)\left(x - \tfrac{1}{2}A\cos 2\pi v_0 t\right)\right]. \tag{7.10}$$

The first exponential factor represents a relatively tall and narrow hump, with the form of a Gaussian error curve at position

$$x = A\cos 2\pi v_0 t. \tag{7.11}$$

According to (7.11) this narrow hump behaves like a particle of mass m in linear oscillation, and with energy

$$2\pi^2 a^2 v_0^2 m = \tfrac{1}{2}A^2 hv$$

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

$$u(x, t) = 2\kappa^2 \operatorname{sech}^2 \kappa (x - ct + \delta)$$

---

[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
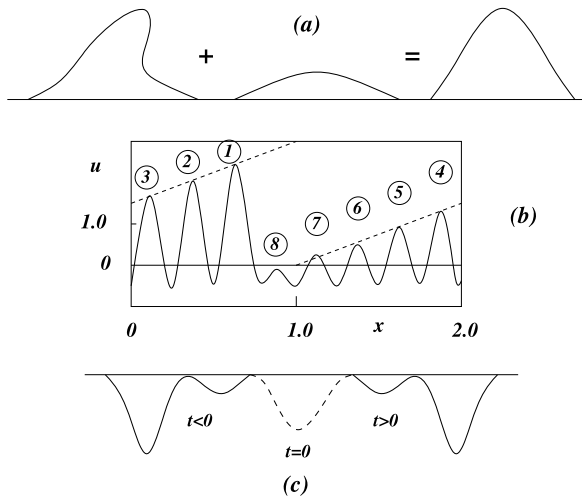
with arbitrary δ and $c = 4\kappa^2$, describing a hump-like shape as described by Scott Russell and moving at constant velocity without change in shape. As the velocity is amplitude dependent it follows that a taller wave moves faster than a small one.

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
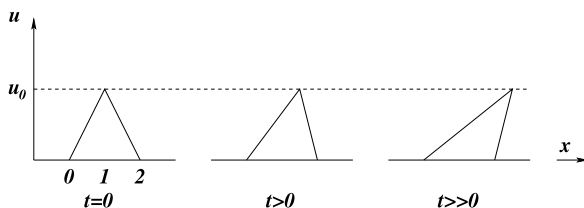
is dispersive, with $\omega = k - k^3$. It is the u_{xxx} term that introduces dispersive effects into the dispersionless equation: $u_t + u_x = 0$. To model the effect of a nonlinear term we next consider the equation

$$u_t + (u + 1)u_x = 0.$$

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,

$$u(x, 0) = -p(p + 1)\operatorname{sech}^2 x, \quad p > 0,$$

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]
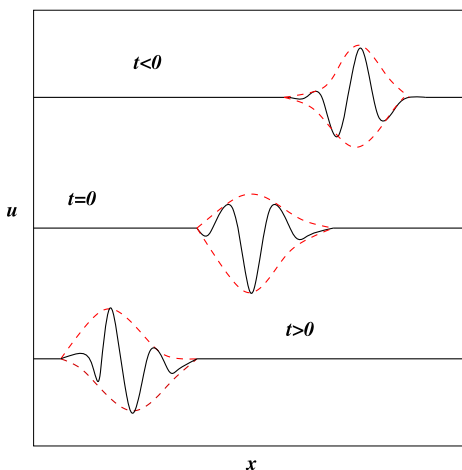
with the single-soliton solution

$$u(x, t) = \pm 2k \operatorname{sech}(2kx - 8k^3 t).$$

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:

$$i F_t + F_{xx} + 2|F|^2 F = 0.$$

This equation is of the same form as Schrödinger's equation

$$i \hbar \psi_t + (\hbar^2/2m) \psi_{xx} - V \psi = 0$$

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]

$$i \hbar \frac{\partial \Psi}{\partial t} = -\left(\frac{\hbar^2}{2m} \right) \nabla^2 \Psi - \epsilon^2 (\Psi^* \Psi) \Psi, \tag{7.13}$$

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]:

$$i\frac{\partial E}{\partial t} + \frac{\partial^2 E}{\partial x^2} + |E|^2 E = 0$$

to describe a soliton that moves through an optical fibre. It should describe a conduction electron equally well.

The linear Klein–Gordon equation

$$\frac{\partial^2 u}{\partial t^2} - c^2 \frac{\partial^2 u}{\partial x^2} + m^2 u = 0, \quad m = m_0 c^2 / \hbar$$

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*.
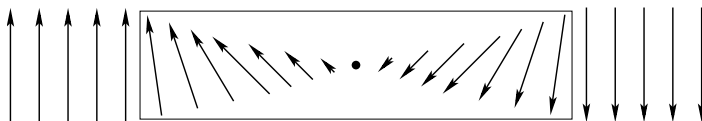
Fig. 7.6 Bloch wall

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

$$F_K = K \sin^2 \theta, \quad \text{where } K \text{ measures energy per unit volume.}$$

---

[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 $x' = Lx + a$, where a is an arbitrary translation vector of the origin and L is the orthogonal matrix of the homogeneous Lorentz transformation $x' = Lx$ (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 $\pm\pi$ 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 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-
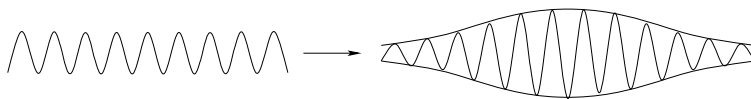
Fig. 7.7   KdV elastic modulation of a sinusoidal wave

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

$$\nabla^2 \phi - (1/c^2)(\partial\phi^2)(\partial t^2) = (1/2)\sin 2\phi$$

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 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 consid-

ered 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 $\varepsilon = 3\alpha d^2$, $\xi = x - c_0 t$, $\tau = \tfrac{1}{2}\varepsilon c_0 t$, $\mu = 1/36\alpha$, $v = \partial y/\partial \xi$:

$$\frac{\partial v}{\partial \tau} + v^2 \frac{\partial v}{\partial \xi} + \mu \frac{\partial^3 v}{\partial \xi^3} = 0,$$

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 $V_q = -\frac{\hbar^2 \nabla^2 R}{2m R}$, 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, $V_q \to 0$ 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 ($m \to 0$) 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

$$\int_{-\infty}^{\infty} \big|\Psi(x,t)\big| dx < \infty$$

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

$$\Psi(x,t) = F(\eta_1, \epsilon) \cdot \exp\big[f_1(x - \bar{x}_0), \eta_1\big] \cdot \mathrm{sech}\big[f_2(x - x_0), \eta_1\big]$$

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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