1

Quantum Mechanics

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1.1
Introduction

Quantum mechanics (QM), also called *wave mechanics*, is the modern theory of matter, of atoms, molecules, solids, and of the interaction of electromagnetic fields with matter. It supersedes the classical mechanics embodied in Newton's laws and contains them as a limiting case (the so-called classical limit of QM). Its development was stimulated in the early part of the twentieth century by the failure of classical mechanics and classical electrodynamics to explain important discoveries, such as the photoelectric effect, the spectral density of blackbody radiation, and the electromagnetic absorption and emission spectra of atoms. QM has proven to be an extremely successful theory, tested and confirmed to an outstanding degree of accuracy for physical systems ranging in size from subatomic particles to macroscopic samples of matter, such as superconductors and superfluids. Despite its undisputed success in the description of physical phenomena, QM has continued to raise many conceptual and philosophical questions, in part due to its counterintuitive character, defying common-sense interpretation.

One distinguishes between nonrelativistic quantum mechanics and relativistic quantum mechanics depending on the characteristic speed v of the constituents of the system under study. The domain of nonrelativistic QM is characterized by speeds that are small compared with the speed of light:

$$v \ll c \tag{1}$$

where $c = 3 \times 10^8 \, \text{m s}^{-1}$ is the speed of light. For v approaching c, relativistic extensions are necessary. They are referred to as *relativistic wave equations.* Because of the possibility of production and destruction of particles by conversion of relativistic energy E into mass M (or vice versa) according to the relation (*see* chapter 2)

$$E = Mc^2 \tag{2}$$

a satisfactory formulation of relativistic quantum mechanics can only be developed within the framework of quantum field theory. This chapter focuses primarily on nonrelativistic quantum mechanics, its formalism and techniques as well as applications to atomic, molecular, optical, and condensed-matter physics. A brief discussion of extensions to relativistic wave equations is given at the end of the chapter.

The new "quantum world" will be contrasted with the old world of classical mechanics. The bridge between the latter and the former is provided by the

semiclassical mechanics, whose rigorous formulation and application have only recently been developed.

1.2
Particle-Wave Duality and the Uncertainty Principle

The starting point of modern quantum mechanics is the hypothesis of the particle-wave duality put forward by de Broglie (1924): the motion of each particle of mass M is associated with a wave ("matter wave") of wavelength

$$\lambda = \frac{h}{p} \tag{3a}$$

where $h = 6.63 \times 10^{-34}$ J s is Planck's constant, discovered by M. Planck in 1900 in his investigation of blackbody radiation, and $p = Mv$ is the classical momentum of the particle. Similarly, the frequency v of the wave is associated with the mechanical energy of the particle through the expression

$$v = \frac{E}{h} \tag{3b}$$

These relations, ascribing wave properties to particles, are the logical complements to postulates put forward 20 years earlier by Einstein (1905), assigning the characteristics of particles ("photons," particles of zero rest mass) to electromagnetic radiation. In fact, Einstein employed, in his explanation of the "photoelectric effect," the expression $E = hv$ (Eq. 3b) to find the energy E of each photon associated with electromagnetic radiation of frequency v. Photons can eject electrons from the atoms of a material provided that the energy exceeds the binding energy of the electron. This particle-wave duality of QM unifies the description of distinct entities of classical physics: mechanics and electromagnetism. Particles, the fundamental constituents of matter, possess, in addition to mechanical properties such as momentum and angular momentum, wave character. Conversely, electromagnetic radiation, successfully described by Maxwell's theory of electromagnetic waves, takes on, under appropriate conditions, the property of quasiparticles, the photons, carrying mechanical energy and momentum. The particle and wave character are complementary to each other. An object behaves either like a particle or like a wave.

The hypothesis of particle-wave duality has been experimentally verified in remarkable detail. Interference of matter waves due to the indistinguishability of paths was demonstrated first for electrons (Davisson and Germer, 1927), later for neutrons, and, most recently, for neutral atoms. The particle-wave duality of electromagnetic radiation and its complementarity have been explored through modern versions of Young's double-slit experiment using state-of-the-art laser technology and fast switches. Hellmuth and colleagues (1987) succeeded, for example, in switching from particle to wave character and vice versa even after the photon has passed through the slit (in the experiment, a beam splitter) by activating a switch (a Pockels cell) in one of the two optical paths of the interferometer. By use of the switch, the interference patterns are made to appear or disappear, as expected for a wavelike or particlelike behavior of the photon, respectively. This "delayed choice" experiment not only demonstrates the particle-wave duality for photons but also elucidates important conceptual aspects of the nonlocality of quantum mechanics. The decision as to whether the photon will behave like a particle or a wave need not be

made at the double slit itself but can be spatially separated and temporarily postponed.

The consequences of the wave-particle duality for the description of physical phenomena are far reaching and multifaceted. One immediate consequence that represents the most radical departure from classical physics is the *uncertainty principle* (Heisenberg, 1927). One deeply rooted notion of classical physics is that all dynamical observables can be measured, at least in principle, with arbitrary accuracy. Uncertainties in the measurement are a matter of experimental imperfection that, in principle, can be overcome. The wave nature of particles in QM imposes, however, fundamental limitations on the simultaneous accuracy of measurements of dynamical variables that cannot be overcome, no matter how much the measurement process can be improved. This uncertainty principle is an immediate consequence of the wave behavior of matter. Consider a wave of the form

$$\psi(x) = Ae^{i(kx-\omega t)} \tag{4}$$

traveling along the x coordinate (Figure 1.1). Equation (4) is called a *plane wave* because the wave fronts form planes perpendicular to the direction of propagation. The physical interpretation of the amplitude A was provided by Born (1926) in terms of a probability density

$$P(x) = |\psi(x)|^2 = |A|^2 \tag{5}$$

for finding the particle at the coordinate x. The matter wave (Eq. 4) is further characterized by the wave number $k = 2\pi/\lambda = p/\hbar$ and the angular frequency $\omega = 2\pi\nu = E/\hbar$. The "rationalized" Planck's constant $\hbar = h/2\pi = 1.05 \times 10^{-34}$ J s is frequently used in QM.

The uncertainty principle is inherent to all wave phenomena. Piano tuners have exploited it for centuries. They sound a vibrating tuning fork of standard frequency in unison with a piano note of the same nominal frequency and listen to a beat tone between the struck tune and the tuning fork. For a fork frequency of $\nu = 440$ Hz and a string frequency of $\nu' = 441$ Hz, one beat tone will be heard per second ($\delta\nu = \nu' - \nu = 1$ Hz). The goal of the tuner is to reduce the number of beats as much as possible. To achieve an accuracy of $\delta\nu = 0.010.01$ Hz, the tuner has to wait for at least about $\delta t = 100$ s (in fact, only a fraction of this time since the frequency mismatch can be detected prior to completion of one beat period) to be sure no beat had
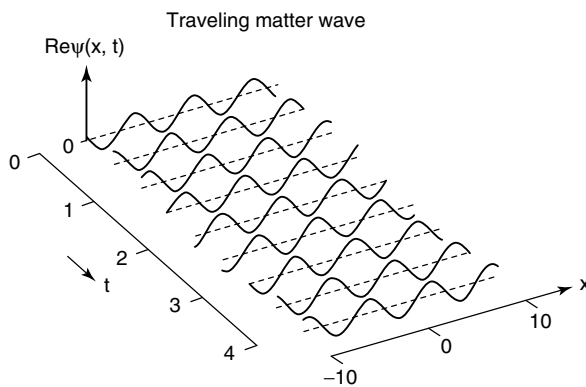

Traveling matter wave

Fig. 1.1 Matter wave traveling along the *x* direction; the figure shows the real part of $\psi(x)$, Eq. (4) (after Brandt and Dahmen, 1989).

occurred. Piano tuning therefore relies on the frequency–time uncertainty

$$\Delta \nu \, \Delta t \gtrsim 1 \qquad (6)$$

Measurement of the frequency with infinite accuracy ($\Delta \nu \to 0$) requires an infinite time period of measurement ($\Delta t \to \infty$), or equivalently, it is impossible within any finite period of time to determine the frequency of the string exactly since time and frequency are *complementary variables*. Similarly, the variables characterizing the matter wave (Eq. 4) are complementary:

$$\Delta k \, \Delta x \geq 1$$
$$\Delta \omega \, \Delta t \geq 1 \qquad (7)$$

These relations, well known from classical theory of waves and vibrations, have unexpected and profound consequences when combined with the de Broglie hypothesis (Eq. 3) for quantum objects:

$$\Delta p \, \Delta x \geq \hbar$$
$$\Delta E \, \Delta t \geq \hbar \qquad (8)$$

The momentum and the position of a particle, its energy and the time, and more generally, any other pair of complementary variables, such as angular momentum and angle, are no longer simultaneously measurable with infinite precision. The challenge to the classical laws of physics becomes obvious when one contemplates the fact that Newton's equation of motion uses the simultaneous knowledge of the position and of the change of momentum.

Since $\hbar$ is extremely small, the uncertainty principle went unnoticed during the era of classical physics for hundreds of years and is of little consequence for everyday life. Its far-reaching

implications become obvious only in the microscopic world of atoms, molecules, electrons, nuclei, and elementary particles. More generally, whenever the size of an object or mean distance between constituents becomes comparable to the de Broglie wavelength λ, the wave nature of matter comes into play. The size of λ also provides the key for quantum effects in macroscopic systems such as superfluids, superconductors, and solids.

1.3
Schrödinger Equation

The Schrödinger equation for matter waves ψ describes the dynamics of quantum particles. In the realm of quantum physics, it plays a role of similar importance to that which Newton's equation of motion does for classical particles. As with Newton's laws, the Schrödinger equation cannot be rigorously derived from some underlying, more fundamental principles. Its form can be made plausible, however, by combining the Hamiltonian function of classical mechanics,

$$H = T + V = E \qquad (9)$$

which equals the mechanical energy, with the de Broglie hypothesis of matter waves (Eq. 4). The potential energy is denoted by V and the kinetic energy by $T = p^2/2M$. Formally multiplying the wave function $\psi(x,t)$ by Eq. (9) yields

$$H\psi(x, t) = \frac{p^2}{2M}\psi(x, t) + V\psi(x, t) \qquad (10)$$

In order to connect the de Broglie relations for energy and momentum appearing in the arguments of the plane wave (Eq. 4) with the energy and momentum in the

Hamiltonian function, H and p in Eq. (10) must be taken as differential operators,

$$H \longleftrightarrow i\hbar \frac{\partial}{\partial t}$$
$$p \longleftrightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} \tag{11}$$

This substitution into Eq. (10) leads to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = H\psi(x, t)$$
$$= \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + V(x) \right)$$
$$\times \psi(x, t) \tag{12}$$

which describes the time evolution of the matter wave. For physical systems that are not explicitly time dependent, i.e., that have time-independent potentials $V(x)$, the energy is conserved and $i\hbar \, \partial/\partial t$ can be replaced by E, giving the time-independent Schrödinger equation

$$E\psi(x) = \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) \tag{13}$$

If no interaction potential is present ($V(x) = 0$), Eq. (12) is referred to as the *free-particle Schrödinger equation*. The plane waves of Eq. (4) are solutions of the free-particle Schrödinger equation with eigenenergies $E = (\hbar k)^2/2M$.

The *correspondence principle*, first formulated by Bohr, provides a guide to quantizing a mechanical system. It states that in the limit of large quantum numbers or small de Broglie wavelength, the quantum-mechanical result should be the same, or nearly the same, as the classical result. One consequence of this postulate is that the quantum-mechanical Hamiltonian operator in the Schrödinger equation (Eq. 12) should be derived from its corresponding classical analog, the

classical Hamiltonian function (Eq. 9), through the replacement of the classical observable by the operator equivalents (Eq. 11).

The replacement of dynamical variables by differential operators leads to the *noncommutativity* of pairs of conjugate variables in QM, for example,

$$[x, p_x] \equiv x\frac{\hbar}{i} \frac{\partial}{\partial x} - \frac{\hbar}{i} \frac{\partial}{\partial x} x = i\hbar \tag{14}$$

with similar relations for other complementary pairs, such as Cartesian coordinates of position and momentum (y, p_y), (z, p_z), or energy and time. It is the noncommutativity that provides the basis for a formal proof of the uncertainty principle, Eq. (8). The Schrödinger equation (Eqs. 12 and 13) is a linear, homogeneous, and (in general) partial differential equation. One consequence of this fact is that matter waves ψ satisfy the *superposition principle*. If ψ_1 and ψ_2 are two acceptable solutions of the Schrödinger equation, called *states*, a linear combination

$$\psi = c_1\psi_1 + c_2\psi_2 \tag{15}$$

is an acceptable solution, as well. The physical implication of Eq. (15) is that the quantum particle can be in a ''coherent superposition of states'' or ''coherent state,'' a fact that leads to many strange features of QM, such as destructive and constructive interference, the collapse of the wave function, and the revival of wave packets.

A solution of a linear, homogeneous differential equation is determined only up to an overall amplitude factor, which is arbitrary. The probability interpretation of the matter wave (Eq. 5), however, removes this arbitrariness. The probability for finding the particle somewhere

is unity,

$$\int dx P(x) = \int dx |\psi(x)|^2 = 1 \qquad (16)$$

Equation (16) and its generalization to three dimensions are referred to as the *normalization condition* on the wave function and eliminate the arbitrariness of the modulus of the wave function. A wave function that can be normalized according to Eq. (16) is called *square integrable*. The only arbitrariness remaining is the overall "phase factor" of the wave function, $e^{i\phi}$, i.e., a complex number of modulus 1.

1.4
Boundary Conditions and Quantization

In order to constitute a physically acceptable solution of the Schrödinger equation, i.e., to represent a state, ψ must satisfy appropriate boundary conditions. While their detailed forms depend on the coordinates and symmetry of the problem at hand, their choice is always dictated by the requirement that the wave function be normalizable and unique and that physical observables take on only real values (more precisely, real expectation values) despite the fact that the wave function itself can be complex. Take, as an example, the Schrödinger equation for a rotator with a moment of inertia I, constrained to rotate about the z axis. The classical Hamiltonian function $H = L_z^2/2I$, with L_z the z component of the angular momentum,

$$L_z = xp_y - yp_x = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \qquad (17)$$

gives rise, according to the correspondence principle, to the following time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2I}\frac{\partial}{\partial\phi^2}\psi(\phi) = E\psi(\phi) \qquad (18)$$

where ϕ is the angle of rotation about the z axis. Among all solutions of the form

$$\psi(\phi) = Ae^{i(m\phi+\phi_0)} \qquad (19)$$

only those satisfying the periodic boundary conditions

$$\psi(\phi + 2\pi) = \psi(\phi) \qquad (20)$$

are admissible in order to yield a uniquely defined single-valued function $\psi(\phi)$. (The implicit assumption is that the rotator is spinless, as discussed below.) The magnetic quantum number m therefore takes only integer values $m = -\infty, \ldots, -1, 0, 1, \ldots \infty$. Accordingly, the z component of the angular momentum

$$L_z\psi(\phi) = m\hbar\psi(\phi) \qquad (21)$$

takes on only discrete values of multiples of the rationalized Planck's constant $\hbar$. The real number on the right-hand side that results from the operation of a differential operator on the wave function is called the *eigenvalue* of the operator. The wave functions satisfying equations that are of the form of Eqs (18) or (21) are called *eigenfunctions*. The eigenvalues and eigenfunctions contain all relevant information about the physical system; in particular, the eigenvalues represent the measurable quantities of the systems.

The amplitude of the eigenfunction follows from the normalization condition

$$\int_0^{2\pi} d\phi |\psi(\phi)|^2 = 1 \qquad (22)$$

as $A = (2\pi)^{-1/2}$. The eigenvalues of E in Eq. (18) are $E_m = \hbar^2 m^2 / 2I$. Just like for a vibrating string, it is the imposition of boundary conditions (in this case, periodic boundary conditions) that leads to "quantization," that is, the selection of an infinite but discrete set of modes of matter waves, the eigenstates of matter, each of which is characterized by certain quantum numbers.

Different eigenstates may have the same energy eigenvalues. One speaks then of *degeneracy*. In the present case, eigenstates with positive and negative quantum numbers $\pm m$ of L_z are degenerate since the Hamiltonian depends only on the square of L_z. Degeneracies reflect the underlying symmetries of the Hamiltonian physical system. Reflection of coordinates at the x–z plane, ($y \rightarrow -y$, $p_y \rightarrow -p_y$ and therefore $L_z \rightarrow -L_z$) is a symmetry operation, i.e., it leaves the Hamiltonian invariant. In more general cases, the underlying symmetry may be dynamical rather than geometric in origin.

1.5
Angular Momentum in Quantum Mechanics

The quantization of the projection of the angular momentum, L_z, is called *directional quantization*. The Hamiltonian function for the interaction of an atom having a magnetic moment $\boldsymbol{\mu} = \gamma \mathbf{L}$ with an external magnetic field $\mathbf{B}$ reads

$$H = -\boldsymbol{\mu} \cdot \mathbf{B} = -\gamma \mathbf{L} \cdot \mathbf{B} \qquad (23)$$

The proportionality constant γ between the magnetic moment and the angular momentum is called the *gyromagnetic ratio*. According to the correspondence principle, the Schrödinger equation for the magnetic moment in a field with field lines oriented along the z axis becomes

$$-\gamma B L_z \psi(\phi) = E_m \psi(\phi) \qquad (24)$$

The eigenenergies

$$E_m = -\gamma B \hbar m \qquad (25)$$

are quantized and depend linearly on the magnetic quantum number. Depending on the sign of γ, states with positive m for $\gamma > 0$, or negative m for $\gamma < 0$, correspond to states of lower energy and are preferentially occupied when the atomic magnetic moment is in thermal equilibrium. This leads to an alignment of the magnetic moments of the atoms along one particular direction and to paramagnetism of matter when its constituents carry a net magnetic moment.

The force an atom experiences as it passes through an inhomogeneous magnetic field depends on the gradient of the magnetic field, ∇B. Because of the directional quantization of the angular momentum, a beam of particles passing through an inhomogeneous magnetic field will be deflected into a set of discrete directions determined by the quantum number m. A deflection pattern consisting of a few spots rather than a continuous distribution of a beam of silver atoms was observed by Stern and Gerlach (1921, 1922) and provided the first direct evidence of directional quantization.

In addition to the projection of the angular momentum along one particular axis, for example, the z axis, the total angular momentum $\mathbf{L}$ plays an important role in QM. Here, one encounters a conceptual difficulty, the noncommutativity of different angular momentum components.

Application of Eq. (14) leads to

$$\left[L_x, L_y\right] = i\hbar L_z, \quad \left[L_y, L_z\right] = i\hbar L_x$$
$$\left[L_z, L_x\right] = i\hbar L_y \qquad (26)$$

As noncommutativity is the formal expression of the uncertainty principle, the implication of Eq. (26) is that different components of the angular momentum cannot be simultaneously determined with arbitrary accuracy. The maximum number of independent quantities formed by components of the angular momentum that have simultaneously ''sharply'' defined eigenvalues is two. Specifically,

$$[L^2, L_z] = 0 \qquad (27)$$

with $L^2 = L_x^2 + L_y^2 + L_z^2$ being the square of the total angular momentum. Therefore, one projection of the angular momentum vector (conventionally, one chooses the z projection) and the L^2 operator can have simultaneously well-defined eigenvalues, unaffected by the uncertainty principle. The differential operator of L^2 in spherical coordinates gives rise to the following eigenvalue equation:

$$L^2 Y(\theta, \phi) = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) \right.$$
$$\left. + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y(\theta, \phi)$$
$$= \hbar^2 l(l + 1) Y(\theta, \phi) \qquad (28)$$

The solutions of Eq. (28), $Y_l^m(\theta, \psi)$, are called *spherical harmonics*. The superscript denotes the magnetic quantum number of the z component, as above, while the quantum number $l = 0, 1, \ldots \infty$ is called the *angular momentum quantum number*. Since $|L_z| \leq |L|$, we have the restriction $|m| \leq l$, that is, for given angular momentum quantum number l, the z component varies between $-l$ and l: $m =$ $-l, \ldots, -1, 0, 1, \ldots l$. The total number of quantized projections of L_z is $2l + 1$. The eigenvalue of the L^2 operator is, however, $\hbar^2 l(l + 1)$ and not $\hbar^2 l^2$. The latter can be understood in terms of the uncertainty principle and can be illustrated with the help of a vector model (Figure 1.2). Because of the uncertainty principle, the projections L_y and L_x do not take a well-defined value and cannot be made to be exactly zero, when L_z possesses a well-defined quantum number. Therefore, the z projection $m\hbar$ will always be smaller than the magnitude of $L = \hbar\sqrt{l(l + 1)}$ in order to accommodate the nonzero fluctuations in the remaining components.

The spherical harmonics are given in terms of associated Legendre functions $P_l^m(\cos\theta)$ by

$$Y_l^m(\theta, \phi) = (-1)^m \left[\frac{(2l + 1)}{4\pi} \frac{(l - m)!}{(l + m)!} \right]^{1/2}$$
$$\times P_l^m(\cos\theta) e^{im\phi} \qquad (29)$$

The eigenfunctions of L_z (Eq. 19) can be recognized as one factor in the expression for Y_l^m. The probability densities $|Y_l^m|^2$ of the first few eigenfunctions are represented by the polar plots in Figure 1.3.

In addition to the orbital angular momentum operator **L**, which is the quantum-mechanical counterpart to the classical angular momentum, another type of angular momentum, the spin angular momentum, plays an important role for which, however, no classical analog exists. The spin is referred to as an *internal degree of freedom*. The Stern–Gerlach experiment discussed above provided the major clue for the existence of the electron spin (Goudsmit and Uhlenbeck, 1925). The orbital angular momentum quantization allows only for an odd number of discrete values of L_z ($2l + 1 = 1, 3, 5, \ldots$) and therefore an odd number of spots in
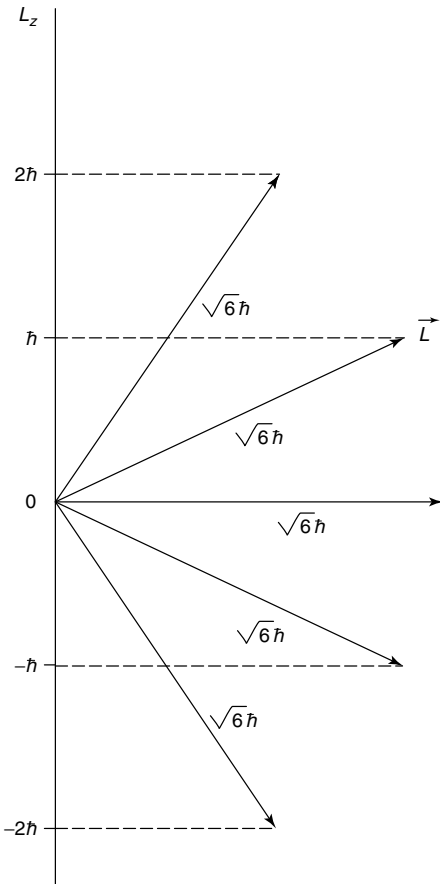
Fig. 1.2 Vector model of angular momentum **L** for quantum number $l = 2$ and $|\mathbf{L}| = \sqrt{6}\,\hbar$.

the deflection pattern. Stern and Gerlach observed, however, two discrete directions of deflection (see schematic illustration in Figure 1.14). The spin hypothesis solved this mystery. The outermost electron of a silver atom has a total orbital angular momentum of zero but has a spin angular momentum of $s = \frac{1}{2}$. The number of different projections of the spin is therefore $2s + 1 = 2$ in accordance with the number of components into which the beam was magnetically split. Within nonrelativistic quantum mechanics, the spin must be introduced as an additional degree of freedom on empirical grounds. A conceptually satisfactory description is provided

by relativistic quantum mechanics (see Section 1.11). The identification of the spin as an angular momentum rests on the validity of the commutation rules (Eq. 26),

$$\left[S_x, S_y\right] = i\hbar S_z, \quad \left[S_y, S_z\right] = i\hbar S_x,$$
$$\left[S_z, S_x\right] = i\hbar S_y \tag{30}$$

identical to those of the orbital angular momentum. Any set of the components of a vector operator satisfying Eq. (26) has a spectrum of eigenvalues (quantum numbers) of an angular momentum with quantum numbers $j = 0, \frac{1}{2}, 1, \ldots$ and $m = -j, -j + 1 \ldots, +j$. The quantum number j is an integer in systems with an even
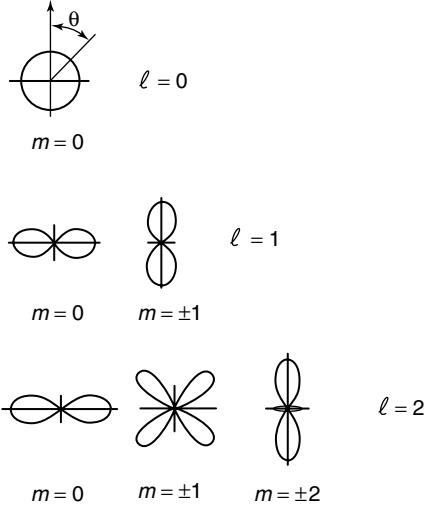
Fig. 1.3 Polar plots of the probability distributions $|Y_l^m(\theta, \phi)|^2$ of angular momentum eigenfunctions.

number of spin $\frac{1}{2}$ particles (including zero) and half-integer in systems with an odd number of spin $\frac{1}{2}$ particles. The Hamiltonian for the interaction of an electron spin with an external magnetic field is given in direct analogy to Eq. (23) by

$$H = -\gamma g \mathbf{S} \cdot \mathbf{B} \qquad (31)$$

The only difference is the "anomalous" gyromagnetic ratio represented by the factor g. An approximate value of g can be deduced from the relativistic wave equation (Dirac's equation) for the electron (see Section 1.11).

1.6
Formalism of Quantum Mechanics

The quantum-mechanical description outlined in the previous section with the help of specific examples can be expanded to a general formalism of quantum mechanics. The starting point is the identification of wave functions with vectors in an infinite-dimensional vector space, the Hilbert space,

$$\psi \longrightarrow |\psi\rangle \qquad (32)$$

with the vectors represented by a "ket." The ket notation was first introduced by Dirac (1930). The coherent superposition illustrated by Eq. (15) can be recognized as vector addition in Hilbert space. Physical observables such as the Hamiltonian or the angular momentum can be represented by linear and Hermitian operators. Linearity of an operator B means

$$B(c_1|\psi_1\rangle + c_2|\psi_2\rangle) = c_1 B|\psi_1\rangle + c_2 B|\psi_2\rangle \qquad (33)$$

for all complex numbers c_1, c_2 and all vectors $|\psi_1\rangle$, $|\psi_2\rangle$. Hermitian operators are defined as those for which

$$B^\dagger = B \qquad (34)$$

that is, the operator is equal to its Hermitian adjoint. The Hermiticity assures that the eigenvalue equation

$$B|\psi\rangle = \lambda|\psi\rangle \qquad (35)$$

possesses real eigenvalues λ, which can be identified with measurable quantities. The time-independent Schrödinger equation, Eq. (13), is of the form in Eq. (35) with B being the Hamiltonian operator H and λ being the eigenenergy E. The result of a measurement of a physical observable yields an eigenvalue λ of the corresponding operator, B.

The noncommutativity of operators (Eq. 14) corresponds to the well-known noncommutativity of matrices in linear algebra. The overlap of wave functions can be identified with the scalar product in Hilbert space:

$$\langle \phi | \psi \rangle \equiv \int d^3 r \; \phi^*(\mathbf{r}) \psi(\mathbf{r}) \tag{36}$$

The adjoint of a vector in Hilbert space $\langle \psi |$ is called a *bra* and the scalar product a *bracket* (Dirac, 1930). The normalization requirement imposed on the wave function can be expressed in terms of the scalar product as $\langle \psi | \psi \rangle = 1$. The requirement of normalizability (Eq. 22) implies that the Hilbert space is spanned by square-integrable functions. Since eigenstates of Hermitian operators belonging to different eigenvalues are orthogonal to each other, each physical dynamical variable possesses a complete orthonormal set of eigenstates:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \tag{37}$$

The operator B is a diagonal matrix in a basis consisting of its eigenstates, the "eigenbasis" $|\psi_i\rangle$ with $i = 1, \ldots, \infty$. In its eigenbasis, the operator B possesses the following "spectral representation":

$$B = \sum_i \lambda_i |\psi_i\rangle\langle\psi_i| \tag{38}$$

containing only its eigenstates $\{\psi_i\}$ and its eigenvalues λ_i. Two operators possess the same eigenbasis when they commute with each other. Physical observables whose operators commute with each other are called *compatible observables*. A state of a physical system is therefore specified to the maximum extent possible, consistent with the uncertainty principle, by one common eigenstate of a maximum set of compatible observables. For example, the set $\{L^2, L_z\}$ is the maximum set of compatible observables for the angular momentum with the common eigenstate $|lm\rangle$.

The probability amplitude for finding the system in a particular state $|\psi_1\rangle$ is given by the projection of the state vector onto this state, i.e., by the scalar product $\langle \psi_1 | \psi \rangle$. The corresponding probability is

$$P(\psi_1) = |\langle \psi_1 | \psi \rangle|^2 \tag{39}$$

Formally, Eq. (39) can be viewed as the expectation value of the projection operator $\overline{P} = |\psi_1\rangle\langle\psi_1|$ in the state $|\psi\rangle$. The process of a measurement is therefore associated with a projection in Hilbert space. This projection is sometimes referred to as the *collapse of the wave function*. The process of measurement thus influences the quantum system to be measured.

The state of a physical system is often not completely specified by a "pure" state described by a single Dirac ket $|\psi\rangle$ or a coherent superposition of kets $\sim c_1 |\psi_1\rangle + c_2 |\psi_2\rangle$. The limited information available may only allow us to specify a statistical mixture of states. Such a mixture is described by the statistical operator or density operator

$$\rho = \sum_i P_i |\psi_i\rangle\langle\psi_i| \tag{40}$$

with P_i denoting the probability for the system to be found in a particular state $|\psi_i\rangle$. The result of the measurement of an observable B is then given by the statistical expectation value

$$\langle B \rangle = \text{Tr}(\rho B) = \sum_i \langle \psi_i | B | \psi_i \rangle P_i \qquad (41)$$

i.e., by the diagonal elements of the operator B, each weighted with the probability to find the system in the corresponding state. The preferred set of states, $|\psi_i\rangle$, for which the density matrix is "diagonal," that is, of the form in Eq. (40), is sometimes referred to as the *set of pointer states*.

In light of the expression for the probability as a projection, Eq. (39), we can rewrite Eq. (5) as

$$P(\mathbf{r}) = |\psi(\mathbf{r})|^2 = |\langle \mathbf{r} | \psi \rangle|^2 \qquad (42)$$

where $|\mathbf{r}\rangle$ is formally treated as a vector ("ket") in Hilbert space. This definition leads to the difficulty that $|\mathbf{r}\rangle$ cannot be defined as a square-integrable function. Nevertheless, it can be consistently incorporated into the formalism by employing the concept of generalized functions ("distributions"; see Lighthill, 1958; Schwartz, 1965). One defines a scalar product through

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}')$$
$$= \delta(x - x')\delta(y - y')\delta(z - z') \qquad (43)$$

where the right-hand side is called *Dirac's δ function*. The δ function is zero almost everywhere:

$$\delta(x) = \begin{cases} 0, & x \neq 0 \\ \infty, & x = 0 \end{cases} \qquad (44)$$

with the strength of the singularity such that the area underneath the peak is

$$\int dx \delta(x) = 1 \qquad (45)$$

While the δ function is not an ordinary (Riemann integrable) function, it can be approximated as a limit of Riemann integrable functions, for example,

$$\lim_{\varepsilon \to 0} \frac{1}{\pi} \frac{\varepsilon}{x^2 + \varepsilon^2} = \delta(x) \qquad (46)$$

Equation (46) satisfies Eq. (45) provided one evaluates the integral first and takes the limit $\varepsilon \to 0$ afterward. As the order of the operations of integration and taking the limit is not interchangeable, Eq. (46) is said to converge "weakly" toward a δ function in the limit $\varepsilon \to 0$. δ functions play an important role in the quantum theory of scattering.

The time evolution of the Hilbert-space vectors is given by Schrödinger's equation written in Dirac's ket notation:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = H|\psi\rangle \qquad (47)$$

For systems with a classical analog, the Hamiltonian operator is given, according to the correspondence principle, by the classical Hamiltonian function $H(\mathbf{r}, \mathbf{p})$ upon treating the canonical variables $(\mathbf{r}, \mathbf{p})$ as noncommuting operators (see Eq. 14). There are, however, additional dynamical variables in quantum mechanics, such as spin, for which no classical counterparts exist.

A vector in Hilbert space can be expanded in terms of any basis (a "representation"),

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle = \sum_i \langle \phi_i | \psi \rangle |\phi_i\rangle \qquad (48)$$

where $c_i = \langle \phi_i | \psi \rangle$ are the expansion coefficients of the ket $|\psi\rangle$ in the basis

$\{|\phi_i\rangle\}$. Switching from one representation to another $|\psi\rangle \to |\psi'\rangle = U|\psi\rangle$ amounts to a unitary transformation, U, since the norm of a state vector must be conserved,

$$\langle\psi'|\psi'\rangle = \langle\psi|U^\dagger U|\psi\rangle$$
$$= \langle\psi|\psi\rangle \tag{49}$$

or $U^\dagger U = 1$. Transformations among representations play an important role in QM. While the maximum number of compatible observables is determined by commutation rules, the choice of observables that are taken to be diagonal or to have "good" quantum numbers depends on the specific problem under consideration. Unitary transformations provide the tool to switch from a basis within which one set of observables is diagonal to another. The transformation law for state vectors $|\psi'\rangle = U|\psi\rangle$ implies the transformation law for operators

$$A' = UAU^\dagger \tag{50}$$

The latter follows from the invariance of the expectation value $\langle\psi'|A'|\psi'\rangle = \langle\psi|U^\dagger A'U|\psi\rangle$ under unitary transformations.

Classical Hamiltonian functions as well as quantum-mechanical Hamiltonian operators possess discrete symmetries. For example, the Hamiltonian function of the harmonic oscillator,

$$H(x,p) = \frac{p^2}{2M} + \frac{1}{2}M\omega^2 x^2 \tag{51}$$

is invariant under reflection of all spatial coordinates $(x \to -x,\ p \to -p)$ since H depends only on the square of each canonical variable. In classical mechanics, this symmetry is of little consequence since the solution of Newton's equation of motion depends on the initial conditions $x(t=t_0),\ p(t=t_0)$, which are not subject to any symmetry constraint. They may "break" the symmetry and usually do so. In quantum mechanics, however, the parity of a state vector becomes a dynamical observable.

We can define a parity operator $\hat{p}$ through

$$\hat{p}H(x,p)\hat{p}^\dagger = H(-x,-p) \tag{52}$$

Since $\hat{p}^2$ is the unit operator (two successive reflections restore the original function), we have $\hat{p} = \hat{p}^\dagger = \hat{p}^{-1}$. Eigenfunctions of $\hat{p}$, $\psi(x) = \langle x|\psi\rangle$, can now be characterized by their parity:

$$\langle x|\hat{p}|\psi\rangle = \langle -x|\psi\rangle = \pm\langle x|\psi\rangle \tag{53}$$

The $\pm$ sign in Eq. (53) is referred to as *indicating positive* or *negative parity*. A wave function cannot always be assigned a well-defined parity quantum number ± 1. However, when $\hat{p}$ commutes with H,

$$\hat{p}H(x,p)\hat{p} = H(x,p) \tag{54}$$

there exists a common eigenbasis in which both the Hamiltonian operator and the parity operator are diagonal and, consequently, ψ is an eigenstate of $\hat{p}$ with a well-defined parity. A similar argument can be developed for symmetry with respect to the time-reversal operator T: $t \to -t$, $\mathbf{p} \to -\mathbf{p}$, $\mathbf{r} \to \mathbf{r}$.

An additional discrete symmetry, which is of fundamental importance for the quantum mechanics of identical particles, is the permutation symmetry. Consider a wave function describing the state of two identical particles $\psi(\mathbf{r}_1, \mathbf{r}_2)$. The permutation operator $\hat{p}_{12}$ exchanges the two particles in the wave function:

$$\hat{p}_{12}\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1) \tag{55}$$

The spin-statistics postulate of quantum mechanics makes a general statement concerning the permutation symmetry. A many-body system consisting of identical particles of integer spin ("bosons") possesses wave functions that are even under all interchanges of two particles, whereas the wave function is odd for half-integer spin particles ("fermions"). The eigenvalue of $\hat{p}_{ij}$, the operator of permutation for any two particles of an N-body system, is $+1$ for bosons and -1 for fermions. Wave functions are totally symmetric under particle exchange for bosons and totally antisymmetric for fermions. An immediate consequence is that two fermions cannot be in identically the same state for which all quantum numbers agree (the so-called Pauli exclusion principle) since the antisymmetric wave function would vanish identically.

1.7
Solution of the Schrödinger Equation

1.7.1
Methods for Solving the Time-Dependent Schrödinger Equation

1.7.1.1 Time-Independent Hamiltonian
If the Hamilton operator is not explicitly time dependent, i.e., the total energy is conserved, the time-dependent Schrödinger equation can be reduced to the time-independent Schrödinger equation. Equation (47) can be formally solved by

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle \qquad (56)$$

where $U(t, t_0)$ is called the *time-evolution operator*, a unitary transformation describing the translation of the system in time. Substitution of Eq. (56) into Eq. (47) shows

that

$$U(t, t_0) = \exp\left[\frac{-iH(t - t_0)}{\hbar}\right] \qquad (57)$$

where the exponential function of the operator H is defined through its power-series expansion

$$U(t, t_0) = 1 - i\frac{t - t_0}{\hbar}H \\ -\frac{1}{2}\left(\frac{t - t_0}{\hbar}\right)^2 H \cdot H + \cdots \quad (58)$$

If one is able to solve the time-independent Schrödinger equation

$$H|\psi_n\rangle = E_n|\psi_n\rangle \qquad (59)$$

where n labels the eigenstate, one can calculate the time evolution of the eigenstate:

$$U(t, t_0)|\psi_n\rangle = e^{-iH(t-t_0)/\hbar}|\psi_n\rangle \\ = e^{-iE_n(t-t_0)/\hbar}|\psi_n\rangle \qquad (60)$$

using the definition in Eq. (58). The phase factor in Eq. (60) is called the *dynamical phase*. The explicit solution for an arbitrary state can then be found by expanding $|\psi(t_0)\rangle$ in terms of eigenstates of the Hamilton operator:

$$|\psi(t_0)\rangle = \sum_n |\psi_n\rangle\langle\psi_n|\psi(t_0)\rangle \\ |\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle \\ = \sum_n e^{-iE_n(t-t_0)/\hbar}|\psi_n\rangle \\ \times \langle\psi_n|\psi(t_0)\rangle \qquad (61)$$

Hence, for time-independent systems, the solution of the energy eigenvalue problem (Eq. 59) is sufficient to determine the time evolution for any initial state.

1.7.1.2 **Time-Dependent Hamiltonian**

For a time-dependent Hamiltonian $H(t)$, the solution of the time-evolution operator U in terms of the exponential function Eq. (57) must be redefined in order to take into account that the Hamiltonian operator at different instances of time may not commute, $[H(t), H(t')] \neq 0$. We have

$$
\begin{aligned}
U(t, t_0) &= 1 - \frac{i}{\hbar} \int_{t_0}^{t} dt' H(t') \\
&\quad - \frac{1}{\hbar^2} \int_{t_0}^{t} dt' H(t') \\
&\quad \times \int_{t_0}^{t'} dt'' H(t'') \cdots \\
&= T \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t} H(t') dt'\right)
\end{aligned}
\tag{62}
$$

Equation (62) is called the *time-ordered exponential function* and T is called the *time-ordering operator*. In two limiting cases, the evolution operator for time-dependent Hamiltonian systems can be easily calculated by reducing the problem to the time-independent Hamiltonian. One is the adiabatic limit. If the temporal changes in $H(t)$ are very slow compared with the changes in the dynamical phases of Eq. (60) for all t, the U matrix is diagonal in the slowly changing eigenbasis of $H(t)$ at each instant t,

$$
|\psi_n(t)\rangle = e^{i\gamma_n(t)} \exp\left[-\frac{i}{\hbar} \int_{t_0}^{t} dt' E_n(t')\right] |\phi_{n,t}\rangle
\tag{63}
$$

The dynamical phase factor is determined by $E_n(t')$, the energy eigenvalue of the stationary Schrödinger equation for the Hamiltonian operator $H(t')$ at time t'. In Eq. (63), the state $|\psi_n(t)\rangle$ denotes the evolved state and the state $|\phi_{n,t}\rangle$ represents the stationary eigenstate for the Hamiltonian $H = H(t)$ at the time t, where the time plays the role of a parameter.

The additional phase $\gamma_n(t)$ is called *Berry's phase* (Berry, 1984) or the *geometric phase*, since it records the information on the excursion of the Hamiltonian $H(t')$ in parameter space in the case of adiabatic evolution. The role of $\gamma_n(t)$ is to relate the phases of the adiabatic wave function $|\psi_n(t)\rangle$ at different points in time. Insertion of Eq. (63) into Schrödinger's equation yields the equation that defines the real phase function $\gamma_n(t)$,

$$
\dot{\gamma}_n(t) - i\left\langle \phi_{n,t} \left| \frac{d}{dt} \phi_{n,t} \right. \right\rangle = 0
\tag{64}
$$

The analogy to the parallel transport of vectors on a sphere (Figure 1.4) can give a glimpse of the concept underlying Berry's phase. Consider a quantum-mechanical state to be represented by a vector at point A. By infinitely slowly (adiabatically) varying an external parameter, for example, the direction of the magnetic field, one can "transport" state vectors successively from point A to B, then to C, and finally back to A. After completion of the closed loop, the vector does not coincide with its original orientation but is rotated by an angle γ that is proportional to the solid angle subtended by the loop. This angle gives rise to a geometric phase, $\exp(i\gamma)$, which depends on the geometry of a loop, but unlike the dynamical phase, Eq. (60), it is independent of the time it takes to complete the transport of the state along the closed loop. If one is now able to form in a physical system a coherent superposition of two states, one accumulating the geometric phase along the adiabatic change of the external field while the other is subject to a constant field, an interference pattern will arise. The Berry phase has been observed in interference experiments involving neutron spin rotation, in molecules, in light transmission through twisted optical-fiber cables, and in the quantum Hall effect.
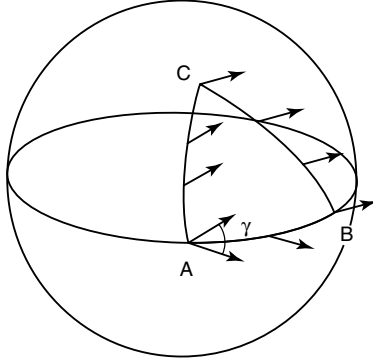
Fig. 1.4 Parallel transport of a vector on a sphere along a closed loop leads to a rotation of the vector. The vector's orientation relative to its local environment remains unchanged during parallel transport. The angle of rotation is related to Berry's phase.

In the opposite limit, where a sudden change of the Hamiltonian from $H(t) = H_0$ for all $t < 0$ to another Hamiltonian $H(t) = \overline{H}_0$ for all $t > 0$ occurs, no dynamical or geometric phase can be accumulated during the instantaneous change of the Hamiltonian at $t = 0$. The initial eigenstate of H_0, ψ_n, in which the system is prepared at $t = 0$, evolves for $t > 0$ as

$$|\psi_n(t)\rangle = \sum_{n'} \exp\left(-\frac{i\overline{\varepsilon}_{n'}t}{\hbar}\right) |\overline{\psi}_{n'}\rangle\langle\overline{\psi}_{n'}|\psi_n\rangle$$

(65)

In the sudden limit, the matrix U is non-diagonal. The eigenstate belonging to the "old" Hamiltonian forms a coherent superposition of eigenstates $|\overline{\psi}_n\rangle$ of the new Hamiltonian. The "sudden" formation of coherent states causes "quantum beats," observable oscillations in amplitudes and probabilities.

Consider, for example, an atom that is excited at the time $t = 0$ to a state that is a coherent superposition of a state $|\psi_1\rangle$, with energy E_1, and a state $|\psi_2\rangle$, with energy E_2, that is, $|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$. At a later point in time, t, the state acquires a phase factor as a function of time according to Eq. (65):

$$|\psi(t)\rangle = c_1 e^{-iE_1 t/\hbar}|\psi_1\rangle + c_2 e^{-iE_2 t/\hbar}|\psi_2\rangle$$

(66)

The projection onto a final state $|f\rangle$ representing, for example, the atom in the ground state and the emission of a photon,

$$\begin{aligned}
P_f(t) &= |\langle f|\psi(t)\rangle|^2 \\
&= |c_1|^2|\langle f|\psi_1\rangle|^2 + |c_2|^2|\langle f|\psi_2\rangle|^2 \\
&\quad + c_1 c_2^* \exp\left[\frac{it}{\hbar}(E_2 - E_1)t\right] \\
&\quad \times \langle f|\psi_1\rangle\langle f|\psi_2\rangle^* \\
&\quad + \text{complex conjugate}
\end{aligned}$$

(67)

will display oscillations ("quantum beats") due to the time dependence of the relative phases of the two states. These quantum beats due to dynamical phases have been observed, for example, in the Lyman-α ($n = 2 \rightarrow n = 1$) radiation of hydrogen excited in the $n = 2$ level subsequent to fast collisions with a foil (Figure 1.5).

The standard computational method of solving the time-dependent Schrödinger equation for time-dependent interactions consists of expanding a trial wave function $|\psi(t)\rangle$ in terms of a conveniently chosen truncated time-independent basis of finite size:

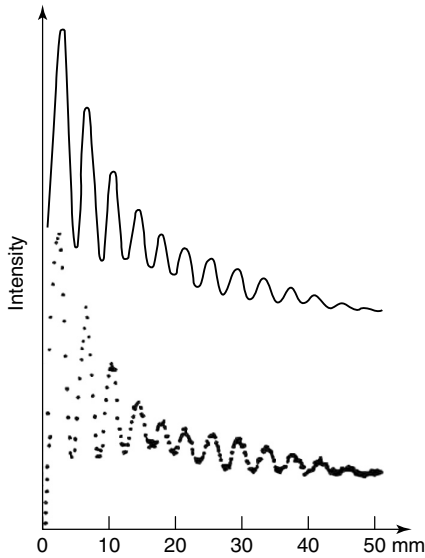$$|\psi(t)\rangle = \sum_{n=1}^{N} a_n(t)|\psi_n\rangle$$

(68)

Fig. 1.5 Quantum beats in the Lyman-α photon intensity of hydrogen after collision with a carbon foil: ●, experimental data from Andrä (1974); − , theory from Burgdörfer (1981). The theory curve is shifted relative to the data for clarity.

with unknown, time-dependent coefficients $a_n(t)$. Insertion of Eq. (68) into Eq. (47) leads to a system of coupled first-order differential equations, which can be written in matrix notation as

$$i\hbar\dot{\mathbf{a}} = \mathbf{H}(t)\,\mathbf{a}(t) \tag{69}$$

using the vector notation $\mathbf{a} = (a_1, \dots a_n)$ with $\mathbf{H}$ the matrix of the Hamiltonian in the basis $\{|\psi_n\rangle\}$, $H_{n,\,n'} = \langle \psi_n \,|\, H \,|\, \psi_{n'} \rangle$. The solution of Eq. (69) is thereby reduced to a standard problem of numerical mathematics, the integration of a set of N coupled first-order differential equations with variable (time-dependent) coefficients.

1.7.2
Methods for Solving the Time-Independent Schrödinger Equation

The solution of the stationary Schrödinger equation, Eq. (59), proceeds mostly in the $\{|\mathbf{r}\rangle\}$ representation, i.e., using wave functions $\psi(\mathbf{r})$. Standard methods include the method of separation of variables and variational methods.

1.7.2.1 **Separation of Variables**
The energy eigenvalue problem, Eq. (59), requires the solution of a second-order partial differential equation. It can be reduced to an ordinary second-order differential equation if the method of separation of variables can be applied, i.e., if the wave function can be written in a suitable coordinate system (q_1, q_2, q_3) in factorized form

$$\psi(\mathbf{r}) = f(q_1)g(q_2)h(q_3) \tag{70}$$

with obvious generalizations for an arbitrary number of degrees of freedom. Equation (70) applies only to a very special but important class of problems for which the Hamiltonian possesses as many constants of motion or compatible observables as there are degrees of freedom (in our example, three). In this case, each factor function in Eq. (70) is associated with one ''good'' quantum number belonging to one compatible observable. This class of Hamiltonians permits an exact solution of the eigenvalue problem and is called *separable* (or *integrable*).

Consider the example of the isotropic three-dimensional harmonic oscillator. The Hamiltonian is

$$H = \frac{p_x^2}{2M} + \frac{p_y^2}{2M} + \frac{p_z^2}{2M}$$
$$+ \tfrac{1}{2}M\omega^2(x^2 + y^2 + z^2) \tag{71}$$

In this case, one suitable set of coordinates for the separation are the Cartesian coordinates $(q_1 = x,\ q_2 = y,\ q_3 = z)$. Each of the three factor functions of Eq. (70) satisfies a one-dimensional Schrödinger equation of the form

$$\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + \tfrac{1}{2}M\omega^2 x^2\right)f(x) = E_x f(x) \tag{72}$$

and $E = E_x + E_y + E_z$. The simplest solution of Eq. (72) satisfying the boundary conditions $f(x \to \pm\infty) \to 0$ for a normalizable wave function is a Gaussian wave function of the form

$$f(x) = \left(\frac{M\omega}{\pi\hbar}\right)^{1/4} e^{-(M\omega/2\hbar)x^2} \tag{73}$$

It corresponds to the lowest possible energy eigenstate, with $E_x = \tfrac{1}{2}\hbar\omega$. Ground-state wave functions are, in general, node free, i.e., without a zero at any finite x. The Schrödinger equation possesses an infinite number of admissible solutions with an increasing number $n = 0, 1, \ldots$ of nodes of the wave function and increasing eigenenergies

$$E_x = \hbar\omega\left(n + \tfrac{1}{2}\right) \tag{74}$$

The fact that wave functions belonging to higher states of excitation have an increasing number of zeros can be understood as a consequence of the orthogonality requirement, Eq. (37). Only through the additional change of sign of the wave function can all contributions in the orthogonality integral (Eq. 36) be made to cancel. The wave functions for excited states of a harmonic oscillator are given in terms of Hermite polynomials H_n by

$$f_n(x) = (2^n n!)^{-1/2}\left(\frac{M\omega}{\hbar\pi}\right)^{1/4}$$
$$\times e^{-(M\omega/2\pi)x^2} H_n\left(\sqrt{\frac{M\omega}{\hbar}}x\right) \tag{75}$$

Examples of the first few eigenstates are shown in Figure 1.6 With increasing n, the probability density $|f_n(x)|^2$ begins to resemble the classical probability density for finding the oscillating particle near the coordinate x, $P_{cl}(x)$ (Figure 1.7). The latter is proportional to the time the particle spends near x or inversely proportional to its speed:

$$P_{c1}(x) = \left(\frac{\omega}{\pi}\right)\left(2E_x/M - \omega^2 x^2\right)^{-1/2} \tag{76}$$

The increasing similarity between the classical and quantal probability densities as $n \to \infty$ is at the core of the correspondence principle. This example highlights the nonuniformity of the convergence to the classical limit: the quantum probability density oscillates increasingly rapidly around the classical value with decreasing de Broglie wavelengths λ (compared with the size of the classically allowed region). Furthermore, the wave function penetrates the classically forbidden region ("tunneling"). While the amplitude decreases exponentially, $\psi(x)$ possesses significant nonvanishing values outside the domain of classically allowed trajectories of the same energy over a distance of the order of the de Broglie wavelength λ. Only upon averaging over regions of the size of λ can the classical–quantum correspondence be
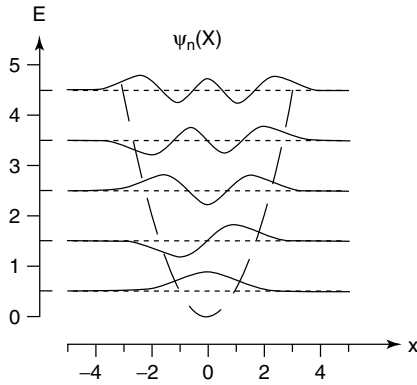
Fig. 1.6 Wave functions $f_n(x)$ for the first five eigenstates of the harmonic oscillator.
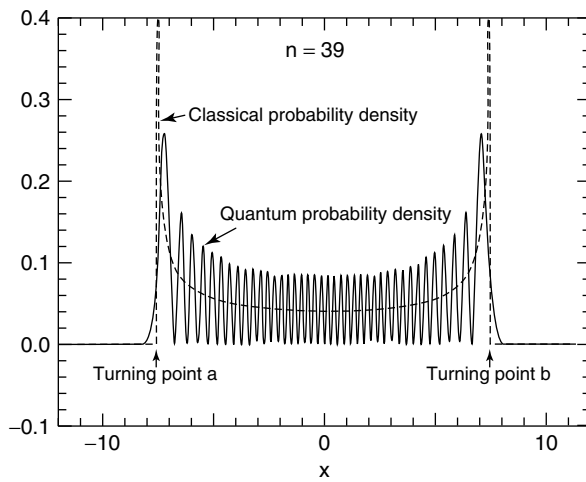

Fig. 1.7 Probability density $|f_n(x)|^2$ of a harmonic oscillator in $n = 39$ compared with the classical probability density $P_{cl}(x) = (\omega/\pi)(2E/M - \omega^2 x^2)^{-1/2}$ indicated by the dashed line. Classical turning points are denoted by a and b.

recovered. As λ tends to zero in the classical limit, classical dynamics emerges. It is the smallness of λ that renders the macroscopic world as being classical for all practical purposes.

The complete wave function for the three-dimensional isotropic oscillator (Eq. 71) consists of a product of three wave functions each of which is of the form of Eq. (75),

$$\psi_{n_x n_y n_z}(x, y, z) = f_{n_x}(x) f_{n_y}(y) f_{n_z}(z) \qquad (77)$$

with eigenenergies

$$E_{n_x n_y n_z} = \hbar\omega\left(n_x + n_y + n_z + \tfrac{3}{2}\right) \qquad (78)$$

The energy depends only on the sum of the three quantum numbers,

$$n = n_x + n_y + n_z \qquad (79)$$

but not on the individual quantum numbers n_x, n_y, and n_z, separately. Different combinations of quantum numbers yield the same energy; the spectrum is therefore degenerate. The degeneracy factor g_n, the number of different states having the same energy E_n, is

$$g_n = \frac{(n+1)(n+2)}{2} \qquad (80)$$

Only the ground state ($n = 0$) is nondegenerate, a feature generic to quantum systems and the origin of the third law (Nernst's theorem) of statistical mechanics. The degeneracy signals that alternative complete sets of commuting observables (instead of the energies in each of the three Cartesian coordinates E_x, E_y, and E_z) and corresponding alternate sets of coordinates should exist in which the problem is separable. One such set of coordinates is the spherical coordinates.

Consider the example of the hydrogen atom. One of the most profound early successes of quantum mechanics was the interpretation of the line spectrum emitted from the simplest atom, the hydrogen atom, consisting of an electron and a proton. The Schrödinger equation (in the center-of-mass frame) for the electron interacting with the proton through a Coulomb potential $V(r) = -e^2/4\pi\varepsilon_0 r$ reads as

$$\left[\frac{-\hbar^2 \nabla^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad (81)$$

where $m_e = 9.1 \times 10^{-31}$ kg is the reduced mass of the electron, $\mathbf{r}$ is the vector that points from the nucleus to the electron, $e = 1.6 \times 10^{-19}$ C is the electric charge of the nucleus, and $-e$ is the charge of the electron. If we express the Laplace operator ∇^2 (defined as $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$) in polar spherical coordinates (r, θ, ϕ), the Schrödinger equation becomes

$$\left[\frac{-\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{L^2}{2m_e r^2}\right.$$
$$\left. - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \qquad (82)$$

Since the angular coordinates enter only through the square of the angular momentum operator (see Eq. 28), the Schrödinger equation is separable in spherical coordinates and the wave function can be written as a product $\psi(r, \theta, \phi) = R_{nl}(r)Y_\ell^m(\theta, \phi)$ with one factor being the spherical harmonics Y_l^m and the $R_{nl}(r)$ being the radial wave function satisfying the second-order differential equation

$$\left[\frac{-\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2m_e r^2}\right.$$
$$\left. - \frac{e^2}{4\pi\varepsilon_0 r}\right]R_{nl}(r) = ER_{nl}(r) \qquad (83)$$

The negative-energy eigenvalues of bound states can be found as

$$E_n = -\frac{m_e e^4}{2\hbar^2 n^2 (4\pi\varepsilon_0)^2} = -\frac{E_\mathbf{H}}{2n^2} \qquad (84)$$

where $E_H = m_e e^4/\hbar^2(4\pi\varepsilon_0)^2$ is called a *Hartree* or an *atomic unit of energy*. The energy depends only on the "principal" quantum number n, being independent of the angular momentum

$$l = 0, 1, \ldots, n - 1 \qquad (85)$$

and of the magnetic quantum number m. The m independence can be found for any isotropic potential $V(|\mathbf{r}|)$ that depends only on the distance of the interacting particles. The degeneracy in l is a characteristic feature of the Coulomb potential (and of the isotropic oscillator), and it reflects the fact that the Schrödinger equation is separable not only in polar spherical coordinates but also in parabolic coordinates. The Coulomb problem possesses a dynamical symmetry that allows the choice of alternative complete sets of compatible observables. The separability in spherical coordinates is related to the set $\{H, L^2, L_z\}$ while the separability in parabolic coordinates is related to the set $\{H, L_z, A_z\}$ where $\mathbf{A}$ is the Runge–Lenz (or perihelion) vector, which, as is well known from
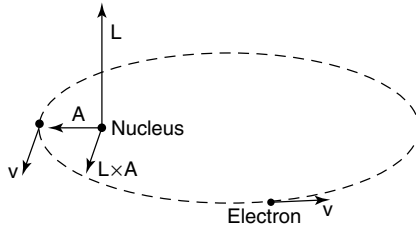
Fig. 1.8 The Runge–Lenz vector **A** and the angular momentum **L** for the classical orbit in an attractive $-1/r$ potential.

astronomy, is a constant of motion for a $1/r$ potential (Figure 1.8). The emission spectrum follows from Eq. (84) as

$$\nu = \frac{(E_n - E_{n_0})}{h}$$
$$= \frac{E_H}{2h}\left(\frac{1}{n_0^2} - \frac{1}{n^2}\right) \tag{86}$$

with $n_0 = 1$ and $n = 2, 3, \ldots$ giving rise to the Lyman series of spectral lines, $n_0 = 2$ and $n = 3, 4, \ldots$ giving rise to the Balmer series, and so on. The radial probability densities $r^2 R_{nl}(r)^2$ are shown in Figure 1.9

1.7.2.2 **Variational Methods**

For all but the few separable Hamiltonians, the time-independent Schrödinger equation is only approximately and numerically solvable. The accuracy of approximation can, however, be high. It may only be limited by the machine precision of modern computers. The most successful and widely used method in generating accurate numerical solutions is the variational method. The solution of the Schrödinger equation can be recognized as a solution to the variational problem of finding an extremum (in practice, a minimum) of the energy functional $\langle E \rangle = \langle \psi \mid H \mid \psi \rangle / \langle \psi \mid \psi \rangle$ by varying $|\psi\rangle$ until $\langle E \rangle$ reaches a stationary point at an approximate eigenvalue. The wave function at the minimum is an approximate solution to the Schrödinger equation. In practice, one chooses functional forms called *trial functions* $\psi(\mathbf{r})$ that depend linearly and/or

nonlinearly on parameters $(c_1, \ldots, c_k)$. The trial function is optimized by minimizing the energy in the k-dimensional parameter space according to

$$\frac{d}{dc_i}\langle E \rangle = 0 \quad (1 \leq i \leq k) \tag{87}$$

Provided the trial function is sufficiently flexible to approximate a complete set of states in Hilbert space, ψ becomes exact in the limit as $k \to \infty$. The ground state of the helium atom consisting of an α particle as a nucleus (nuclear charge number $Z = 2$) and two electrons provides one of the most striking illustrations of the success of the variational method. The Hamiltonian (neglecting the motion of the nucleus)

$$H = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}$$
$$- \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|} \tag{88}$$

is nonseparable, an analytic solution is unknown, and no perturbation solution is possible since all interactions are of comparable strength. The variational method pioneered by Hylleraas (1929) and further developed by Pekeris (1958, 1959) achieves, however, a virtually exact result for the ground-state energy, $E = 2.903\,724\,377\,03\ldots E_H$, for which the accuracy is no longer limited by the method of solution but rather by the approximate nature of the Hamiltonian itself (for example, the neglect of the finite
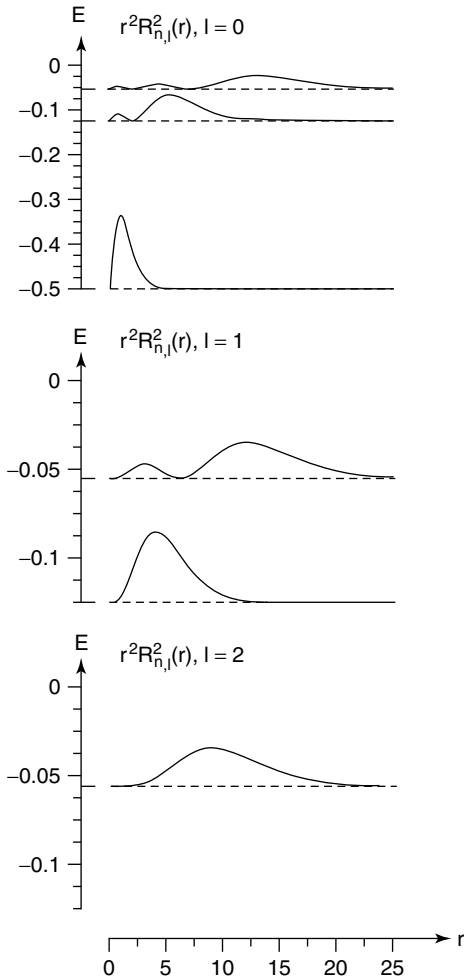
Fig. 1.9 Radial densities $r^2 R_{nl}(r)$ for $n = 1$, 2, 3 and $l = 0$, 1, and 2 of the hydrogen atom.

size of the nucleus and of relativistic effects).

1.7.3
Perturbation Theory

A less accurate method, which is, however, easier to implement, is perturbation theory. The starting point is the assumption that the Hamiltonian H can be decomposed into a ''simple,'' separable (or, at least, numerically solvable) part H_0 plus a perturbation gV,

$$H = H_0 + gV \tag{89}$$

which is nonseparable, but ''small'' such that it causes only a small modification of the spectrum and of the eigenstates of H_0. The control parameter g $(0 \leq g \leq 1)$ is used as a convenient formal device for controlling the strength of the perturbation and keeping track of the order of the perturbation. At the end of the calculation, g can be set equal to unity if V itself is small.

Two cases can be distinguished: stationary perturbation theory and time-dependent perturbation theory.

1.7.3.1 **Stationary Perturbation Theory**

The Rayleigh–Schrödinger perturbation theory involves the expansion of both the perturbed energy eigenvalue $E_0(g)$ and the perturbed eigenstate $|\psi_0(g)\rangle$ in powers of the order parameter g (or, equivalently, in powers of V),

$$E_0(g) = E_0 + gE^{(1)} + g^2 E^{(2)} + \cdots$$
$$|\psi_0(g)\rangle = |\psi_0\rangle + g|\psi^{(1)}\rangle + g^2|\psi^{(2)}\rangle + \cdots$$
$$(90)$$

Inserting Eq. (90) into the Schrödinger equation

$$H(g)|\psi_0(g)\rangle = E_0(g)|\psi_0(g)\rangle \qquad (91)$$

yields recursion relations ordered in ascending powers of g for the successive corrections to $E_0(g)$ and $|\psi_0(g)\rangle$. In practice, the first few terms are most important: Thus the first-order corrections for a non-degenerate eigenvalue E_0 are

$$E^{(1)} = \langle\psi_0|V|\psi_0\rangle \qquad (92)$$

and

$$|\psi^{(1)}\rangle = \sum_{n\neq 0} |\psi_n\rangle \frac{\langle\psi_n|V|\psi_0\rangle}{E_0 - E_n} \qquad (93)$$

where the sum over $\{|\psi_n\rangle_{n\neq 0}\}$ extends over the complete set of eigenstates of the unperturbed Hamiltonian excluding the state $|\psi_0\rangle$ for which the perturbation expansion is performed. The second-order correction to the eigenenergy is

$$E^{(2)} = \langle\psi_0|V|\psi^{(1)}\rangle = \sum_{n\neq 0} \frac{|\langle\psi_0|V|\psi_n\rangle|^2}{E_0 - E_n}$$
$$(94)$$

Alternative perturbation series can be devised. For example, in the Brillouin–Wigner expansion, the perturbed $E_0(g)$, rather than the unperturbed energy E_0, appears in the energy denominator of Eq. (94). The energy is therefore only implicitly given by this equation.

1.7.3.2 **Time-Dependent Perturbation Theory**

Time-dependent perturbation theory deals with the iterative solution of the system of coupled equations, Eq. (69), representing the time-dependent Schrödinger equation. One assumes again that the Hamiltonian consists of an unperturbed part H_0 and a time-dependent perturbation $V(t)$. Expansion in the basis of eigenstates of the unperturbed Hamiltonian (Eq. 68) yields a matrix **H** consisting of a diagonal matrix $\langle i|H_0|j\rangle = E_j\delta_{ij}$ and a time-dependent perturbation matrix $V_{ij} = \langle i|V(t)|j\rangle$.

The dynamical phases associated with the unperturbed evolution can be easily included in the perturbative solution of Eq. (69) by making the phase transformation

$$a_j(t) = c_j(t)e^{-iE_j t/\hbar} \qquad (95)$$

This transformation, often referred to as the *transformation* to the *interaction representation*, removes the diagonal matrix $\langle i|H_0|j\rangle$ from Eq. (69), resulting in the new system of equations

$$i\hbar\frac{d}{dt}\mathbf{C}(t) = \mathbf{V}_I(t)\,\mathbf{C}(t) \qquad (96)$$

with matrix elements

$$\langle i|V_I(t)|j\rangle = \exp\left(\frac{i}{\hbar}t(E_i - E_j)\right)\langle i|V(t)|j\rangle$$
$$(97)$$

and $\mathbf{C} = (c_1, c_2, \ldots, c_N)$. The perturbative solution of Eq. (96) proceeds now by assuming that initially, say at $t = 0$, the
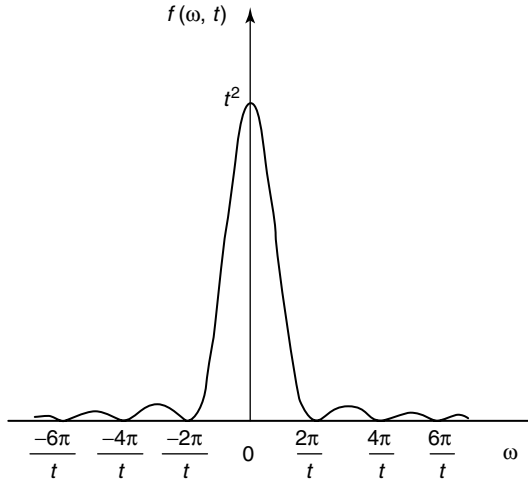
$f(\omega, t)$

Fig. 1.10 The function $f(\omega, t)$ as a function of ω.

system is prepared in the unperturbed state $|j\rangle$ with unit amplitude, $c_j(0) = 1$. Since the perturbation is assumed to be weak, the system at a later time t will still be approximately in this state. However, small admixtures of other states will develop with amplitudes

$$c_i(t) = \frac{1}{i\hbar} \int_0^t dt' \langle i| V_I(t')|j\rangle c_j(t')$$

$$\approx \frac{1}{i\hbar} \int_0^t dt' \langle i| V_I(t')|j\rangle \quad (98)$$

Therefore, to first order, the time-dependent perturbation induces during the time interval $[0, t]$ transitions $|j\rangle \rightarrow |i\rangle$ with probabilities

$$P_i(t) = |c_i(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t dt' \langle i| V_I(t')|j\rangle \right|^2 \quad (99)$$

In the special case that V is time independent, Eq. (99) gives

$$P_i(t) = \frac{1}{\hbar^2} |\langle i| V|j\rangle|^2 \frac{|e^{i\omega_{ij}t} - 1|^2}{\omega_{ij}^2}$$

$$= \frac{1}{\hbar^2} |\langle i| V|j\rangle|^2 \frac{4 \sin^2(\omega_{ij}t/2)}{\omega_{ij}^2} \quad (100)$$

with $\omega_{ij} = (\varepsilon_i - \varepsilon_j)/\hbar$. Plotted as a function of ω, the function $f(\omega, t) = 4 \sin^2(\omega t/2)/\omega^2$ (Figure 1.10) is strongly peaked around $\omega = 0$. The peak height is t^2 and the width of the central peak is given by $\Delta\omega \simeq 2\pi/t$. In other words, f describes the energy–time uncertainty governing the transition: The longer the available time, the more narrowly peaked is the transition probability around $\omega_i - \omega_j = 0$, that is, for transition into states that are almost degenerate with the initial state. In the limit $t \rightarrow \infty$, the time derivative of Eq. (100), that is, the transition probability per unit time, or transition rate w, has the well-defined limit

$$w = \frac{d}{dt} P_i(t)_{t \rightarrow \infty} = \frac{2\pi}{\hbar} |\langle i| V|j\rangle|^2 \delta(\varepsilon_i - \varepsilon_j) \quad (101)$$

where the representation of the δ function, $\pi\delta(\omega) = \lim_{t \rightarrow \infty} (\sin\omega t/\omega)$, has been used. Equation (101) is often called *Fermi's golden rule* and provides a simple, versatile tool to calculate transition rates to first order. The physical meaning of the δ function is such that in the limit $t \rightarrow \infty$ only those transitions take place for which energy is conserved, as we would have expected since

the interaction in Eq. (100) was assumed to be time-independent (after being switched on at time $t = 0$). For example, in scattering processes, many final states with energies very close to that of the initial states are accessible. The δ function is then evaluated within the sum (or integral) over these final states.

1.8
Quantum Scattering Theory

Scattering theory plays, within the framework of quantum mechanics, a special and important role. Its special role is derived from the fact that scattering deals with unbound physical systems: two (or more) particles approach each other from infinity, scatter each other, and finally separate to an infinite distance. Obviously, one cannot impose upon the wave function the boundary condition $\psi(r = |\mathbf{r}_2 - \mathbf{r}_2| \to \infty) \to 0$ since the probability of finding the scattered particles at large interparticle distances r is, in fact, nonvanishing. This has profound consequences: energies are not quantized since the corresponding boundary condition is missing. The energy spectrum consists of a continuum instead of a set of discrete states. The states describing the unbound motion, the "scattering states," are not square integrable and do not, strictly speaking, belong to the Hilbert space. They can only be orthonormalized in terms of a δ function,

$$\langle \psi_E | \psi_{E'} \rangle = \delta(E - E') \qquad (102)$$

Mathematically, they belong to the space of distributions and can be associated with states in Hilbert space only upon forming "wave packets," that is, by convoluting the scattering state with a well localized

function. Nevertheless, most of the time one can manipulate scattering states using the same rules valid for Hilbert-space vectors (see Section 1.6) except for replacing the ordinary orthonormalization condition, Eq. (37), by the δ normalization condition, Eq. (102).

The strategy for solving the Schrödinger equation, which governs both bounded and unbounded motion, is different for scattering states. Rather than determining the energy eigenvalues or the entire wave function (which is, in many cases, of no interest), one aims primarily at determining the asymptotic behavior of the wave function emerging from the interaction region, which determines the flux of scattered particles. The central quantity of both classical and quantum scattering is the cross section σ, defined as

$$\sigma = \frac{\begin{array}{c}\text{number of scattered particles}\\\text{per unit time}\end{array}}{\begin{array}{c}\text{number of incident particles}\\\text{per unit area and per unit time}\end{array}}$$

$$(103)$$

A cross section σ has the dimension of an area and can be visualized as an effective area that the target presents to the incoming projectile. Using the probabilistic description of quantum mechanics, one can replace in the definition Eq. (103) all particle currents by corresponding probability currents. Accordingly, σ can be expressed in terms of the transition rate w as

$$\sigma = \frac{w}{j} \qquad (104)$$

where $j = |\psi|^2 v$ represents the incoming probability current density. For an incoming plane particle wave (Eq. 4), $j = \hbar k / M$ (with M the reduced mass and the amplitude A set equal to unity). Calculations of

total cross sections σ proceed typically by first calculating differential cross sections for scattering into a particular group of final states and then summing over all possible final states. For elastic scattering of particles with incident wave vectors $\mathbf{k}_{in}$ pointing in the z direction, a group of final states is represented by a wave vector $\mathbf{k}_{out}$ of the outgoing particles pointing in a solid angle centered around the spherical angles (θ, ϕ),

$$\frac{d\sigma}{d\Omega} = \frac{M}{\hbar k_{in}} w_{\mathbf{k}_{in} \longrightarrow \mathbf{k}_{out}} \tag{105}$$

Equation (105) gives the differential cross section per unit solid angle.

1.8.1
Born Approximation

The evaluation of $d\sigma/d\Omega$ is most straightforward in the Born approximation. The first Born approximation is nothing but the application of Fermi's "golden rule," Eq. (101), to scattering:

$$\frac{d\sigma}{d\Omega} = \frac{2\pi M}{\hbar^2 k_{in}} \int_0^\infty \frac{k_{out}^2}{(2\pi)^3} dk_{out} \tag{106}$$
$$|\langle \mathbf{k}_{out} | V | \mathbf{k}_{in} \rangle|^2 \times \delta(E_{in} - E_{out})$$

where the integral is taken over the magnitude of k_{out} but not over the solid angle and where $k_{out}^2 dk_{out} \, d\Omega/(2\pi)^3$ represents the number of final states available for the scattered particles in the interval $dk_{out} d\Omega$. Since $k_{out}^2 dk_{out} = (M/\hbar^2) k_{out} dE_{out}$, we have

$$\frac{d\sigma}{d\Omega} = \frac{M^2}{\hbar^4 (2\pi)^2} |\langle \mathbf{k}_{out} | V | \mathbf{k}_{in} \rangle|^2 \tag{107}$$

with $|\mathbf{k}_{out}| = |\mathbf{k}_{in}|$. The first Born approximation to elastic scattering, Eq. (107), is only valid if the potential V is sufficiently weak to allow for a perturbative treatment

and vanishes sufficiently rapidly at large distances for the matter wave to become a plane wave. In such cases, the matrix element in Eq. (107) can be expressed as the Fourier component of the potential,

$$\langle \mathbf{k}_{out} | V | \mathbf{k}_{in} \rangle = \int d^3 r \, e^{i\mathbf{r} \cdot (\mathbf{k}_{out} - \mathbf{k}_{in})} V(\mathbf{r}) \tag{108}$$

For a Coulomb potential $V(\mathbf{r}) = Z_1 Z_2 e^2 / 4\pi \varepsilon_0 r$ representing two charged particles with charges $Z_1 e$ or $Z_2 e$ scattering each other, Eq. (107) yields – coincidentally – the Rutherford cross section

$$\left(\frac{d\sigma}{d\Omega} \right)_R = \frac{Z_1^2 Z_2^2 e^4}{16 E^2 (4\pi \varepsilon_0)^2 \sin^4(\theta/2)} \tag{109}$$

This expression provided essential clues as to an internal structure and charge distribution of atoms. Two remarkable features should be noted: Prior to the advent of quantum theory, Rutherford (1911) used classical mechanics instead of quantum mechanics to derive Eq. (109). He could do so since, for Coulomb scattering, classical and quantum dynamics happen to agree. Keeping in mind that the classical limit entails the limit $\hbar \to 0$, the QM and classical cross sections should agree, since $(d\sigma/d\Omega)_R$ does not depend on $\hbar$. The equivalence of the classical and the QM Rutherford cross sections is due to the long range (in fact, infinite range) of the Coulomb potential. In this case, the de Broglie wavelength of the particle wave is negligibly small compared to the "size" of the target at all energies. A second coincidence lies in the fact that the first Born approximation yields the exact quantum result even though the Born approximation is, strictly speaking, not even applicable in the case of a Coulomb potential. The infinite range of the Coulomb potential distorts the matter

wave at arbitrarily large distances so that it never becomes the plane wave that is assumed in Eq. (108). It turns out that all high-order corrections to the Born approximation can be summed up to give a phase factor that drops out from the expression for the cross section.

1.8.2
Partial-Wave Method

For elastic scattering by a spherically symmetric potential, that is, a potential that depends only on the distance between the particles, $V(\mathbf{r}) = V(|\mathbf{r}|)$, phase-shift analysis provides a versatile nonperturbative method for calculating differential and integral cross sections. For each angular momentum l (which is a good quantum number for a spherically symmetric potential), the phase shift for a radial wave function $u(r) = rR(r)$ can be determined from the radial Schrödinger equation

$$\left(-\frac{\hbar^2}{2M}\frac{d^2}{dr^2} + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2} + V(r) \right) u(r) = Eu(r) \tag{110}$$

The idea underlying the phase-shift analysis can be best illustrated for the phase shift δ_l for $l = 0$. In absence of the scattering potential $V(r)$, Eq. (110) represents a one-dimensional Schrödinger equation of a free particle in the radial coordinate,

$$-\frac{\hbar^2}{2M}\frac{d^2}{dr^2}u(r) = Eu(r) \tag{111}$$

whose solution is $u(r) = \sin(kr)$ with $k^2 = 2ME/\hbar^2$. Since the matter wave cannot reach the unphysical region of negative r, we have to impose the boundary condition $u(0) = 0$, which excludes the alternative solution $\sim \cos kr$. In the presence of the

potential $V(r)$, the wave function will be modified within the region of the nonvanishing potential. At large distances $r \to \infty$, however, when $V(r) \to 0$, the wave function will again become $u(r) = \sin(kr + \delta_0)$ since in this region it must satisfy Eq. (111). The only effect that the potential can have on the scattered wave function at large distances is to introduce a phase shift δ_0 relative to the unperturbed wave.

Simple arguments give a clue as to the origin and the sign of the phase shift. For an attractive potential (negative V), the wave number $k(r) = \sqrt{2M(E - V(r))/\hbar^2}$ increases locally and the de Broglie wavelength $\lambda(r) = 2\pi/k(r)$ becomes shorter compared with that of a free particle of the same energy. The phase of the matter wave is therefore advanced compared with the wave of a free particle and δ_0 is positive (Figure 1.11). Similarly, if V is a repulsive potential, λ increases in the interaction region causing a phase delay and, hence, a negative phase shift δ_0. Including all angular momenta, or all ''partial waves,'' the differential cross section can be expressed in terms of the partial-wave phase shifts δ_l as

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l+1)e^{i\delta_l} \sin \delta_l P_l(\cos \theta) \right|^2 \tag{112}$$

A particularly simple expression can be found for the total cross section:

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (l+1) \sin^2 \delta_l \tag{113}$$

For short-ranged potentials, δ_l decreases with increasing l such that only a small number of terms must be included in this sum. The scattering phase shifts $\delta_l(E)$ depend sensitively on the energy E of the incident particle.
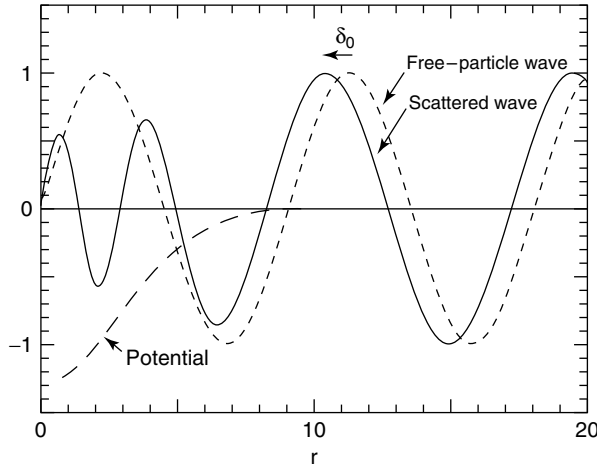
Fig. 1.11 Comparison between the scattered wave in an attractive potential and a free-particle wave (the scattering phase δ_0 is shown modulo π).

1.8.3
Resonances

Often, one phase shift $\delta_l(E)$ increases by π within a narrow energy range. This corresponds to a phase shift of one-half of a wave length, or to the addition of one node to the wave function. A sudden increase of the scattering phase by π is a signature of a "resonance" in the cross section. A resonance is characterized by a sharp maximum in the partial-wave cross section at the energy $E_{\text{res}} = \hbar^2 k_{\text{res}}^2/2M$:

$$(\sigma_l)_{\text{max}} = \left(\frac{4\pi}{k_{\text{res}}^2}\right)(2l+1) \qquad (114)$$

where the phase shift passes through $\pi/2$ (or an odd multiple thereof). Resonances appear when the scattering potential allows for the existence of "virtual levels" or quasi-bound states inside the potential well, whose probability density can leak out by tunneling through the potential well. The additional node that the scattering wave function acquires as the energy passes through E_{res} reflects the presence of a quasi-bound state. An isolated resonance can be parametrized by a formula due to Breit and Wigner. One assumes that

the rapid change of the scattering phase near the resonance can be modeled by

$$\delta_l(E) \simeq \tan^{-1}\frac{\Gamma}{2(E_{\text{res}} - E)} \qquad (115)$$

and that the energy dependence of the non-resonant (smooth part) of the phase shift can be neglected. The term Γ denotes the width over which the phase jump occurs. Inserting Eq. (115) into the lth term of Eq. (113) yields, for the shape of the resonant cross section, the Breit–Wigner formula

$$\sigma_l(E) = (\sigma_l)_{\text{res}}\frac{\Gamma^2/4}{(E_{\text{res}} - E)^2 + \Gamma^2/4} \qquad (116)$$

The shapes of resonant cross sections become more complicated when interferences between the resonant and the nonresonant parts of the scattering amplitude come into play. The cross section can then exhibit a variety of shapes (Beutler–Fano profile; Fano, 1961), including asymmetric peaks or dips ("window resonance") depending on the relative phases of the amplitudes. In the limit that a large number of resonances with energies $E_{\text{res},i}$ ($i = 1,\ldots,N$)

are situated within the width Γ ("overlapping resonances"), the cross section displays irregular fluctuations ("Ericson fluctuations") (*see* Chapter 10). These play an important role in scattering in complex systems, for example, in nuclear compound resonances (Ericson and Meyer-Kuckuk, 1966) as well as in scattering in chaotic systems Burgdörfer *et al.*, 1995).

1.9
Semiclassical Mechanics

While the correspondence principle postulates that in the limit of large quantum numbers (or, equivalently, $\hbar \to 0$), quantum mechanics converges to classical mechanics, the approach to this limit is highly nonuniform and complex. The description of dynamical systems in the limit of small but nonzero $\hbar$ is called *semiclassical mechanics*. Its importance is derived not only from conceptual but also from practical aspects since a calculation of highly excited states with large quantum numbers involved becomes difficult because of the rapid oscillations of the wave function (see Figure 1.7). Semiclassical mechanics has been developed only recently. The old Bohr–Sommerfeld quantization rules that preceded the development of quantum mechanics are now understood as an approximate form of semiclassical mechanics applicable to separable (or integrable) systems.

The wave function of the time-independent Schrödinger equation for a single particle,

$$E\psi(\mathbf{r}) = -\left(\frac{\hbar^2}{2M}\right)\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r})$$

(117)

can be written as

$$\psi(\mathbf{r}) = A\exp\left[\frac{iS(\mathbf{r})}{\hbar}\right]$$

(118)

where the unknown function $S(\mathbf{r})$ replaces the exponent $\mathbf{k}\cdot\mathbf{r}$ of a plane wave (Eq. 4) for a free particle in the presence of the potential. The idea underlying the semiclassical approximation is that in the limit $\hbar \to 0$, or likewise, in the limit of small de Broglie wavelength $\lambda \to 0$ (compared with the distance over which the potential changes), $\psi(\mathbf{r})$ should behave like a plane wave with, however, a position-dependent de Broglie wavelength. Inserting Eq. (118) into Eq. (117) leads to

$$E = \frac{1}{2M}[\nabla S(\mathbf{r})]^2 + V(\mathbf{r}) - \frac{i\hbar}{2M}\nabla^2 S(\mathbf{r})$$

(119)

with $\mathbf{p} = \nabla S$. Equation (119) is well suited for taking the classical limit $\hbar \to 0$ and yields the classical Hamilton–Jacobi equation. In this limit, S is the action or Hamilton's principal function. Quantum corrections enter through the term linear in $\hbar$. Approximate solutions of Eq. (119) can be found by expanding S in ascending powers of $\hbar$. The apparent simplicity of the classical limit is deceiving: the principal function S appears inside the exponent Eq. (118) with the prefactor $\hbar^{-1}$ and this causes the wave function to oscillate infinitely rapidly as $\hbar \to 0$.

1.9.1
The WKB Approximation

For problems that depend only on one coordinate, retention of the first two terms of the expansion of Eq. (119),

$$S(x) = S_0(x) + \hbar S_1(x)$$

with

$$S_0(x) = \pm \int^x p(x')dx'$$

$$S_1(x) = \tfrac{1}{2}i \ln|p(x)| + c \tag{120}$$

leads to the Wentzel–Kramers–Brillouin (WKB) approximation where c is an integration constant to be determined by normalization of the wave function,

$$\psi^{\text{WKB}}(x) = \frac{A}{\sqrt{|p(x)|}} \exp\left[\frac{\pm i}{\hbar} \int^x p(x')dx'\right] \tag{121}$$

Several features of Eq. (121) are worth noting: the WKB wave function is an asymptotic solution of Schrödinger's equation in the limit of small λ and satisfies all rules of QM, including the superposition principle. All quantities in Eq. (121) can be calculated, however, purely from classical mechanics. In particular, the quantum probability density $|\psi^{\text{WKB}}(x)|^2$ can be directly associated with the inverse classical momentum $\sim |p(x)|^{-1}$ or, equivalently, the time the particle spends near x. This result was already anticipated for the highly excited state of the harmonic oscillator (Figure 1.7). Furthermore, $S_0(x)$ is a double-valued function of x corresponding to the particle passing through a given point moving either to the right or to the left with momentum $\pm p(x)$. It is the multiple-valuedness of $p(x)$ or $S(x)$ that is generic to semiclassical mechanics and that poses a fundamental difficulty in generalizing the WKB approximation to more than one degree of freedom.

For describing bound states, a linear combination of ψ^{WKB} with both signs of the momentum in Eq. (121) is required in order to form a standing rather than a traveling wave:

$$\psi^{\text{WKB}}(x) = \frac{A}{\sqrt{|p(x)|}} \sin$$
$$\times \left(\frac{1}{\hbar} \int_a^x p(x')dx' + \frac{\pi}{4}\right) \tag{122}$$

Here a is the left turning point, the boundary of the classically allowed region (Figure 1.7). The additional phase of $\pi/4$ is required to join $\psi(x)$ smoothly with the exponentially decaying solution in the classically forbidden region where $p(x)$ becomes purely imaginary ("tunneling"). With equal justification, we could have started from the classically forbidden region to the right of the turning point b and would find

$$\psi^{\text{WKB}}(x) = \frac{A}{\sqrt{|p(x)|}} \sin$$
$$\times \left(\frac{1}{\hbar} \int_x^b p(x')dx' + \frac{\pi}{4}\right) \tag{123}$$

The uniqueness of $\psi^{\text{WKB}}(x)$ mandates the equality of Eqs (122) and (123). The two are equal if the integral over the whole period of the trajectory (from a to b and back to a) equals

$$\left(\int_a^b + \int_b^a\right) p(x)dx = \oint p(x)dx$$
$$= (n + \tfrac{1}{2})2\pi\hbar \tag{124}$$

Equation (124) can be recognized as the Bohr–Sommerfeld quantization rule of the "old" quantum theory put forward prior to the development of quantum mechanics. Quantization rules were successful in exploring the discrete spectrum of hydrogen, one of the great puzzles that classical dynamics could not resolve. The additional term $\tfrac{1}{2} \times 2\pi\hbar$ in Eq. (124) was initially introduced as an empirical correction. Only within the semiclassical limit of QM does
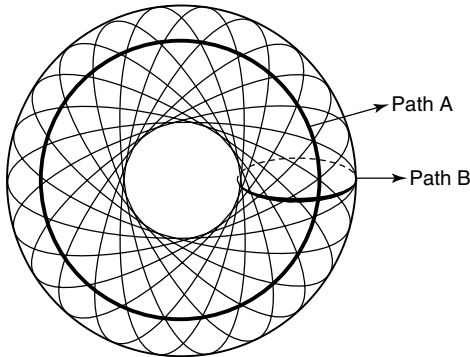
Fig. 1.12 Confinement of trajectories of an integrable Hamiltonian for constant energy E to the surface of a torus, shown here for a system with two degrees of freedom ($N = 2$) (after Noid and Marcus, 1977).

its meaning become transparent: it is the phase loss in units of $h = 2\pi\hbar$ of a matter wave upon reflection at the turning points (in multidimensional systems, at caustics). These phase corrections are of the form $\alpha(\pi/4)$ with $\alpha = 2$ in the present case. The quantity α is called the *Maslov index* and it is used to count the number of encounters with the caustics (in general, the number of conjugate points) during a full period of the classical orbit.

1.9.2
The EBK Quantization

The generalization of the WKB approximation to multidimensional systems faces fundamental difficulties: the momentum vector $\mathbf{p}(\mathbf{r})$ is, in general, not smooth but it is a highly irregular function of the coordinate vector $\mathbf{r}$ and takes on an infinite number of different values. Take, for example, a billiard ball moving in two dimensions on a stadium-shaped billiard table. A ball of a fixed kinetic energy $T = p^2/2M$ can pass through any given interior point $\mathbf{r}$ with a momentum vector $\mathbf{p}$ pointing in every possible direction. Consequently, the generalization of Eq. (121),

$$\psi(\mathbf{r}) = \sqrt{|D(\mathbf{r})|} \times \exp\left[\frac{i}{\hbar}\int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{p}(\mathbf{r}') \cdot d\mathbf{r}'\right]$$

(125)

is well defined only under special circumstances, that is, when $\mathbf{p}(\mathbf{r})$ is smooth and the action $S(\mathbf{r}_0, \mathbf{r}) = \int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{p} \cdot d\mathbf{r}'$ is either single valued or (finite-order) multiple valued (called a *Lagrangian manifold*; Gutzwiller, 1990). Einstein pointed out, as early as 1917, that the smoothness applies only to integrable systems, i.e., systems for which the number of constants of motion equals the number of degrees of freedom, N. For such a system, classical trajectories are confined to tori in phase space (as shown in Figure 1.12 for $N = 2$) and give rise to smooth vector fields $\mathbf{p}(\mathbf{r})$ (Figure 1.13). The corresponding quantization conditions are

$$\oint_{C_i} \mathbf{p}(\mathbf{r}) \cdot d\mathbf{r} = 2\pi\hbar\left(n + \frac{\alpha}{4}\right) \quad (i = 1, \ldots, N)$$

(126)

where C_i ($i = 1, \ldots, N$) denote N topological distinct circuits on the torus, that is, circuits that cannot be smoothly deformed into each other without leaving the torus (for example, the paths *A* and *B* in Figure 1.12). The conditions of Eq. (126) are called the *Einstein–Brillouin–Keller* (*EBK*) quantization rules and are the generalization of the WKB approximation (Eq. 124). The amplitude of Eq. (125) is given by the projection of the point density of the torus in phase space onto the coordinate space. Since the point density is
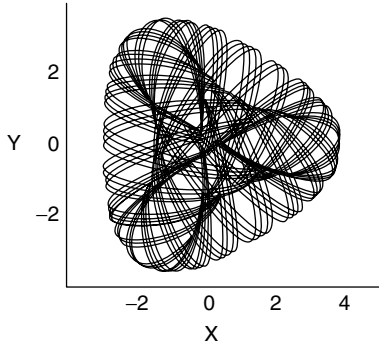
Fig. 1.13 Regular trajectory in coordinate space for an integrable system. The vector field **p(r)** is multiple valued but smooth (after Noid and Marcus, 1977).

uniform in the classical angle variables θ_i conjugate to the action (Goldstein, 1959), the amplitude is given by

$$|D(\mathbf{r})| \propto \det \left| \frac{\partial\theta_1 \partial\theta_2 \partial\theta_3}{\partial x \partial y \partial z} \right| \qquad (127)$$

For a system with one degree of freedom ($N = 1$), Eq. (125) reduces to Eq. (121) since

$$\left| \frac{\partial\theta}{\partial x} \right|^{1/2} = \left| \frac{\partial t}{\partial x} \frac{\partial\theta}{\partial t} \right|^{1/2}$$
$$= \left| \frac{M}{p}\omega \right|^{1/2} \propto \frac{1}{|p|^{1/2}} \qquad (128)$$

1.9.3
Gutzwiller Trace Formula

As already anticipated by Einstein (1917), tori do not exist in many cases of practical interest – for example, for the motion of an electron in a stadium-shaped semiconductor heterostructure (Marcus *et al.*, 1992). WBK or EBK approximations are not applicable since the classical motion of such an electron is chaotic, destroying the smooth vector field **p(r)** as in the billiard discussed above. The semiclassical mechanics for this class of problems was developed only recently (Gutzwiller, 1967, 1970, 1971). The starting point is the

semiclassical Van Vleck propagator (Van Vleck, 1928),

$$K^{\text{SC}}(\mathbf{r}_1, \mathbf{r}_2, t_2 - t_1)$$
$$= \sqrt{|D(\mathbf{r}_1, \mathbf{r}_2, t_2 - t_1)|}$$
$$\times \exp\left[\frac{i}{\hbar} \int_{t_1}^{t_2} L(\mathbf{r}(t'))dt' - \frac{i\alpha\pi}{2} \right] \quad (129)$$

where L is the classical Lagrange function for the particle traveling along the classically allowed path from $\mathbf{r}_1$ at time t_1 to $\mathbf{r}_2$ at time t_2 and α counts the number of singular points of the amplitude factor D (similar to the Maslov index). If more than one path connects $\mathbf{r}_1(t_1)$ with $\mathbf{r}_2(t_2)$, the coherent sum of terms of the form in Eq. (129) must be taken. The Van Vleck propagator was recognized only 20 years later (Feynman, 1948) as the semiclassical limit of the full Feynman quantum propagator

$$K(\mathbf{r}_1, \mathbf{r}_2, t_2 - t_1)$$
$$= \int \{D\mathbf{r}\} \exp\left[\frac{i}{\hbar} \int_{t_1}^{t_2} L(\mathbf{r}, t')dt' \right] \quad (130)$$

where $\{D\mathbf{r}\}$ stands for the path integral, that is the continuous sum over all paths connecting $\mathbf{r}_1$ and $\mathbf{r}_2$ including all those that are classically forbidden. In the semiclassical limit $\hbar \to 0$, the rapid oscillations in the phase integral cancel all contributions except for those stemming from the classically allowed paths for which

the actions $\int L dt$ possess an extremum or, equivalently, for which the phase in Eq. (130) is stationary.

Equation (129) provides a method for investigating the semiclassical time evolution of wave packets in time-dependent problems. The Fourier–Laplace transform of Eq. (129) with respect to t yields the semiclassical Green's function $G(\mathbf{r}_1, \mathbf{r}_2, E)$. The spectral density of states of a quantum system can be shown to be

$$
\begin{aligned}
n(E) &= \sum_i \delta(E - E_i) \\
&= -\frac{1}{\pi} \mathrm{Tr}\, \mathrm{Im}\, G(\mathbf{r}_1 = \mathbf{r}_2, E)
\end{aligned}
\tag{131}
$$

where the trace implies integration over the variables $\mathbf{r}_1$, $\mathbf{r}_2$ with constraint $\mathbf{r}_1 = \mathbf{r}_2$. Note that each of these eigenenergies causes a sharp peak (resembling the singularity of the δ function) in $n(E)$. Calculation of $n(E)$ therefore allows the determination of eigenenergies of quantum systems. It is possible to evaluate Eq. (131) in the semiclassical limit by using the semiclassical Green's function and evaluating the trace in the limit $\hbar \to 0$ by the stationary-phase method. The result is the trace formula

$$
\begin{aligned}
n(E) = n_{\mathrm{av}}(E) &+ \mathrm{Im}\, \frac{1}{i\hbar\pi} \\
&\times \sum_{\substack{\text{periodic} \\ \text{orbits}}} \frac{T_i}{2\sinh(T_i \lambda_i / 2)} \\
&\times \exp\left[i \left(\frac{S_i}{\hbar} - \alpha_i \frac{\pi}{2} \right) \right]
\end{aligned}
\tag{132}
$$

The sum extends over all unstable classical periodic orbits, each characterized by the period T_i, the instability (or ''Lyapunov'') exponent λ_i, and the action S_i, all of which are functions of the energy E. An orbit is unstable if its Lyapunov exponent is positive. The term λ_i measures the rate of exponential growth of the distance from the orbit when the initial condition is ever so slightly displaced (Gutzwiller, 1990). The smooth average density of states,

$$
n_{\mathrm{av}}(E) = \frac{d}{dE} \left(\frac{V(E)}{(2\pi\hbar)^N} \right)
\tag{133}
$$

is given by the rate of the change of the classical phase-space volume with energy in units of the volume of Planck's unit cell $(2\pi\hbar)^N$ associated with each quantum state. The derivation of Eq. (132) assumes two degrees of freedom and makes explicit use of the fact that the physical system is completely chaotic and integrable regions are absent. Only (hyperbolic) unstable periodic orbits are assumed to exist, each with a positive Lyapunov exponent $\lambda_i > 0$ that measures the instability of each periodic orbit. Equation (132) is therefore complementary to the EBK quantization formula (Eq. 126). This formula of ''periodic orbit quantization'' is an asymptotic series, that is, the sum over all periodic orbits is, in general, divergent. For several systems, the sum over the first few orbits has been shown to reproduce the position of energy levels quite well. The mathematical and physical properties of the Gutzwiller trace formula are still a topic of active research in quantum mechanics.

1.10
Conceptual Aspects of Quantum Mechanics

QM has proved to be an extraordinarily successful theory and, so far, has never been in contradiction to experimental observation. The Schrödinger equation has cleared every test carried out so far, including a precision test of its linearity: the upper bound for corrections due to nonlinear terms in the wave functions,

$\psi(x)^n$ ($n > 1$), in the Schrödinger equation stands currently at one part in 10^{27} (Majumder *et al.*, 1990). Even so, the conceptual and philosophical aspects of QM have remained a topic of lively discussion stimulated, to a large part, by the counterintuitive consequences of QM that apparently defy common-sense interpretation. The debate, which can be traced to the origins of QM and Einstein's objections summarized in his famous quote ''Gott würfelt nicht'' (''God does not play dice''), is centered around two aspects: the superposition principle, Eq. (15), and the probability interpretation of the wave function, Eq. (39).

1.10.1
Quantum Mechanics and Physical Reality

The counterintuitive aspects of the superposition principle are highlighted by the thought experiment of ''Schrödinger's cat.'' The coherent superposition of two states, each of which is presumably an eigenstate of an extremely complex many-body Schrödinger equation, describes the state of the cat, being either dead, $|d\rangle$, or alive, $|a\rangle$:

$$|\psi_{\text{cat}}\rangle = c_d|d\rangle + c_a|a\rangle \qquad (134)$$

with $|c_d|^2 + |c_a|^2 = 1$. Only by way of measurement, that is, by projection onto the states $|a\rangle$ or $|d\rangle$,

$$P_a = |\langle a|\psi_{\text{cat}}\rangle|^2, \quad P_d = |\langle d|\psi_{\text{cat}}\rangle|^2 \quad (135)$$

can we find out about the fate of the cat. While the meaning of two sharply different outcomes of Eq. (135), ''dead'' or ''alive,'' is deeply engraved in our classical intuition, the quantum state of a coherent superposition, Eq. (134), defies any classical interpretation. Yet it is an accessible state

of the system. The point to be emphasized is that it is not our incomplete knowledge of an independently existing objective reality, but the fate of the cat itself, that can only be resolved by the measurement. Such a measurement is therefore, quite literally, a ''demolition'' measurement leading to the ''collapse'' of the wave function to one of the two possible states. In hypothetical thought experiments for macroscopic systems such as Schrödinger's cat problem, the average over a huge number ($\sim 10^{23}$) of uncontrolled degrees of freedom will, for all practical purposes, destroy any well-definded phase relation or coherence between the ''states'' dead and alive. In contrast, the axioms of QM can be put to a rigorous test for microscopic systems, for example, by performing correlation measurements on two particles emitted from the same source. Examples along these lines were, for example, put forward by Einstein, Podolsky and Rosen (1935) to challenge the purely probabilistic interpretation of QM.

Consider the emission of two electrons from, for example, a helium atom (Figure 1.14). The spin of each electron $i = 1,2$ can be in a coherent superposition state of spin up $|+\rangle$ and spin down $|-\rangle$,

$$|\psi_i\rangle = \alpha_i|+\rangle + \beta_i|-\rangle \qquad (136)$$

relative to one particular Cartesian axis, for example, the z axis. One possible spin state of the electron pair (ignoring here the antisymmetrization requirement for fermions) would be an uncorrelated product state,

$$|\psi\rangle = |+\rangle_1|-\rangle_2 \qquad (137)$$

Already Schrödinger pointed out that quantum theory allows to be alternatively
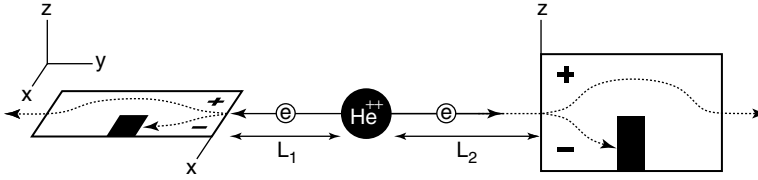
Fig. 1.14 Two-electron emission from helium with the electrons being spin-analyzed in two Stern–Gerlach-type filters with different orientations (along the x and z axis, respectively). The difference in length, $L_1 < L_2$, makes the spin selection in the left detector happen first (inducing a "wave function collapse") and in the right detector later.

in an entangled (or quantum-correlated) superposition state,

$$|\psi\rangle = \alpha|+\rangle_1|-\rangle_2 + \beta|-\rangle_1|+\rangle_2 \qquad (138)$$

In fact, the electron pair in the (singlet) ground state of helium with total spin $S = 0$ forms such an entangled pair with $\alpha = -\beta = 1/\sqrt{2}$. The hallmark of entangled states of the form Eq. (138) is that they cannot be represented as a factorized product in the form of Eq. (137).

The consequences of such quantum correlations are profound: when measuring the spin of particle 1 to be up ($+$), we know with certainty that particle 2 has its spin down ($-$). The "collapse" of the entangled wave function when measuring particle 1 forces particle 2 to switch its spin from a completely undetermined state to a well-defined value. We therefore obtain information about the orientation of spin 2 without actually performing a measurement on this particle. This correlation, often referred to as the *nonlocality of QM*, is a consequence of the probabilistic description and superposition of wave functions in QM. The emergence of a definite physical property or physical reality by "postselection" through the measurement of an entangled state goes even further. For example, the entangled state Eq. (138) with

$\alpha = -\beta = 1/\sqrt{2}$,

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|+\rangle_1|-\rangle_2 - |-\rangle_1|+\rangle_2) \qquad (139)$$

is rotationally symmetric and equally applies when we inquire about the spin orientation along the x rather than along the z axis. If we postselect the spin-up direction ($+$) along the x axis for the first particle, the second particle will have spin down ($-$) along the same axis. If we, instead, measured for the second particle the polarization relative to the z axis as before (Figure 1.14), we would find both spin up and down with 50% probability, and thus a vanishing average spin. Different projection protocols for the first spin imply entirely different results for the second. The emergence of a specific "physical reality" out of a specific measurement context is often referred to as *quantum contextuality* and is unknown in classical physics. It has therefore been questioned whether the quantum mechanical description of a state such as in Eq. (138) can be considered a complete picture of physical reality (Einstein, Podolsky and Rosen, 1935). In particular, it was conjectured that particles may have additional properties that are underlying the quantum-mechanical picture but which are hidden from our view. Such "hidden variables" would ensure that physical systems

have only properties that are "real," that is, independent of a measurement and that the result of any measurement is only dependent on "local" system properties rather than on a remote detection of another observable. The knowledge of "hidden variables" would allow one to remove the probabilistic aspects of QM. The role of probability in QM could then be the same as in statistical mechanics: a convenient way to quantify our incomplete knowledge of the state of a system. The hidden-variable hypothesis, or alternatively, the quantum correlation built into entangled states, Eq. (138), has been probed by testing the violation of Bell's inequality (Bell, 1969; Clauser *et al.*, 1969). Experiments with correlated pairs of particles, in particular photon pairs – for example, by Aspect and coworkers (1982) – have falsified the hidden-variable hypothesis by showing that entangled states can violate Bell's inequality while being in full agreement with the predictions of QM. More recent experiments have succeeded in measuring entangled photons at a distance of several hundred meters apart and with light polarizers (used as photon analyzers), which switch their axes so rapidly that during the photons' time of flight the polarizers have no chance to exchange information on their respective orientation. (The "collapse" of the wave function by measuring one of the two photons occurs instantaneously for both photons, but cannot be used to transmit any information and therefore does not violate the relativistic causality relations.) Even under such stringent conditions, a violation of Bell's inequality by more than 30 standard deviations was observed experimentally (Weihs *et al.*, 1998). Also so-called noncontextual hidden-variable theories and realistic models that assume a certain type

of "nonlocality" are untenable (Hasegawa *et al.*, 2006; Gröblacher *et al.*, 2007).

1.10.2
Quantum Information

The most fundamental unit of information in classical information theory is the so-called bit, which can take on only one of two mutually exclusive values (typically labeled as "0" and "1"). In conventional computers, all numbers and operations with them are encoded in this binary system. The corresponding quantum analog of the bit – named *qubit* – is given by a two-state system with the two states $|+\rangle$ and $|-\rangle$ from Eq. (136), now labeled as $|0\rangle$ and $|1\rangle$. What sets the qubit apart from the conventional classical bit is precisely the ability to be in a coherent superposition of both basis states,

$$|Q\rangle = \alpha|0\rangle + \beta|1\rangle \tag{140}$$

with $|\alpha|^2 + |\beta|^2 = 1$. In quantum information theory, the intrinsic indeterminacy of the qubit's value before a measurement is exploited as a resource rather than treated as a deficiency.

One potential application of qubits is subsumed under the name "quantum computation". The basic building block of a so-called quantum computer would be a number of N entangled qubits that can be in any superposition of 2^N basis states. An example for $N = 2$ is just the maximally entangled pair in Eq. (139). While a collection of N classical bits can only be in a single one of the 2^N possible states at a given time, N qubits can be in any superposition state and thus can clearly have a much higher information content. Owing to the superposition principle, any of the (unitary) logic operations of the

quantum computer performed on the initial state could process all the involved 2^N basis states simultaneously. Several algorithms have been suggested (Shor, 1994; Grover, 1996) for how this inherently quantum feature of "parallel processing" could be used to solve fundamental computational problems much faster, i.e., with much fewer operations than with the corresponding classical computations.

The manipulation of quantum states within the framework of quantum computation and quantum information processing involves a set of rules as, for example, the so-called no cloning theorem (Wootters and Zurek, 1982), which states the impossibility to create identical copies of an arbitrary unknown quantum state. Although only imperfect "clones" of a quantum state are possible, a transfer of a quantum state from one system to a second, possibly distant, system is allowed according to QM. Such a "teleportation" of a quantum state involves the destruction of the original state during the teleportation procedure and is typically performed through an intermediate entangled state of three particles (Bennett *et al.*, 1993; Bouwmeester *et al.*, 1997).

The laws of QM can also be used for secure information transfer. In classical cryptography, secret messages are enciphered by way of a code that the recipient of a message must know in order to decipher a message's content. To prevent the breaking of the code by a third unauthorized party, the key for the encoding algorithm is preferably defined as a random sequence of numbers, which is generated anew for each message transmitted.

Challenges to classical cryptography are the need of a truly random key and the risk of key corruption through the interception by a third party. Both of theses challenges can be met by intrinsic quantum features.

A truly random sequence of numbers can be generated, for example, by repeatedly measuring the spin orientation (or photon polarization) of an unpolarized spin, a situation that may be realized by first projecting the first spin of an entangled pair along a perpendicular direction (see the example of Fig. 1.14 above).

Interception of a message shared with the recipient through an entangled pair by a third party would require a measurement, which leads to a wave function collapse and to a detectable reduction in quantum correlations. Using the principles of QM for the generation and transmission of a secure encryption key – a technique that is referred to as *quantum cryptography* – has been successfully implemented for setups involving very large distances (144 km) between the sender and recipient (Ursin *et al.*, 2007).

1.10.3
Decoherence and Measurement Process

One fundamental obstacle in practically implementing quantum computation and quantum information protocols is the challenge to keep the coherent superposition of a quantum state, in particular of entangled pairs, "alive" for extended periods of time. Any unintentional or intentional interaction of the system inevitably and irreversibly converts the quantum superposition into a classical probability distribution and destroys the operating principle of a quantum information device. The measurement process and the destruction of coherence, frequently called *decoherence*, are closely intertwined. In the early days of quantum theory, the measurement device that caused the "collapse" of the wave function was considered to be a "classical" apparatus decoupled from the quantum dynamics to be observed

(Bohr, 1928). The notion of open quantum systems has superseded this view and provides a widely accepted unified description of measurement and decoherence within the realm of quantum theory. The starting point here is the fundamental insight that the quantum system (S) to be observed is never completely isolated from the environment (E), which itself is quantum rather than classical. The Hamiltonian describing both system and environment is given by $H = H_S + H_E + H_{S-E}$, containing the Hamiltonian of the system (H_S) and its environment (H_E), as well as the interaction between the two (H_{S-E}). A state describing both system and environment, $|\psi\rangle$, even when at the initial time $t = 0$ prepared in a factorizable state, $|\psi(t = 0)\rangle = |\psi_S^i\rangle|\psi_E^j\rangle$, will evolve in the course of time under the influence of the interaction H_{S-E} into an entangled, non-factorizeable state

$$|\psi(t)\rangle = \sum_{i,j} a_{ij}|\psi_S^i\rangle|\psi_E^j\rangle(t) \tag{141}$$

Here, $|\psi_S^i\rangle$ (and $|\psi_E^j\rangle$) are basis states of the system (of the environment), which often, but not always, are eigenstates of the Hamilton operator of the system H_S (of the environment H_E). "Tracing out" the (unobserved) environment degrees of freedom of the entangled state by taking expectation values leads to decoherence in the (observed) system and mimics the effect of a classical measurement device.

Consider, as an illustrative example, a situation in which the system and the environment are each represented by a two-dimensional Hilbert space and described by the following entangled state:

$$|\psi(t)\rangle = \alpha|+\rangle_S|-\rangle_E + \beta|-\rangle_S|+\rangle_E \tag{142}$$

The expectation value of any physical observable represented by an operator A_S acting only on the states in the Hilbert space of the system S gives in the presence of entangled environmental degrees of freedom,

$$\begin{aligned}\langle A_S\rangle &= \langle\psi|A_S|\psi\rangle \\ &= |\alpha|_S^2\langle+|A_S|+\rangle_S \\ &\quad + |\beta|_S^2\langle-|A_S|-\rangle_S \\ &= Tr(\rho A_S)\end{aligned} \tag{143}$$

with $\rho = |\alpha|^2|+\rangle_S {}_S\langle+| + |\beta|^2|-\rangle_S {}_S\langle-|$. It is the coherent entanglement with the environment, Eq. (142), that leads to (partial) decoherence within the system (S) and to a statistical mixture described by the density operator introduced above (Eq. 40) with probabilities $P_+ = |\alpha|^2$ and $P_- = |\beta|^2$. The ubiquitous coupling of a physical system to the environment provides the natural setting for the transition from the quantum indeterminism of superpositions to the definiteness of the classical measurement. The classical limit induced by decoherence is conceptually different from the classical limit of quantum systems of large quantum numbers, which is the focus of semiclassical mechanics (see Section 1.9). In spite of recent progress, it is generally still considered an open question if decoherence concepts alone can fully explain the quantum-to-classical transition and provide definite answers to the widely discussed questions regarding the "quantum measurement problem."

The above considerations demonstrate that it is very unlikely for a macroscopic object such as Schrödinger's cat to ever be in a superposition state "dead and alive" as in Eq. (134) because it is extremely difficult to isolate the cat from its environment. For all practical purposes, an exchange of particles and heat between the cat and

its environment will prevent the cat, for itself, to be in a pure quantum state. It will rather be described by a density matrix with strongly reduced quantum correlations. As both the cat and the environment are macroscopic objects with many degrees of freedom, decoherence sets in at an extremely short timescale. Recent experiments have been able to sufficiently decouple ''mesoscopic'' objects as superconducting rings (Friedman *et al.*, 2000) from their environment to observe these systems in superposition states.

1.11
Relativistic Wave Equations

When the characteristic speed v of particles in a physical system becomes comparable to the speed of light, $v \leq c$, the Schrödinger equation, which incorporates nonrelativistic quantum dynamics, fails. Generalizations to relativistic wave equations face, however, fundamental difficulties due to the possibility of particle creation and destruction in relativistic dynamics (*see* Chapter 2). For example, if photons have energies in excess of twice the relativistic rest energy of electrons, $E_\gamma > 2m_e c^2$, a pair consisting of an electron and its antiparticle, a positron, can be created. Therefore, the interpretation of $|\psi(\mathbf{r})|^2$ as a single-particle probability density is no longer possible. A consistent resolution of the difficulties can be accomplished within the framework of quantum field theory, which is outside the scope of this chapter. The relativistic analogs to the Schrödinger equation discussed in the following section are only applicable to relativistic systems in which particle production and destruction are not yet important.

1.11.1
The Klein–Gordon Equation

We use the same recipe that led us in Section 1.3 to the Schrödinger equation, i.e., we replace the quantities H and $\mathbf{p}$ by differential operators (Eq. 11), motivated by the de Broglie hypothesis. In this case, however, we use the relativistic relation between energy and momentum (*see* Chapter 2) instead of the nonrelativistic one, Eq. (9):

$$E - V(\mathbf{r}) = \sqrt{M^2 c^4 + p^2 c^2} \tag{144}$$

Following this recipe, we are led to

$$i\hbar \frac{d}{dt} \psi(\mathbf{r}, t) = \left[\sqrt{-\hbar^2 \nabla^2 c^2 + M^2 c^4} + V(\mathbf{r}) \right] \psi(\mathbf{r}, t) \tag{145}$$

Equation (145) has a major drawback: it treats the space and time derivatives asymmetrically. The Lorentz invariance of relativistic dynamics requires, however, that space and time coordinates be treated on equal footing. We thus start with the square of Eq. (144) and arrive at

$$\left[i\hbar \frac{\partial}{\partial t} - V(\mathbf{r}) \right]^2 \psi(\mathbf{r}, t) = (-\hbar^2 \nabla^2 c^2 + M^2 c^4) \psi(\mathbf{r}, t) \tag{146}$$

This is the time-dependent Klein–Gordon equation, applicable to particles with integer spin. The corresponding stationary Klein–Gordon equation follows by replacing $i\hbar \partial / \partial t$ by E. Equation (146) gives an eigenvalue equation in E^2 rather than in E itself. Consequently, upon taking the square root of the eigenvalue, solutions with both signs, $\pm\sqrt{p^2 c^2 + M^2 c^4}$, will appear. The physical meaning of negative-energy solutions is discussed

below. For a charged particle with charge q in the presence of an electromagnetic field, both the scalar potential ϕ ($V = q\phi$) and the electromagnetic vector potential $\mathbf{A}$ must be included by "minimum coupling":

$$\mathbf{p} \longrightarrow \mathbf{p} - q\mathbf{A} = \left(\frac{\hbar}{i}\right) \nabla - q\mathbf{A} \qquad (147)$$

With this coupling, the Klein–Gordon equation is invariant under gauge transformations of the electromagnetic field as well as under Lorentz transformations.

1.11.2
The Dirac Equation

Instead of taking the square of Eq. (144), Dirac pursued a different approach in developing a Lorentz-invariant relativistic wave equation. He "linearized" the square root

$$\sqrt{c^2 p^2 + M^2 c^4} \longrightarrow \left(c\,\boldsymbol{\alpha} \cdot \mathbf{p} + \beta M c^2\right) \tag{148}$$

with the subsidiary condition that the square of the linearized operator satisfies

$$\left(c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta M c^2\right)^2 = c^2 p^2 + M^2 c^4 \qquad (149)$$

It turned out that solutions to this equation can be found only if all α_i ($i = x,\ y,\ z$) and β are taken as matrices of minimum dimension 4×4. Equation (149) is satisfied if the matrices α_i, β satisfy the relations

$$\alpha_i \alpha_k + \alpha_k \alpha_i = 2\delta_{ik}$$
$$\alpha_i \beta + \beta \alpha_i = 0 \qquad (150)$$

Accordingly, ψ is now a four-component entity (called a *spinor*), $\psi = \{\psi_i,\ i = 1, \ldots, 4\}$. The resulting Dirac equation describes spin $\frac{1}{2}$ particles. When a charged spin $\frac{1}{2}$ particle interacts with an electromagnetic field as described by minimal coupling, the stationary Dirac equation becomes

$$[E - q\phi(\mathbf{r})]\psi(\mathbf{r})$$
$$= \left[c\boldsymbol{\alpha}\left(\frac{\hbar}{i}\nabla - q\mathbf{A}\right) + \beta M c^2\right]\psi(\mathbf{r}) \tag{151}$$

Dirac spinors permit the probability-density interpretation, that is, $|\psi(x)|^2 = \sum_{i=1}^{4} |\psi_i(x)|^2$. The physical meaning of the four components can be easily understood by considering a free particle. The energy eigenvalues are $E = \pm\sqrt{p^2 c^2 + M^2 c^4}$. In addition to the positive energies we find negative eigenenergies, which are a feature of relativistic quantum mechanics and which result from the fact that the square-root operator permits both the positive and negative sign of E. The four-spinor can be decomposed into two 2-spinors $\psi = (\phi_1,\ \phi_2)$ one of which represents the positive-energy solution and the other the negative-energy solution. Each component of the two-spinor wave function can be understood as a product of a configuration-space wave function $e^{i\mathbf{kr}}$ and a spin 1/2 eigenstate $|m_s = \pm 1/2\rangle$. A major success of the Dirac theory was that the intrinsic degree of an electron spin, which was a mere add-on within the Schrödinger theory, is incorporated into the Dirac equation from the outset. Furthermore, the g factor for the magnetic moment of the electron as well as the spectrum of the hydrogen atom can be derived from the Dirac equation to a very high degree of approximation. The pieces still missing are the quantum electrodynamic (QED) corrections that lead to small energy shifts of atomic levels ("Lamb shift") and the deviations of the g factor for the anomalous magnetic moment from
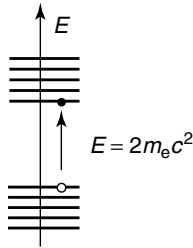
Fig. 1.15 Particle–antiparticle production visualized as the excitation of a negative-energy particle to positive energies leaving behind a hole.

2, $g = 2 \times 1.001\,16$. These corrections can be determined only within quantum field theory, the theory of the interactions of charged particles with the quantized electromagnetic field.

The negative-energy states, according to Dirac, can be interpreted in terms of antiparticle states. The vacuum state of empty space is represented by a fully occupied ''sea'' of negative-energy states. While this ''sea'' itself is not observable, ''holes'' created in the sea by exciting negative-energy electrons to positive energies (Figure 1.15) are observable and appear as antiparticles. For example, a missing electron with charge $-e$, energy $-E$, and momentum $\mathbf{p}$ represents a positron with charge e, energy E, and momentum $-\mathbf{p}$. The negative-energy states of electrons therefore offer a simple explanation of particle–antiparticle pair production in terms of the excitation of a negative-energy particle to a positive-energy state (the particle) leaving a hole in the negative-energy ''sea'' (the antiparticle) behind.

Glossary

Coherence and Decoherence: In QM, the term *coherence* stands for the ability of a particle's state to interfere. Perfectly coherent states (''pure states'') are subject to the superposition principle of QM, whereas imperfections in the coherence are described by a density matrix with (partially) classical correlations. Decoherence stands for the loss of coherence as induced, for example, by coupling an isolated quantum system to its environment.

Correspondence Principle: The principle that quantum-mechanical and classical description of physical phenomena should become equivalent in the limit of vanishing de Broglie wavelength $\lambda \to 0$, or equivalently, of large quantum numbers.

de Broglie Wave: According to de Broglie, the motion of a particle of mass M and velocity v is associated with a matter wave with wavelength $\lambda = h/(Mv)$. h is Planck's quantum.

Delta (δ) Function: A particular case of a distribution, frequently used in quantum mechanics to formulate the orthogonality and normalization conditions of states with a continuous spectrum of eigenvalues.

Distributions: Also called *generalized functions*. Linear-continuous functionals operating on a metric vector space. They form the dual space of the metric vector space. In the context of quantum mechanics, the space is a Hilbert space and the operation of the functional on an element of the Hilbert space is called *formation of a wave packet*.

Eigenvalue Problem: The solution of the eigenvalue equation for the matrix A, $A\psi = \lambda\psi$ where λ is a number called

an *eigenvalue* and ψ is the *eigenvector*. In quantum mechanics, ψ is a vector in Hilbert space.

Entanglement: An intrinsic feature of QM, occurring when particles or subsystems (in either case more than one), are correlated beyond a degree allowed by classical physics. Entangled systems, even when far apart, cannot be described independently of each other.

Hamilton–Jacobi Equation: A particular canonical transformation in classical dynamics that leads to the vanishing of the Hamiltonian function in the new coordinates. The transformation equation for the original Hamiltonian function is called the *Hamilton–Jacobi equation* and is equivalent to equations of motion.

Hilbert Space: Infinite-dimensional complete vector space over the complex numbers endowed with a metric induced by a scalar product that satisfies Schwartz's inequality.

Laser: <u>L</u>ight <u>a</u>mplification by <u>s</u>timulated <u>e</u>mission of <u>r</u>adiation. Modern source for high-intensity coherent electromagnetic radiation in the infrared, visible, and ultraviolet spectral region.

Schrödinger Equation: Fundamental equation governing the dynamics of a nonrelativistic quantum system, playing a similar role in quantum mechanics as do Newton's equations of motion in classical dynamics.

State: A mechanical system is at any given time completely characterized in quantum mechanics by the state ψ. The projection onto coordinate space, $\psi(\mathbf{r})$, is called a *wave function*. States are vectors in Hilbert space.

Superposition Principle: Any superposition in Hilbert space, $\psi = a\psi_1 + b\psi_2$, of two states ψ_1 and ψ_2 forms another physically realizable state of a physical system.

Uncertainty Principle: Two canonically conjugate variables, such as position x and momentum p, can be simultaneously measured only with an intrinsic uncertainty of at least $\Delta x \Delta p \gtrsim \hbar/2$.

Wave Function: The representation of the state $|\psi\rangle$ in coordinate space, $\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle$.

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