Introduction to Quantum Mechanics

4

4.1 The Quantum Concepts

In Chapter 1 we saw that classical mechanics was incapable of explaining the optical spectra emitted by atoms or even the existence of atoms. Bohr developed a model for the atom of hydrogen by assuming the quantization of the angular momentum, which was an introduction to wave or quantum mechanics. Quantum mechanics is a more precise approach to describe nearly all physical phenomena which reduces to classical mechanics in the limit where the masses and energies of the particles are large or macroscopic.

In this section, we will illustrate the success of quantum mechanics through the historically important examples of blackbody radiation, wave-particle duality, the photoelectric effect, and the Davisson and Germer experiment.

4.1.1 Blackbody Radiation

As introduced in Chap. 1, a blackbody is an ideal source of electromagnetic radiation, and the radiated power dependence was depicted as a function of wavelength in Fig. 1.3 for several temperatures of the blackbody.

When the temperature of the body is at or below room temperature, the radiation is mostly in the infrared spectral region, i.e., not detectable by the human eye. When the temperature is raised, the emission power increases, and its peak shifts toward shorter wavelengths as shown in Fig. 1.3. Several attempts to explain this observed blackbody spectrum were made using classical mechanics in the latter half of the nineteenth century, and one of the most successful ones was proposed by Rayleigh and Jeans.

In their classical model, a solid at thermal equilibrium is seen as consisting of vibrating atoms which are considered harmonic electric oscillators which generate standing waves, or modes, through reflections within the cavity. A *continuous*

M. Razeghi, *Fundamentals of Solid State Engineering*,
https://doi.org/10.1007/978-3-319-75708-7_4

spectrum of vibrational mode frequencies $\nu = \omega/2\pi = c/\lambda$ where c denotes the velocity of light and λ the wavelength of the oscillations. These atomic vibrations cause the emission of electromagnetic radiation in a continuous frequency range too. To determine the power radiated, one has to first determine the energy distribution for each frequency. According to the classical law of equipartition of energy, the average energy per degree of freedom for a blackbody in equilibrium is equal to k_bT, where k_b is the Boltzmann constant ($k_b = 8.614 \times 10^{-5}$ eV·K^{-1}) and T the absolute temperature in degrees K. The number of modes per unit volume is the number of degrees of freedom for an electromagnetic radiation.

To calculate this number, a simple model can be used which involves propagating waves in a rectangular box. Only certain frequencies of waves are allowed as a result of boundary conditions at the limits of the box. In addition, there are two possible polarization directions for the waves, corresponding to what are called "TE" and "TM" propagation modes. The total number of modes per unit volume and per unit frequency interval is $\frac{8\pi\nu^2}{c^3}$. Therefore, the distribution of energy radiated by a blackbody per unit volume and per unit frequency interval is $u(\nu, T) = \frac{8\pi\nu^2}{c^3}k_bT$. Considering that this energy is radiated at the speed of light, and by expressing this distribution in terms of wavelength, we get the distribution of power radiated per unit area and per unit wavelength interval as $w(\lambda, T) = \frac{8\pi c}{\lambda^4}k_bT$. Both expressions $u(\nu, T)$ and $w(\lambda, T)$ are called the Rayleigh-Jeans law. This law is illustrated by a dashed line in Fig. 1.3 for $T = 2000$ K. It shows that this classical theory was in reasonably good agreement with experimental observations at longer wavelengths. However, over the short-wavelength portion of the spectrum, there was significant divergence between experiment and theory. This is because we assumed the classical law of equipartition of energy was valid at all wavelengths. This discrepancy came to be known as the "ultraviolet catastrophe" because the integration of the Rayleigh-Jeans law over all frequencies or wavelengths would theoretically lead to an infinite amount of radiated power.

These experimental observations could therefore not be explained until 1901, when Max Planck provided a detailed theoretical explanation of the observed blackbody spectrum by introducing the hypothesis that the atoms vibrating at a frequency v in a material could only radiate or absorb energy in discrete or *quantized* packages proportional to the frequency:

$$E_n = nh\nu = n\hbar\omega \qquad n = 0, 1, 2, \ldots \tag{4.1}$$

where n is an integer used to express the quantization, h is Planck's constant, and $\hbar = h/2\pi$ is the reduced Planck's constant, obtained by matching theory to experiment and is called Planck's constant. This also means that the energy associated with each mode of the radiated electromagnetic field at a frequency ν did not vary continuously (with an average value kT) but was an integral multiple of $h\nu$. Planck then made use of the Boltzmann probability distribution to calculate the average energy associated with each frequency mode. This Boltzmann distribution states that the probability for a system in equilibrium at temperature T to have an energy E is proportional to $e^{-E/kT}$ and can be expressed as:

$$P(E_n) = \frac{e^{-E_n/k_bT}}{\sum\limits_E e^{-E/k_bT}} \tag{4.2a}$$

and is normalized because the total probability after summation over all possible values of E has to be unity. Taking into account the quantization condition in Eq. (4.1), the average energy <E> associated with each frequency mode ν can thus be written as:

$$\langle E \rangle = \sum_{E_n} E_n P(E_n) = \frac{\sum\limits_{n=0}^{\infty} (nh\nu) e^{-nh\nu/k_bT}}{\sum\limits_{n=0}^{\infty} e^{-nh\nu/k_bT}} = \frac{h\nu}{e^{h\nu/kT} - 1}. \tag{4.2b}$$

Therefore, after multiplying by the number of modes per unit volume and frequency $\frac{8\pi\nu^2}{c^3}$, we obtain the distribution of energy radiated by a blackbody at frequency of ν in this model:

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_bT} - 1} \tag{4.2c}$$

This expression is found to be in good agreement with experimental observations. Actually, there is apparently no other physical law which fits experiments with a higher degree of precision. In the limit of small frequencies, or long wavelengths, this relation simplifies into the Rayleigh-Jeans law because we can make the approximation:

$$e^{h\nu/kT} - 1 \approx {}^{h\nu}\!/_{k_bT}$$

We can thus see that the classical equipartition law is no longer valid whenever the frequency is not small compared with k_bT/h. Moreover, this expression shows that high-frequency modes have very small average energy.

This example of the blackbody radiation already shows that, for atomic dimension systems, the classical view which always allows a continuum of energies is incorrect. Discrete steps in energy, or energy quantization, must occur and is a central feature of the quantum approach to real-life phenomena.

4.1.2 The Photoelectric Effect

In 1902, Philipp Lenard studied the emission of electrons from a metal under illumination. And, in particular, he studied how their energy varied with the intensity and the frequency of the light.

A simplified setup of his experiment is schematically depicted in Fig. 4.1. It involved a chamber under vacuum, two parallel metal plates on which a voltage was applied. Light was shone onto a metal plate. The electrons in it were then excited by

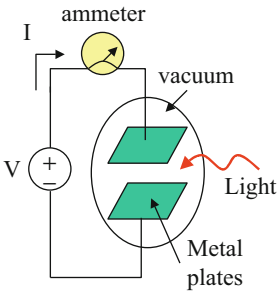


Fig. 4.1 Simplified experimental setup used by Lenard. A chamber in vacuum contains two parallel metal plates on which a voltage is applied. Light shining onto a metal plate gives enough energy to the electrons of the plate to make them leave the plate and be accelerated by the electric field

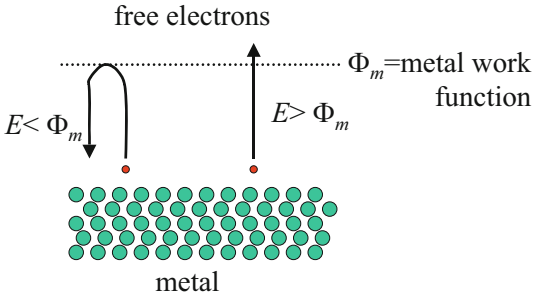


Fig. 4.2 The work function of a metal, denoted Φ_m, is the minimum amount of energy that an electron needs to acquire to leave the metal

this incident light and could gain enough energy to leave the metal surface into the vacuum. This was called the photoelectric effect. These electrons can then be accelerated by the electric field between the metal plate and reach the opposite plate, thus leading to an electrical current that can be measured using a sensitive ammeter.

It was known at the time that there existed a minimum energy, called the metal work function and denoted by Φ_m, which was required to have an electron break free from a given metal, as illustrated in Fig. 4.2. One had to give an energy $E > \Phi_m$ to an electron in order to enable it to escape the attraction of the metal ions.

Example

Q: In the photoelectric effect, the stopping potential V_0, which is the potential required to bring the emitted photoelectrons to rest, can be experimentally determined. This potential is related to the work function Φ_m through $qV_0 = \frac{hc}{\lambda} - \Phi_m$, where λ is the wavelength of the incident photon. For a photon with a wavelength of 2263 Å, incident on the surface of lithium, we experimentally find $V_0 = 3.00$ V. Determine the work function of Li.

A: Using the above formula, we get:

$$\begin{aligned}\Phi_m &= \frac{hc}{\lambda} - qV_0 \\ &= \frac{\left(6.62617 \times 10^{-34}\right)\left(2.99792 \times 10^{8}\right)}{2263 \times 10^{-10}} - \left(1.60218 \times 10^{-19}\right)(3) \\ &= 3.97 \times 10^{-19}\,\text{J} \\ &= 2.48\,\text{eV}\end{aligned}$$

As his light source, Lenard used a carbon-arc lamp emitting a broad range of frequencies and was able to increase its total intensity a thousandfold. With such a powerful arc lamp, it was then possible to obtain monochromatic light at various arbitrary frequencies and each with reasonable power. Lenard could then investigate the photoelectric effect when the frequency of the incident light was varied. To his surprise, he found that below a certain frequency (i.e., certain color), no current could be measured, suggesting that the electrons could not leave the metal any more even when he increased the intensity of light by several orders of magnitude.

In 1905, Albert Einstein successfully interpreted Lenard's results by simply assuming that the incident light was composed of indivisible quanta or packets of energy, each with an energy equal to $h\nu$ where h is Planck's constant and ν is a frequency. He called each quantum a photon. The electrons in the metal could then receive an energy E equal to that of a quantum of light or a photon, i.e., $E = h\nu$. Therefore, if the frequency ν was too low, such that $E = h\nu$ was smaller than Φ_m, the electrons would not have enough energy to escape the metal plate, independently of how high the intensity of light was, as shown in Fig. 4.3. However, if the frequency was high enough, such that $E = h\nu$ was higher than Φ_m, electrons could escape the metal. Albert Einstein won the Nobel Prize in Physics in 1921 for his work on the photoelectric effect.

It is interesting to know that an American experimental physicist, Robert Millikan, who did not accept Einstein's theory, worked for 10 years to show its failure. In spite of all his efforts, he found a rather disappointing result as he ironically confirmed Einstein's theory by measuring Planck's constant to within 0.5%. One consolation was that he did get awarded the Nobel Prize in Physics in 1923 for his experiments!

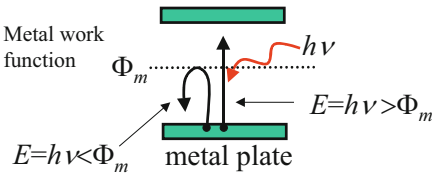


Fig. 4.3 Schematic diagram of the escape mechanism of an electron in the metal plate receiving a photon with energy $h\nu$. If the photon energy is lower than the work function, the electron does not escape. If the photon energy is higher than the work function, the electron receives enough energy to reach the vacuum level and leave the metal

4.1.3 Wave-Particle Duality

The previous discussions on the Bohr atom in Chap. 1, the blackbody radiation and the photoelectric effect, led to the conclusion that the electromagnetic radiation has a quantum nature because it exhibits particle-like properties.

In 1925, Louis de Broglie conjectured that, since the electromagnetic radiation had particle-like properties, particles (e.g., electrons) should have wave-like properties as well. This was called the wave-particle duality. He postulated that a particle with a momentum p can be viewed as a wave with a wavelength given by:

$$\lambda = \frac{h}{p} \tag{4.3}$$

This relation establishes the relationship between a particle and a wave in nature. This concept, as well as the others introduced in the previous examples, clearly proves that classical mechanics was limited and that a new theory was required which would take into account the quantum structure of matter, electromagnetic fields, and the wave-particle duality. In 1927 such a theory was created and called wave or quantum mechanics (Liboff 1998; Davydov 1965).

4.1.4 The Davisson-Germer Experiment

The first complete and convincing evidence of de Broglie's hypothesis came from an experiment that Clinton Davisson and Lester Germer did at the Bell Laboratories in 1926. Using an electron gun, they directed beams of electrons onto a nickel crystal plate from where they were then reflected, as schematically depicted in Fig. 4.4. A sensitive screen, such as a photographic film, was put above the nickel target to get information on the directions in which the electrons reflected most. On it, they observed concentric circular rings, showing that the electrons were more likely to appear at certain angles than others. This was similar to a diffraction pattern and confirmed that these electrons had a wave-like behavior.

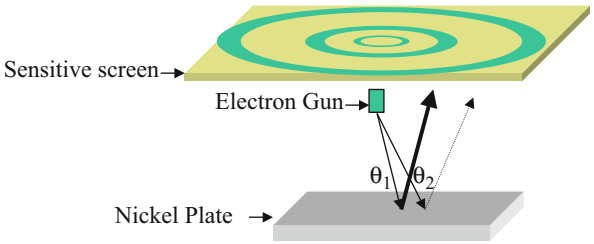


Fig. 4.4 Schematic of the experimental setup in the Davisson-Germer experiment. A beam of electrons is directed on a nickel plate from which the electrons are reflected. They then hit a sensitive screen and create a ring pattern

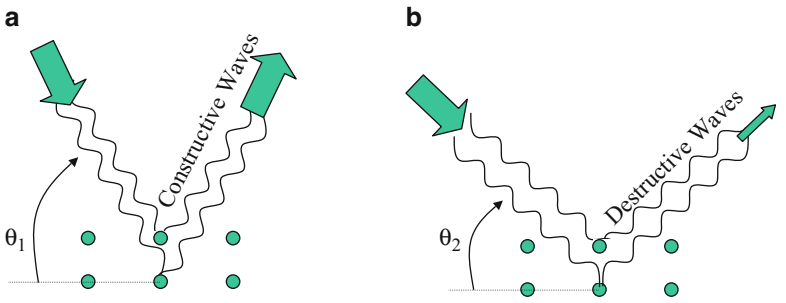


Fig. 4.5 (**a**) Constructive diffraction and (**b**) destructive diffraction condition for the waves reflected from a crystal surface. In the constructive diffraction situation, $2d \sin(\theta) = n\lambda$, where d is the distance between two planes, λ, θ are wavelength and angle to the normal, respectively, n is an integer, the waves are in phase, whereas in the destructive diffraction configuration, the waves have opposite phases

Analyzing the resulting pattern and the geometry of the experiment, in particular the angles of incidence and reflection, they found that the positions of the rings corresponded to angles such that two waves reflected from different atomic layers in the crystal were in phase, i.e., had their phases different by an integer multiple of 360°, as shown in Fig. 4.5a. The darkest areas corresponded to the situations when the reflected waves were out of phase, i.e., their phases were different by an odd integer multiple of 180°, thus canceling each other, as shown in Fig. 4.5b. By quantifying the positions of the rings, Davisson and Germer were able to confirm the de Broglie relation given in Eq. (4.3).

4.2 Elements of Quantum Mechanics

In this section, the essential quantum mechanics formalism and postulates and their mathematical treatment will be introduced. Their purpose will be to provide a general understanding of the behavior of electrons and energy band structures in solids and semiconductors, as discussed in subsequent sections.

4.2.1 Basic Formalism

The contradictions encountered when applying classical mechanics and electrodynamics to atomic processes, e.g., processes involving particles of small masses and at small separation from other particles, could only be resolved through a fundamental modification of basic physical concepts. The formalism which enabled the combining of the particle-like and wave-like properties of matter was created in 1920s by Heisenberg and Schrödinger and was called quantum mechanics, whose basic formalism and postulates we will now review.

1. The state of a system can be described by a definite (in general complex) mathematical function $\Psi(x, y, z, t)$, called the wavefunction of the system, which depends on the set of coordinates (x, y, z) of the quantum system and time t.
2. The wavefunction is a solution of the time-dependent Schrödinger equation (SE):

$$i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t} = H\Psi(x, y, z, t) \tag{4.4a}$$

where the operator H is called the "Hamiltonian" of the system and represents the total energy of the system in the form of mathematical operators. The sum of the kinetic and potential energy operator which make up the Hamiltonian are given by:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(x, y, z, t) \tag{4.4b}$$

Note that the first term represents the kinetic energy of the particle and is a differential operator which acts on the wavefunction. The second term, the potential energy, keeps its classical form. One can think of the action of H on the wavefunction to be one of "measurement" of the total energy of the system.

3. The kinetic energy term is written in terms of the operator ∇^2 which is called the Laplacian and is defined in orthonormal coordinates in three dimensions by:

$$\nabla^2\Psi(x, y, z) = \frac{\partial^2\Psi(x, y, z)}{\partial x^2} + \frac{\partial^2\Psi(x, y, z)}{\partial y^2} + \frac{\partial^2\Psi(x, y, z)}{\partial z^2} \tag{4.4c}$$

$U(x,y,z,t)$ is the potential energy of the system considered, $\hbar$ is Planck's constant, and i is the complex number such that $i^2 = -1$.

The next principle of quantum (SE). Having solved the SE and found the wavefunctions, we have the following properties:

4. The probability that a physical measurement will result in values of the system coordinates in a volume $dxdydz$ around (x, y, z) at a time t is given by $|\Psi(x, y, z, t)|^2 dxdydz$.
5. The sum of the probabilities of all possible values of spatial coordinates of the system must be, by definition, equal to unity:

$$\int |\Psi(x, y, z, t)|^2 dxdydz = 1 \tag{4.5}$$

This equation is the normalization condition for the wavefunction.

4.2.2 General Properties of Wavefunctions and the Schrödinger Equation

The wavefunctions solution of the Schrödinger equation must satisfy a few properties, most of which are direct consequences of the mathematical formalism from which such functions are constructed.

The main property which will be used in the rest of the text is that the wavefunction and its first derivative must be finite, continuous, and single-valued in all space even if the system under consideration contains a surface or interface where the potential $U(x, y, z)$ has a finite discontinuity. But, in the case when the potential becomes infinite beyond this surface, the continuity of the derivative of the wavefunction does not hold anymore. This means that a particle cannot penetrate into a region where an infinite potential exists and therefore that its wavefunction becomes zero there.

Note *In classical physics the state of a system of particles is known when at any given time "t" we know all the spatial coordinates of the particles* $\{\boldsymbol{r}_i(t)\}$ *and all their momenta* $\{\boldsymbol{p}_i(t)\}$. *We can predict completely what is going to happen next when we know all the forces acting on the particles because we know the particles must obey Newton's laws. In principle we can therefore, with the knowledge of an initial state at time* $t = 0$, *compute and predict the exact trajectories that the particles will follow in space and know the momenta at each time. Now consider the difference to quantum, mechanics. In quantum mechanics, all we can possibly know about the system is its wavefunction* $\Psi(x, y, z, t)$ *which is obtainable by solving the Schrödinger equation (SE) given by* Eq. (4.4a). *Solving the SE means solving a differential equation with a given initial condition and only allowing the solutions which satisfy the differentiability and continuity conditions mentioned above. Now let us consider the next set of principles.*

Physical Observables and Measurement Introduction

The next principal of quantum mechanics is that for any physical variable, for example, position, momentum energy, etc., one can associate an operator f which "acts" on a wavefunction, i.e., differentiates, integrates, or simply multiplies it with another function. This operator represents a physical observable. It is like an act of measurement on the system. The mathematical operator in quantum mechanics which represents a physical observable is known and has been extracted by using a procedure which we do not need to discuss at this stage. The most important ones are listed in Table 4.1.

Table 4.1 Examples of common physical quantities and their associated operators

Physical quantity	Operator	Expectation value
x, y, z (coordinates)	x, y, z	$<x> = \int \Psi^* x \Psi dxdydz$
p_x, p_y, p_z (momentum)	$\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}$	$< p_x >= \int \Psi^* \frac{\hbar}{i}\frac{\partial \Psi}{\partial x} dxdydz$
E (energy)	$i\hbar\frac{\partial}{\partial t}$	$< E >= \int \Psi^* i\hbar\frac{\partial \Psi}{\partial t} dxdydz$

Note *In order to proceed further, we are first going to consider situations in which the Hamiltonian of the system does not depend on time. This is the most common situation encountered in practice. It is the situation where we have a closed system and the total energy is conserved. Here we will learn how to extract further information from the solution of the Schrödinger equation and then proceed to some practical examples. At a later stage in* Chap. 10*, we will also consider time-dependent perturbations and return to consider the solutions of the time-dependent Schrödinger equation.*

4.2.3 The Time-Independent Schrödinger Equation

A particular and important situation for the Schrödinger equation is that for a closed system in a time-independent external field. Then, the right-hand side of Eq. (4.4a) does not contain time explicitly. In this case, the states of the system which are described by the wavefunction $\Psi(x, y, z, t)$ are called stationary states, and the total energy of the system is conserved (in time).

Let us now operate on the wavefunction with the energy operator expressed in terms of the time derivative. The action of $i\hbar\frac{\partial}{\partial t}$ on the wavefunction is like asking the question what is the energy of the system? Since we are assuming that energy is a constant, we find that the following relation must be satisfied:

$$i\hbar\frac{\partial\Psi(x, y, z, t)}{\partial t} = E\Psi(x, y, z, t) \tag{4.6}$$

But mathematically this means that the wavefunction $\Psi(x, y, z, t)$ must be a product of a function $\varphi(x, y, z)$ which solely depends on coordinates and an exponential function which depends only on time, such that:

$$\Psi(x, y, z, t) = \varphi(x, y, z)\exp\left(-\frac{i}{\hbar}Et\right) \tag{4.7}$$

This relation follows also directly from the theory of differential equations when the operator $\widehat{H}$ is independent of time. So inserting this expression into the Schrödinger equation in Eq. (4.4a) and eliminating the exponential term on both sides of the equation, we obtain:

$$-\frac{\hbar^2}{2m}\nabla^2\varphi(x, y, z) + U(x, y, z)\varphi(x, y, z) = E\phi(x, y, z) \tag{4.8}$$

which can be rewritten more concisely as:

$$\widehat{H}\,\phi_n = E_n\phi_n \tag{4.9}$$

This last expression is called the time-independent Schrödinger equation. The label "n" denotes the fact that the differential equation can have a spectrum of

solutions each corresponding to an allowed energy state of the system E_n with its corresponding wavefunction ϕ_n. When we know all the wavefunctions ϕ_n, we also know all the possible allowed energy levels of the system. Now we can say that when we measure the energy of the system, we must find the system in one of these eigenstates. We note that when the system is in a stationary state, the time dependence is only a phase factor that means it does not have any effect of the probability distribution. The spatial density is not changing or evolving in time; this is what one would expect.

In the time-independent picture, the total energy operator is $\widehat{H}$ which is also called the Hamiltonian of the system. Even though the total energy of the system does not change with time, the system can be in many different stationary energy states, called eigenstates ϕ_n. Each eigenstate has its own eigenvalue or energy E_n. The action of $\widehat{H}$ is again like an act of measurement of the energy state of the system which can produce, or one also sometimes say forces, the system to adopt an allowed energy state. Once the system has been prepared in an eigenstate φ_n with eigenvalue E_n, it will stay there forever unless it is disturbed by a perturbation which changes its total energy. So in quantum mechanics, and this is indeed fascinating, time may elapse, but the system stays in its eigenstate unless during this elapsing time, it also gets disturbed. So in quantum mechanics, one can say that when one considers a closed system in an eigenstate, time does not elapse for that eigenstate; it does not age, unless something happens which can change the state of the system.

We shall come back to this again later when we consider the "Heisenberg uncertainty principle."

Physical Observables and Measurement

What we did with the energy operator, we can now do with other physical observables. We first recall the following: for any physical variable, for example, position, momentum energy, etc., one can associate an operator f which "acts" on a wavefunction, i.e., differentiates, integrates, or simply multiplies it with another function. Like H the Hamiltonian for the total energy, this operator represents a physical observable. The most important ones are listed in Table 4.1. Every physical observable, or what is now operator, has a set of eigenfunctions and corresponding eigenvalues. Thus the operator $\widehat{f}$, for example (hat denotes that it is an operator), acting on the allowed wavefunction produces a number f_f or "eigenvalue." The eigenvalue corresponds to a possible value of the observable, when the wavefunction on which it operates is an "eigenstate" or also called "eigenfunction" of this operator, in other words if it satisfies the so-called eigenvalue equation:

$$\vec{f}\,\phi_f = f_f \phi_f \tag{4.10}$$

We say ϕ_f is an eigenfunction of $\widehat{f}$ and f_f, the corresponding eigenvalue. Eigenfunctions belonging to different eigenvalues are orthogonal; this means that their inner product is equal to 1 when the wavefunctions belong to the same eigenvalue, and 0 otherwise, or mathematically expressed:

$$\int dxdydz\phi_{f_1}^*(x,y,z)\phi_{f_2}(x,y,z) = \delta_{f_1 f_2} \tag{4.11}$$

Another property is that eigenfunctions of physical observables form a complete set. This means that they can be regarded as an infinite set of vectors which span the so-called Hilbert space such that any function χ can be represented as a linear combination of these eigenfunctions:

$$\chi(x,y,z) = \sum_f a_f \phi_f(x,y,z) \tag{4.12a}$$

Operators which are physical observables must have the property that the expectation value of the operator is a real number. Such operators are called Hermitian operators. For Hermitian operators it follows that the so-called matrix element of an operator f taken between two different eigenstates:

$$f_{ij} = \int d\ \vec{r}\ \Phi_i^* f \Phi_j \tag{4.12b}$$

satisfies the relation $f_{ij} = (f_{ji})^*$.

What we said about physical observables includes of course also the total energy operator $\widehat{H}$. The eigenstates of energy φ_n form a complete set and are orthogonal. Operators can have simultaneous eigenstates but not always. For example a free particle moving unhindered in space has eigenstates of momentum and energy which are the same functions. A particle moving in a box has energy eigenstates, but not momentum eigenstates. We shall see this later more clearly when we solve these problems explicitly.

Admixture of States

Let us imagine we have prepared the system in a stationary state or eigenstate. Then at some time later, it is disturbed by a perturbation which constitutes necessarily a time-dependent change, for example, a light pulse. The system no longer stays in its eigenstate but now goes into an admixture of eigenstates such as:

$$\Psi(x,y,z,t) = \sum_n a_n \varphi_n(x,y,z).\exp\left(-\frac{i}{\hbar}E_n t\right) \tag{4.13}$$

6. The system need not be in a pure state anymore or eigenstate of an observable; it can be in a superposition of such states. In which case if one undertook a measurement, one would find it in any one of the combination of such states as in Eq. (4.13). This leads us to the next definition.
7. The mean value or expectation value of a physical quantity represented by an operator f is what is measured experimentally, is denoted $<\widehat{f}>$, and is given by:

$$<\widehat{f}>= \int \Psi(x,y,z,t)^* f \Psi(x,y,z,t) dxdydz \tag{4.14}$$

where $\Psi(x,y,z,t)$ is the wavefunction of the system considered and $(\ldots)^*$ stands for complex conjugate. Thus if:

$$\Psi(x,y,z,t) = c_{f1}\Psi_{f1}(x,y,z,t) + c_{f2}\Psi_{f2}(x,y,z,t) \tag{4.15}$$

the expectation value $<\widehat{f}>$ is given by:

$$<\widehat{f}>= \left|c_{f1}\right|^2 f_1 + \left|c_{f2}\right|^2 f_2 \tag{4.16}$$

Examples of physical quantities, their associated operators, and expectation values are given in Table 4.1.

Thus one can interpret $|c_{f1}|^2$, $|c_{f2}|^2$ as the probability of finding the particle in the state f_1 and f_2, respectively, and indeed we must also have $|c_{f1}|^2 + |c_{f2}|^2 = 1$.

The problem one is confronted with after the system has been disturbed is to find the coefficients a_n of admixtures in the sum given by Eq. (4.13). This is done by solving the time-dependent Schrödinger equation in the presence of the disturbance and with given initial conditions as shown in Chap. 10.

4.2.4 The Heisenberg Uncertainty Principle

This very important principle says that one of the consequences of quantum mechanics is that one cannot have absolute knowledge of time and energy simultaneously and that this is not a theoretical abstraction but an experimental fact which is verified every day. One of the Heisenberg uncertainty principles (HUP) is therefore:

$$\Delta E \Delta t \sim \hbar \tag{4.17}$$

In other words if one knows the energy E to great accuracy, then one has a large uncertainty Δt, in time t and vice versa. Let us immediately apply this to a stationary state in energy, where clearly by definition, we know the energy level of the particle with absolute accuracy. The meaning of Eq. (4.17) is that in this case, we can say nothing about the time. Indeed the time dependence of the wavefunction as shown by Eq. (4.7) is only a phase, which has no consequence on the probability distribution, for example. Indeed, as we pointed out before, when in an eigenstate of energy, the particle does not evolve in time. It stays in that same energy level until it is disturbed by some perturbation. The perturbation makes the Hamiltonian change in time, and this allows the particle to admix with other eigenstates of different energy, which is the same thing as saying that the system can now evolve in time. The HUP also applies to momentum and space. If one knows the absolute position of a particle in space, then one cannot say anything about its momentum and vice versa, so we also have:

$$\Delta p_\mu \Delta r_\mu \sim \hbar \tag{4.18}$$

where p_μ; r_μ are x,y,z components of momentum space, respectively. We shall see later in more detail that one of the consequences of this rule is that a particle which is confined to a finite size box cannot have zero average momentum or kinetic energy.

4.2.5 The Dirac Notation

A convenient way of writing eigenstates and matrix elements or wavefunction overlap integrals was invented by Dirac. Here are some examples of the *Dirac notation* from which one can deduce the structure:

$$\begin{aligned} &\Psi_n\left(\vec{r}\right) \rightarrow |n\rangle \\ &\Psi_{n,k}\left(\vec{r}\right) \rightarrow |n,k\rangle \\ &\int_{-\infty}^{\infty} d\ \vec{r}\ \Psi_n^* \widehat{A} \Psi_m = \left\langle n \middle| \widehat{A} \middle| m \right\rangle \end{aligned} \tag{4.19}$$

In Eq. (4.19), the right-hand side $|m\rangle$ is called the "Ket vector." The left-hand side $\langle n|$ is called the "Bra vector." When one considers the expectation value of the product of two operators, one can expand over a complete set of eigenstates and write (m,l are arbitrary indices):

$$\left\langle n \middle| \widehat{A}\widehat{B} \middle| n \right\rangle = \int \Psi_n^* \widehat{A}\widehat{B}\, \Psi_n d\ \vec{r} = \sum_m \left\langle n \middle| \widehat{A} \middle| m \right\rangle \left\langle m \middle| \widehat{B} \middle| n \right\rangle \tag{4.20}$$

$$\sum_m |m\rangle\langle m| = 1 \tag{4.21}$$

The operator $P_m = |m\rangle\langle m|$ is called a projection operator because it projects a wavefunction onto a "part" or component of that wavefunction, i.e., it tells us how much of the state ϕ_m is in the wavefunction Ψ:

$$P_m \Psi = \langle m||\Psi\rangle|m\rangle = \phi_m\left(\vec{r}\right) \int d\ \vec{r}\ \phi_m^* \Psi \tag{4.22}$$

Assuming, as must be generally true, that the wavefunction must be in a linear combination of a complete set of basis states or eigenvectors:

$$\Psi = \sum_l a_l |l\rangle = \sum_l a_l \phi_l \tag{4.23}$$

Then it follows by substituting Eq. (4.23) into Eq. (4.22) using the orthogonality of the ϕ_m, and taking the sum, that the total projection reproduces the wavefunction again:

$$\sum_m P_m \Psi = \sum_m \langle m||\Psi\rangle|m\rangle = \sum_m \phi_m(\vec{r}) \int d\,\vec{r}\;\Psi^* \phi_m = \sum_m a_m \phi_m = \Psi \quad (4.24)$$

4.2.6 The Heisenberg Equation of Motion

There is a way of describing the relationship between operators and the time dynamics in quantum mechanics which is very elegant and most useful and called the equation of motion approach. To get there we first recall that the time-dependent Schrödinger equation can be written as:

$$i\hbar \frac{\partial \Psi(x,y,z,t)}{\partial t} = \widehat{H}\;\Psi(x,y,z,t) \quad (4.25)$$

And that the expectation value of an operator $\widehat{A}$ is by definition:

$$<\widehat{A}> = \int \Psi(x,y,z,t)^*\;\widehat{A}\;\Psi(x,y,z,t)dxdydz \quad (4.26)$$

Now consider how this expectation value changes with time, i.e., its time derivative:

$$\begin{aligned} \frac{d}{dt}<\widehat{A}> &= \int \frac{\partial}{\partial t}\Psi(x,y,z,t)^*\;\widehat{A}\;\Psi(x,y,z,t)dxdydz \\ &+ \int \Psi(x,y,z,t)^*\;\widehat{A}\;\frac{\partial \Psi}{\partial t}dxdydz \end{aligned} \quad (4.27)$$

The right-hand side is also in Dirac notation:

$$\frac{d<\widehat{A}>}{dt} = \frac{i}{\hbar}\langle\Psi|\;\widehat{H}\widehat{A} - \widehat{A}\widehat{H}\;|\Psi\rangle \quad (4.28)$$

$$\left[\widehat{H},\widehat{A}\right] = \widehat{H}\widehat{A} - \widehat{A}\widehat{H} \quad (4.29)$$

where the last line is, by definition, the commutator and written as:

$$\frac{d<\vec{A}>}{dt} = \frac{i}{\hbar}\left[\widehat{H},\widehat{A}\right] \quad (4.30)$$

which is called the equation of motion of the operator $\widehat{A}$ and is equivalent to the statement that if the operator commutes with the Hamiltonian, then it is a constant of the motion, which means it does not depend on time. The statement is that the

eigenstates of $\widehat{H}$ are also eigenstates of $\widehat{A}$. One interesting and very important result is, also, that one can define the time derivative of an operator by using the commutator with the Hamiltonian. For example, the velocity operator is indeed:

$$\frac{d\widehat{x}}{dt} = \frac{i}{\hbar}\left[\widehat{H}, \widehat{x}\right] \tag{4.31}$$

For a free particle Hamiltonian, one can check that the right-hand side of Eq. (4.31) is indeed $-i\hbar\frac{1}{m}\frac{\partial}{\partial x}$. Equation (4.31) is of great significance in theoretical physics and has no direct analogy in classical physics; it only has a formal analogue called the Poisson Bracket. In quantum mechanics, Eq. (4.31) is, in particular, a statement that the velocity operator depends on the structure of the Hamiltonian and is not always just given (x-direction) by the operator $-i\hbar\frac{1}{m}\frac{\partial}{\partial x}$. For example, when there are spin-orbit forces or magnetic fields involved, then the velocity operator involves also spin-dependent or magnetic field-dependent terms (we shall see this later in Chap. 5 and also again in Chap. 12). This has no simple analogue in classical physics. Processes or terms contained in $\widehat{H}$ which act on the position of the particle, and therefore do not commute with it, do not just give new energy levels but also give rise to new contributions to the definition of the velocity operator itself. Note that using Eq. (4.31), we can also define acceleration operators, for example, a_x where $a_x = \frac{i}{\hbar}[H, v_x]$. Equation (4.31) is the right and generally valid way of identifying the velocity operator in quantum mechanics. We shall see later that in magnetic field, the velocity operator is different from the free particle form given in Table 4.1; it has an extra term which depends on the field.

4.3 Discussion

As a first summary we note that whereas in classical mechanics one can in principle know energy, position, momentum, and time of a system simultaneously and with absolute accuracy, the same is not true in quantum mechanics. In quantum mechanics one can only at best know the wavefunctions which are the solutions of the Schrödinger equation (SE). Everything that can be known about the system must be deduced from the wavefunctions. This includes the probability distribution in space and the expectation value of the physical observables. Thus in quantum mechanics, the totality of solutions of the SE as we have seen form a complete set; in other words, the system can under all circumstances be found in a linear superposition of this complete set of eigenfunctions, each one belonging to an eigenvalue of energy. Similarly the thermal average of a physical observable $\widehat{A}$ is given by the generalized form of the Boltzmann distribution $<\widehat{A}>= \frac{\sum_n e^{-E_n/k_bT} A_{nn}}{\sum_n e^{-E_n/k_bT}}$ which involves the expectation values of the operator "$\widehat{A}$" A_{nn} over all the eigenstates of energy labeled by n. Unlike in classical mechanics where physical variables are defined irrespective

of the fact that they can be measured or not, in quantum mechanics, only measurable parameters are meaningful. These are the physical observables, and each one has its own operator representation. Measuring the value of a physical observable means calculating the expectation value of the operator, given that one has the wavefunction of the system. If the system is in a pure state, in other words in an eigenstate, then the outcome of this operation, or act of measurement, is the corresponding eigenvalue. In general, however, the system is in a superposition of eigenstates, and the outcome of the measurement is the weighted superposition as given by Eq. (4.13).

Note *The notion that in quantum mechanics, and thus in natural sciences, only measurable parameters are meaningful is also of deep philosophical significance, and the student should think about it carefully.*

4.4 Simple Quantum Mechanical Systems

4.4.1 Free Particle

The simplest example of solution of the Schrödinger equation is for a free particle of mass m and energy E, without external field and thus with a constant potential energy which can then be chosen to be zero $U(x, y, z) = 0$. For further simplicity, we can restrict the mathematical treatment to the one-dimensional time-independent Schrödinger equation. Eq. (4.8) can then be simplified to:

$$\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + E\Psi(x) = 0 \tag{4.32}$$

The solution of Eq. (4.32) which happens to be an eigenstate of both energy and momentum is:

$$\Psi(x) = Ae^{ikx} \tag{4.33}$$

where A is a constant and $k = \frac{2\pi}{\lambda}$ is the wavenumber. By applying the x-momentum operator on the right-hand side of Eq. (4.33), one can see that this state corresponds to a free particle state moving in the positive x-direction with momentum $\hbar k$. Replacing the expression of the wavefunctions into Eq. (4.32), one obtains:

$$-\frac{\hbar^2 k^2}{2m}\Psi(x) + E\Psi(x) = 0 \tag{4.34}$$

which has a nonzero solution for $\Psi(x)$ only if:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{h^2 k^2}{8\pi^2 m} \tag{4.35}$$

or conversely:

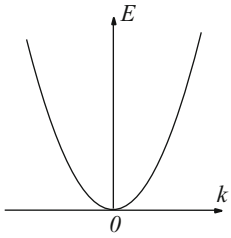


Fig. 4.6 The energy-momentum relationship for a free particle has a parabolic shape

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{4.36}$$

and is plotted in Fig. 4.6. The particle momentum, as defined also by the expectation value, can be expressed in quantum mechanics as:

$$\langle p \rangle = \hbar k \tag{4.37}$$

The energy of the free particle depends therefore on its momentum as $E = \frac{\langle p \rangle^2}{2m}$, which is analogous to the case in classical mechanics. We can think of the system as very large and of size 2 L $\{-L, L)$, as L becomes infinite, so that the normalization constant A is given by $A = \sqrt{\frac{1}{2L}}$.

4.4.2 Degeneracy

The eigenstates with + and –k have the same energy; one says that the level k is twofold degenerate. Whenever an energy eigenstate has more than one quantum number which gives the same energy, one says that the level is degenerate.

4.4.3 Particle in a 1-D Box

Another simple and important illustration of quantum mechanics concepts can be obtained by considering a particle whose motion is confined in space. For simplicity, the analysis will be conducted in one dimension. It involves a particle of mass m and an energy E which evolves in a potential $U(x)$, shown in Fig. 4.7.

This potential can be mathematically expressed such that:

$$\begin{cases} U(x) = \infty & \text{for } x < 0 \text{ and } x > a \\ U(x) = 0 & \text{for } 0 < x < a \end{cases} \tag{4.38}$$

In such a potential, the properties of the wavefunctions and Schrödinger equation lead us to:

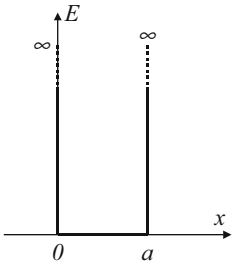


Fig. 4.7 Potential energy corresponding to the 1-D box

$$\begin{cases} \Psi(x) = 0 & \text{for } x < 0 \text{ and } x > a \\ \dfrac{\hbar^2}{2m}\dfrac{d^2\Psi(x)}{dx^2} + E\Psi(x) = 0 & \text{for } 0 < x < a \end{cases} \tag{4.39}$$

which means that the solution $\Psi(x)$ inside the box has the same expression as for the free particle in Eq. (4.33) and can be rewritten as the sum of *sin* and *cos* functions for simplification:

$$\Psi(x) = A\sin(kx) + B\cos(kx) \tag{4.40}$$

but with the boundary conditions:

$$\Psi(0) = \Psi(a) = 0 \tag{4.41}$$

Expressing these conditions using Eq. (4.40), we get, with $k = \frac{2\pi}{\lambda}$:

$$\begin{cases} B = 0 \\ A\sin(ka) = 0 \end{cases} \tag{4.42}$$

Since the wavefunction cannot be identically zero in the entire space, the following condition must be satisfied:

$$\sin(ka) = 0 \text{ or } k = k_n = n\frac{\pi}{a} \quad \text{where } n \text{ is an integer equal to } \pm 1, \pm 2, \ldots$$

Consequently, in contrast to the free particle case, not all values of the wavenumber k are allowed, but only discrete values are allowed. n can also be viewed as a quantum number of the system. Using Eq. (4.42), we can see that the energy of a particle in a 1-D box is also quantized:

$$E_n = n^2\frac{\hbar^2\pi^2}{2ma^2} \tag{4.43}$$

One can see that when $a \to \infty$, the spacing between the quantized energy levels tends toward zero and a quasi-continuous energy spectrum is achieved, as for a free particle. Nevertheless, the energy levels remain strictly discrete (this is why we talk

about a "quasi"-continuous energy spectrum). Combining Eq. (4.40) and Eq. (4.42), we can write the wavefunction as:

$$\Psi_n(x) = A \sin\left(\frac{n\pi x}{a}\right) \tag{4.44}$$

The value of A can be computed by substituting this expression into the normalization condition expressed in Eq. (4.5). One easily finds that:

$$A = \sqrt{\frac{2}{a}} \tag{4.45}$$

so that the complete analytical expression of the wavefunction solution of the infinite potential well problem is:

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \tag{4.46}$$

These functions consist of standing waves as depicted in Fig. 4.8b. One can think of the particle in a 1-D box as bouncing on the walls of the box and the probability of finding a particle at x in the box is shown in Fig. 4.8c.

* Unlike the free particle case, the eigenstates of energy are no longer eigenstates of momentum. Operating with $-i\hbar\frac{\partial}{\partial x}$ on Eq. (4.46) does not give back the same function. Classically the particle is bouncing from the sides of the box and keeps on changing its momentum. The expectation value of the momentum can be evaluated as usual from Eq. (4.26) and can be verified to be zero.

Example

Q: Find the energy levels of an infinite quantum well that has a width of $a = 25$ Å.

A: The energy levels are given by the expression $E_n = n^2 \frac{\hbar^2\pi^2}{2m_0a^2}$, where m_0 is the free electron rest mass. This gives numerically:

$$\begin{aligned} E_n &= n^2 \frac{\left(1.05458 \times 10^{-34}\right)^2 \pi^2}{2\left(0.91095 \times 10^{-30}\right)\left(25 \times 10^{-10}\right)^2} \\ &= 9.63n^2 \times 10^{-21}\,\text{J} \\ &= 0.060n^2\,\text{eV} \end{aligned}$$

4.4.4 Particle in a Finite Potential Well

The infinite-potential analysis conducted previously corresponds to an unrealistic situation, and a finite potential well is more appropriate. Under these conditions, the potential in the Schrödinger equation is shown in Fig. 4.9 and mathematically expressed as:

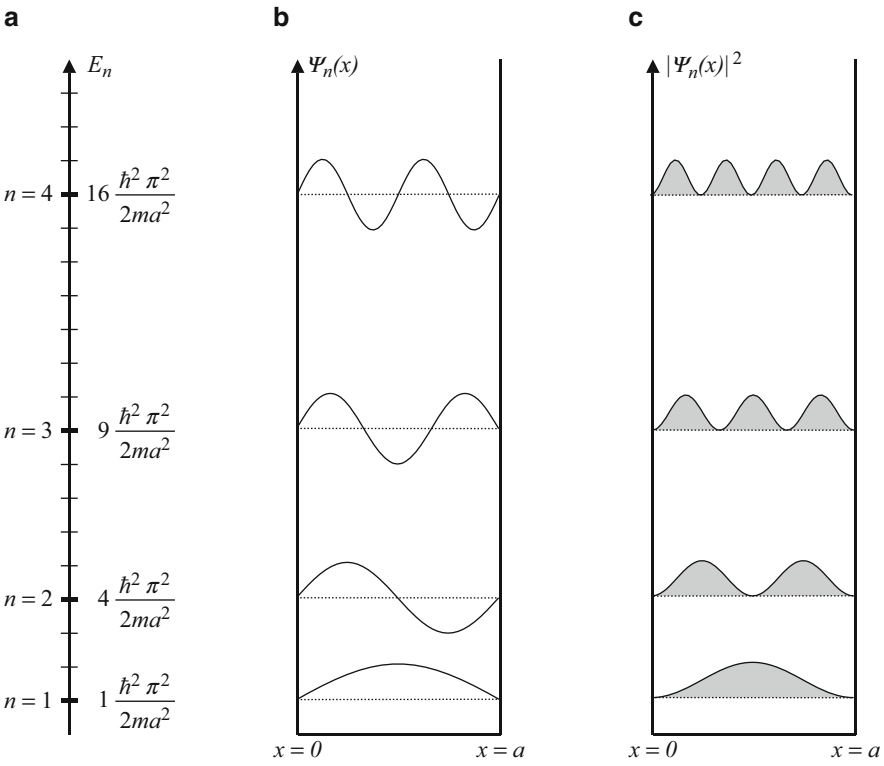


Fig. 4.8 (**a**) Energy levels, (**b**) wavefunctions $\Psi(x)$, and (**c**) $|\Psi(x)|^2$ which is proportional to the probability of finding a particle at a position x in a 1-D quantum box, for the first four allowed levels

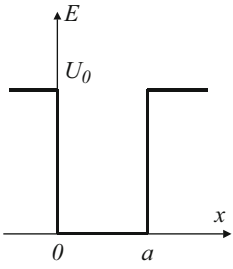


Fig. 4.9 Potential energy in a finite potential well

$$\begin{cases} U(x) = U_0 > 0 & \text{for } x < 0 \text{ and } x > a \\ U(x) = 0 & \text{for } 0 < x < a \end{cases} \tag{4.47}$$

In such a potential, the properties of the wavefunctions and Schrödinger equation lead us to:

$$\begin{cases} \dfrac{\hbar^2}{2m}\dfrac{d^2\Psi(x)}{dx^2} + (E - U_0)\Psi(x) = 0 & \text{for } x < 0 \text{ and } x > a \\ \dfrac{\hbar^2}{2m}\dfrac{d^2\Psi(x)}{dx^2} + E\Psi(x) = 0 & \text{for } 0 < x < a \end{cases} \tag{4.48}$$

We see that two distinct cases must be considered when solving this system of equations. The first one is when $0 < E < U_0$ and the other is when $U_0 < E$.

In the case of $0 < E < U_0$, Eq. (4.48) can be rewritten as:

$$\begin{cases} \dfrac{d^2\Psi(x)}{dx^2} - \alpha^2\Psi(x) = 0 & \text{for } x < 0 \text{ and } x > a \\ \dfrac{d^2\Psi(x)}{dx^2} + k^2\Psi(x) = 0 & \text{for } 0 < x < a \end{cases} \tag{4.49}$$

by defining:

$$\begin{cases} \alpha = \sqrt{\dfrac{2m(U_0 - E)}{\hbar^2}} \\ k = \sqrt{\dfrac{2mE}{\hbar^2}} \end{cases} \tag{4.50}$$

The general solution to Eq. (4.49) is then:

$$\begin{cases} \Psi_-(x) = A_- e^{\alpha x} + B_- e^{-\alpha x} & \text{for } x < 0 \\ \Psi_0(x) = A_0 \sin(kx) + B_0 \cos(kx) & \text{for } 0 < x < a \\ \Psi_+(x) = A_+ e^{\alpha x} + B_+ e^{-\alpha x} & \text{for } x > a \end{cases} \tag{4.51}$$

The boundary conditions include the finite nature of $\Psi(x)$ for $x \to \infty$ and $x \to -\infty$, the continuity of $\Psi(x)$, and its first derivative $\frac{d\Psi(x)}{dx}$ at points $x = 0$ and $x = a$, which can all be mathematically summarized as:

$$\begin{cases} \Psi_-(-\infty) = 0 & \Psi_+(+\infty) = 0 \\ \Psi_-(0) = \Psi_0(0) & \Psi_0(a) = \Psi_+(a) \\ \dfrac{d\Psi_-}{dx}(0) = \dfrac{d\Psi_0}{dx}(0) & \dfrac{d\Psi_0}{dx}(a) = \dfrac{d\Psi_+}{dx}(a) \end{cases} \tag{4.52}$$

Utilizing Eq. (4.52), we obtain:

$$\begin{cases} A_+ = B_- = 0 & \\ A_- = B_0 & A_0 \sin(ka) + B_0 \cos(ka) = B_+ e^{-\alpha a} \\ \alpha A_- = k A_0 & k A_0 \cos(ka) - k B_0 \sin(ka) = -\alpha B_+ e^{-\alpha a} \end{cases} \tag{4.53}$$

From these equations, we see that B_0 can be easily expressed in terms of A_0, and we thus obtain two equations involving only B_+:

$$\begin{cases} A_0\left[\sin(ka)+\dfrac{k}{\alpha}\cos(ka)\right]-B_+[e^{-\alpha a}]=0 \\ A_0\left[k\left(\cos(ka)-\dfrac{k}{\alpha}\sin(ka)\right)\right]+B_+[\alpha e^{-\alpha a}]=0 \end{cases} \tag{4.54}$$

A nonzero solution for A_0 and B_+, and thus a nonzero wavefunction, is possible only if:

$$\left(k^2-\alpha^2\right)\sin(ka)-2\alpha k\cos(ka)=0 \tag{4.55}$$

This condition can be rewritten into:

$$\tan(ka)=\frac{2\alpha k}{k^2-\alpha^2} \tag{4.56}$$

By introducing the constants:

$$\begin{cases} \alpha_0=\sqrt{\dfrac{2mU_0}{\hbar^2}} \\ \zeta=\dfrac{E}{U_0} \qquad (0<\zeta<1) \end{cases} \tag{4.57}$$

we can first rewrite Eq. (4.50) as:

$$\begin{cases} \alpha=\alpha_0\sqrt{1-\zeta} \\ k=\alpha_0\sqrt{\zeta} \end{cases} \tag{4.58}$$

and therefore:

$$\tan\left(a\alpha_0\sqrt{\zeta}\right)=\frac{2\sqrt{\zeta(1-\zeta)}}{2\zeta-1} \tag{4.59}$$

The only variable in Eq. (4.58) is ζ, and any value that satisfies leads to a value of E, k, and α and thus a wavefunction $\Psi(x)$ solution of the Schrödinger equation for the finite potential well problem in the case $0<E<U_0$.

Eq. (4.58) is easiest solved graphically. For example, Fig. 4.10 shows a plot of the two functions on either side of Eq. (4.58). The intersection points correspond to values of ζ which satisfy Eq. (4.58), and the number of intersection points is the number of bound states (i.e., wavefunction and energy level) in the finite potential well. In the example depicted in Fig. 4.10, there are two solutions. As the well potential U_0 increases, α_0 increases as defined by Eq. (4.57), and thus, a higher number of tangent function branches can be fitted for ζ between 0 and 1 (left-hand

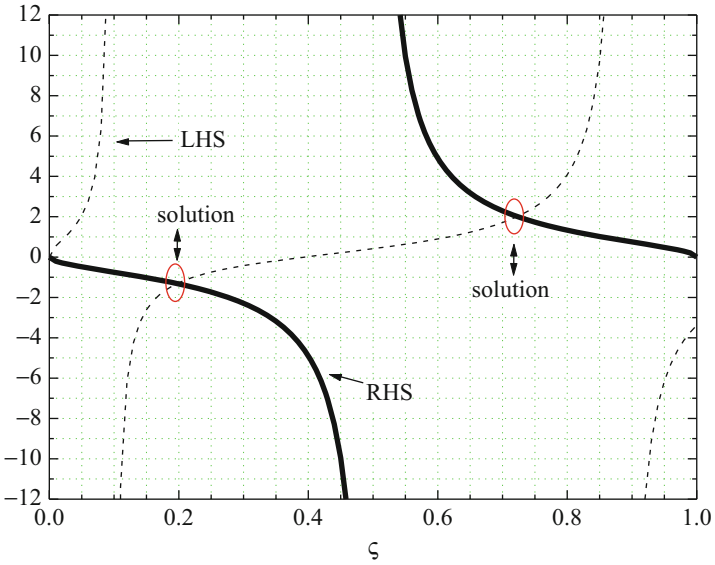


Fig. 4.10 Graphical representations of the functions on the left-hand side (LHS) and right-hand side (RHS) of Eq. (4.59), shown in dashed and solid lines. The intersections between these curves yield the solutions of the finite potential well problem

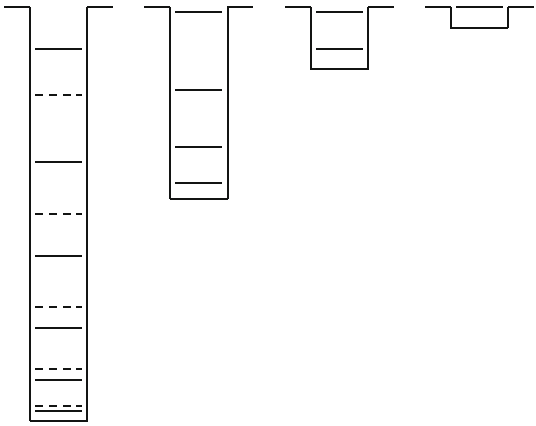


Fig. 4.11 Quantized energy levels in a finite potential well (solid lines) as a function of potential well depth. For comparison, the energy levels of the infinite well case are shown in dashed lines for the quantum well on the left

side of Eq. (4.59)). Consequently, the number of intersections solutions for ζ increases too, which means that there are more bound states in the well. This is schematically shown in Fig. 4.11. This can be understood intuitively because one can "fit" more bound states as the depth of the well increases.

Because there is only a discrete number of values for ζ, there is also a discrete number of energy values E, i.e., the energy levels are quantized similar to the infinite well potential case. In addition, the quantized values of energy here are found to be

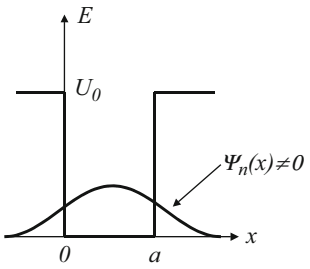


Fig. 4.12 Illustration of the tunneling effect in a finite potential well. The wavefunction is nonzero outside the potential well. This means that there exists a nonzero probability of presence for an electron outside the potential well is even when its energy E is lower than the potential barrier height U_0

lower than those in the infinite well potential case, as shown with the dashed lines in Fig. 4.11.

In addition to the quantization of energy levels, there is another important quantum concept illustrated by the finite potential well: the phenomenon of tunneling. Indeed, a nonzero wavefunction exists in the regions $x < 0$ and $x > a$, which means that the probability of finding a particle there is nonzero. In other words, even if a particle has an energy E lower than the potential barrier U_0, it has a nonzero probability of being found beyond the barrier. This is schematically shown in Fig. 4.12.

In the case of $E > U_0$, the solution of Eq. (4.49) can again as before be written as a sum of a cosine and sine term, for each of the regions defined by Eq. (4.51). Another more elegant way to represent the solution is as a sum of two plane waves, one going to the left and the other to the right. The two plane waves have different wavenumber k. The boundary conditions include the continuity of the wavefunction $\Psi(x)$ and its first derivative $\frac{d\Psi(x)}{dx}$ at points $x = 0$ and $x = a$. Along with the normalization condition expressed in Eq. (4.11), one can analytically determine the wavefunction. This analysis would lead to the same result as for a free particle, that is, there is a continuum of energy states $E > U_0$ allowed.

4.5 Discussion

In this chapter, we have shown the limitations of classical mechanics and the success of quantum mechanics. The basic concepts and formalism of quantum mechanics have been exposed, including the quantized nature of the electromagnetic field, the wave-particle duality, the probability of presence of a particle, the wavefunction, and the Schrödinger equation. Simple quantum mechanical systems have been analyzed to understand these novel major aspects associated with quantum mechanics have been discussed, including the quantization of energy levels and momenta and tunneling effects.

4.6 The Harmonic Oscillator

Recall from classical mechanics the motion of a particle moving in a one-dimensional force field which is linear in the displacement x with force constant K. Newton's law gives:

$$m\frac{d^2x}{dt^2} = -Kx \tag{4.60}$$

We solve this differential equation by noting that the solution is a simple sine function where:

$$x(t) = A\sin\omega_0 t \tag{4.61}$$

$$\omega_0^2 = \frac{K}{m} \tag{4.62}$$

The total energy is:

$$E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}Kx^2 \tag{4.63}$$

and constitutes the classical Hamiltonian of the Harmonic oscillator problem. In quantum mechanics we can rewrite the Hamiltonian by making use of the definition of the momentum operator and keeping the potential energy as it is, to obtain:

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{K}{2}x^2 \tag{4.64}$$

In order to obtain the energy levels and eigenfunctions of the harmonic oscillator, we have to solve the Schrödinger equation:

$$H\Psi_n = \left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{K}{2}x^2\right\}\Psi_n = E_n\Psi_n \tag{4.65}$$

For the mathematician this is a well-known differential equation which was solved long before the ideas of quantum mechanics were developed. We shall therefore here also treat it as a mathematical problem. More detailed developments can be found in specialized textbooks. The solution of Eq. (4.65) can be written with $\varsigma = \sqrt{\frac{m\omega_0}{\hbar}}x$:

$$\Psi_n = A_n H_n(\varsigma)\exp\left[-\frac{\varsigma^2}{2}\right] \tag{4.66}$$

Table 4.2 The first few wavefunctions and energies of the harmonic oscillator problem

n	E_n	Ψ_n
0	$\hbar\omega_0/2$	$A_0 \exp[-\varsigma^2/2]$
1	$3\hbar\omega_0/2$	$A_1 2\varsigma \exp[-\varsigma^2/2]$
2	$5\hbar\omega_0/2$	$A_2.(4\varsigma^2 - 2)\exp[-\varsigma^2/2]$
3	$7\hbar\omega_0/2$	$A_3(8\varsigma^3 - 12\varsigma)\exp[-\varsigma^2/2]$
4	$9\hbar\omega_0/2$	$A_4(16\varsigma^4 - 48\varsigma^2 + 12)\exp[-\varsigma^2/2]$
5	$11\hbar\omega_0/2$	$A_5(32\varsigma^5 - 160\varsigma^3 + 120\varsigma)\exp[-\varsigma^2/2]$
		$A_n = (2^n n!\sqrt{\pi})^{-1/2}$

$$E_n = \hbar\omega_0(n + 1/2) \tag{4.67}$$

where n is an integer which starts at $n = 0$ and A_n is a normalization constant defined by the requirement:

$$\int_{-\infty}^{\infty} dx \Psi_n^* \Psi_n = 1 \tag{4.68}$$

and where the H_n are the so-called Hermite polynomials which are tabulated. The new variable is related to the spatial variable x by:

$$\varsigma = \sqrt{\frac{m\omega_0}{\hbar}} x \tag{4.69}$$

The first few Hermite polynomials are given in Table 4.2 and plotted in Fig. 4.13. It is interesting to note that in the lowest energy, the ground state is not zero but a finite number given by $\hbar\omega_0/2$. This is called "the zero point vibrational energy." It is also a consequence of the Heisenberg uncertainty principle, because it is a manifestation of the fact that when a particle is confined in space by a potential, then its momentum and thus its energy can never be zero. This is one of the truly exciting features of quantum mechanics. The exact solution of the harmonic oscillator problem can be extended to the three-dimensional case without difficulty, provided the potential $V(x,y,z)$ is separable and a sum of the potentials in the three spatial directions:

$$V(x, y, z) = \frac{1}{2}\left\{K_x x^2 + K_y y^2 + K_z z^2\right\} \tag{4.70}$$

4.7 The Hydrogen Atom

As another most important example of the exact solution of a physical problem in quantum mechanics is the solution of the hydrogen atom problem, let us write down the total Hamiltonian of the electron and the proton nucleus with masses m_1 and m_2, respectively:

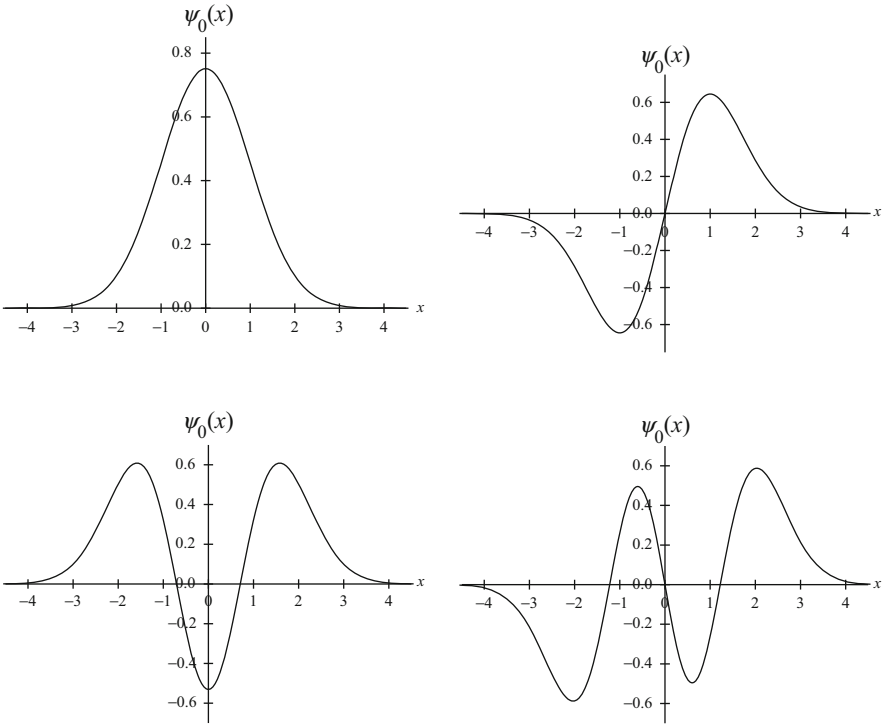


Fig. 4.13 The first few normalized wavefunctions of the harmonic oscillator with $n = 0$, $n = 1$, $n = 2$, and $n = 3$

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{q^2}{4\pi\varepsilon_0 \left| \vec{r}_1 - \vec{r}_2 \right|} \tag{4.71}$$

r_1 and r_2 and p_1 and p_2 are the spatial and momentum coordinates of electron and proton, respectively. The proton mass is 1000 times heavier, and in any case it is useful to work in the relative coordinate system. Using the quantum mechanics operators, Eq. (4.71) becomes:

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2\Psi - \frac{\hbar^2}{2m_2}\nabla_2^2\Psi - \frac{q^2}{4\pi\varepsilon_0 \left| \vec{r}_1 - \vec{r}_2 \right|}\Psi = E\Psi. \tag{4.72}$$

where E is the total energy of the system. Now let us define the new center of mass variables:

$$\begin{aligned}\vec{R} &= [X, Y, Z] = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \\ \vec{r} &= \vec{r}_1 - \vec{r}_2\end{aligned} \tag{4.73}$$

Now we can write for the partial derivatives:

$$\nabla_1 = \nabla + \frac{m}{m_2}\nabla_R \tag{4.74}$$

$$\nabla_2 = -\nabla + \frac{m}{m_1}\nabla_R \tag{4.75}$$

$$\nabla_R = \left[\frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z}\right] \tag{4.76}$$

$$\nabla = \left[\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right] \tag{4.77}$$

$$m = \frac{m_1 m_2}{m_1 + m_2} \tag{4.78}$$

Substituting back in terms of the new coordinates into the original Schrödinger equation, we have:

$$-\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2\Psi - \frac{\hbar^2}{2m}\nabla^2\Psi - \frac{q^2}{4\pi\varepsilon_0|r|}\Psi = E\Psi \tag{4.79}$$

Now in this form, we see that the differential equation is separable in terms of the relative electron-nucleus, and center of mass motion of the atom, so that the total wavefunction can be written mathematically as a product:

$$\Psi\left(\vec{R}, \vec{r}\right) = \Phi\left(\vec{R}\right)\psi\left(\vec{r}\right) \tag{4.80}$$

Substitute back into Eq. (4.79) and rewrite the total equation in terms of two separate ones:

$$-\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2\Phi\left(\vec{R}\right) = E_c\Phi\left(\vec{R}\right) \tag{4.81}$$

$$\begin{aligned}&-\frac{\hbar^2}{2(m)}\nabla^2\psi\left(\vec{r}\right) - \frac{q^2}{4\pi\varepsilon\varepsilon_0 r}\Psi\left(\vec{r}\right) = E_r\psi\left(\vec{r}\right) \\ &E = E_c + E_r\end{aligned} \tag{4.82}$$

The center mass motion is free and can therefore be solved immediately:

$$\Phi(\bar{R}) = C\exp\left[(i/\hbar)\ \vec{P}\cdot\vec{R}\right] \tag{4.83}$$

where $\boldsymbol{P}$ is the center of mass momentum, C the normalization constant, and the magnitude of $\boldsymbol{P}$ is related to the center of mass energy by the equation:

$$\left|\vec{P}\right| = \sqrt{2(m_1+m_2)E_c} \tag{4.84}$$

Now let us consider the relative motion of the electron around the nucleus. It is convenient to work in atomic energy units in which the energy is measured in multiples of the ionization energy of hydrogen which is the Rydberg unit $R = \frac{mq^4}{2(4\pi\varepsilon_0)^2\hbar^2}$ and we measure the coordinates, i.e., lengths, in units of the Bohr radius $a_B = \frac{\hbar^2(4\pi\varepsilon_0)}{mq^2}$. When working in terms of these units, we can put $\hbar = 1$; $q^2 = 2$; $m = /12$ in Eq. (4.82) to find the dimensionless form (we have dropped the index r on the energy for convenience):

$$\nabla^2\psi(\vec{r}) + \left(E + \frac{2}{r}\right\}\Psi(\vec{r}) = 0 \tag{4.85}$$

Equation (4.85) has the special feature that it is now an equation involving a particle moving in a spherically symmetric potential. We can now solve it as a mathematical problem by exploiting the spherical symmetry of the problem. In doing so we will naturally encounter the concept of angular momentum.

4.7.1 Motion in a Spherically Symmetric Potential

Given the symmetry of the problem, it is convenient to work with spherical polar coordinates. The differential Eq. (4.85) can be rewritten using:

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned} \tag{4.86}$$

and thus Eq. (4.85) becomes:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \left(E - \frac{2}{r}\right)\right\}\psi(r,\theta,\phi) = 0 \tag{4.87}$$

Again, this equation has a separable structure, in which the angular part and the radial part can be considered to vary independently so that:

$$\psi = R(r)Y(\theta, \phi) \tag{4.88}$$

Substituting Eq. (4.88) back into Eq. (4.87) allows us to rearrange the equation into the form:

$$\frac{1}{R}\left\{\left[\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right) + \left[E - \frac{2}{r}\right]r^2R(r)\right\} = -\frac{1}{Y}\left\{\frac{1}{\sin\theta\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} \tag{4.89}$$

The left-hand side (LHS) of this equation only depends on r, the right-hand side (RHS), only on the angles. The equation can be satisfied if each side of it is equal to the same constant C_0, so that:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[E - \frac{2}{r} - \frac{C_0}{r^2}\right]R = 0 \tag{4.90}$$

$$\left\{\frac{1}{\sin\theta\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = -C_0Y \tag{4.91}$$

The angular equation for Y can be further separated by writing:

$$Y(\theta, \phi) = P(\theta)\Phi(\phi) \tag{4.92}$$

and thus by substituting into Eq. (4.90) and Eq. (4.91), we have:

$$\frac{1}{P}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)\right] + C_0\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2 \tag{4.93}$$

In anticipation of the mathematical structure, we have introduced a separation constant which we have called m^2, and this allows us to rewrite the right-hand side of Eq. (4.93) as:

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0 \tag{4.94}$$

which has a simple solution of the form (normalization will be handled later):

$$\Phi = \exp[\pm im\phi] \tag{4.95}$$

The LHS of Eq. (4.93) can be conveniently written in terms of a new variable $\mu = \cos\theta$ giving us:

$$\frac{d}{d\mu}\left\{(1-\mu^2)\frac{dP}{d\mu}+\left(C_0-\frac{m^2}{1-\mu^2}\right)P=0\right\} \tag{4.96}$$

This equation is well known to mathematicians, and, indeed, it is one of those fortunate facts that they had looked at this type of equation long before they were of relevance to quantum mechanics and studied them in detail. The scientific community would be very much worse off if these solutions had not be found before, and we had to compute the results numerically. In any case, as it happens, this equation is known as Legendre's equation, and it was discovered that it only had bounded and differentiable solutions if the constant:

$$C_0 = l(l+1) \tag{4.97}$$

where l is a positive integer and the values of m are also restricted to the range $\{-l, -l+1, \ldots .l, l+1\}$. Combining Eq. (4.97) and Eq. (4.96), we can now write down the complete solution of the angular part of the Schrödinger equation as:

$$Y_l^m(\theta,\phi) = A_l^m e^{im\phi} P_l^m(\cos\theta) \tag{4.98}$$

The P_l^m are called the Legendre polynomials, they are tabulated as special functions, and A_l^m are normalization constants which we will now give as the final form:

$$Y_l^m(\theta,\phi) = (-)^m \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}\, e^{im\phi} P_l^m(\cos\theta) \tag{4.99}$$

In order to complete the solution of the hydrogen atom, we still need the solution to the radial part $R(r)$. But before doing that, let us first understand the significance of the angular part.

4.7.2 Angular Momentum

When a system is rotationally invariant, we expect on grounds of symmetry theory, and classical physics, that the particle moving in such a spherically symmetric field should have a well-defined angular momentum. So we ask: What is the angular momentum of an electron moving in the orbital of a hydrogen atom? In order to answer this question, we first have to find the angular momentum operator $\widehat{L}$ in quantum mechanics. We do this as with other operators, we use the classical correspondence principle which says that if:

$$\widehat{\vec{L}} = \vec{r} \times \vec{p} = -\vec{p} \times \vec{r} \tag{4.100}$$

is the classical angular momentum, then the quantum mechanical operator is simply given by replacing the r and p by the corresponding values based on quantum mechanics. Thus, for example:

$$L_z = xp_y - yp_x = x\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right) - y\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) \tag{4.101}$$

Then we note that the angular momentum operators in all three directions commute with the Hamiltonian of the hydrogen atom, i.e., the operators satisfy:

$$[H, L_x] = [H, L_y] = [H, L_z] = 0 \tag{4.102}$$

Equation (4.102) implies that eigenfunctions of $\widehat{H}$ are simultaneous eigenfunctions of $\widehat{L}$. An electron which is in an eigenstate of the Hydrogen atom is also in an eigenstate of angular momentum. In other words, the particle has both a well-defined energy and angular momentum. So we ask the question what is the angular momentum of the electron in the state $Y_l^m(\cos\theta)$ since we know this to be an eigenfunction? To answer this question, we make a measurement or apply the operator $\widehat{L}$ on the wavefunction. It is convenient and easier to work with the square of the angular momentum rather than the angular momentum itself. So we consider the operator:

$$L^2 = L_x^2 + L_y^2 + L_z^2 \tag{4.103}$$

and note that:

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0 \tag{4.104}$$

Also we have that:

$$[H, L^2] = 0 \tag{4.105}$$

It now follows that the energy eigenstates are simultaneous eigenstates of both L_z and L^2, but from vector algebra, it follows also that:

$$L^2\Psi = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\theta}\right] \tag{4.106}$$

and this is exactly the same differential form as Eq. (4.91). So from Eq. (4.91) and Eq. (4.99), it follows that a measurement of the squared angular momentum on the state Y_l^m must give the output $\hbar^2 l(l+1)$ or in other words:

$$L^2 Y_l^m = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_l^m}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_l^m}{\partial\theta}\right] = l(l+1)\hbar^2 Y_l^m \tag{4.107}$$

with the amplitude $\left|\vec{L}\right| = \hbar\sqrt{l(l+1)}$. Also a measurement of the z-component gives:

$$L_z Y_l^m = \frac{\hbar}{i}\frac{\partial}{\partial \phi} Y_l^m = m\hbar Y_l^m \tag{4.108}$$

so that a measurement of the projection of the angular momentum in the z-direction of the state $\left(Y_l^m\right)$ gives an eigenvalue $m\hbar$.

Now we understand the physical significance of the solutions that we derived in Sect. 4.7.1, and we also note the generality of the result. The eigenfunctions of angular momentum are the functions $\left(Y_l^m\right)$ and this is true in general. It happens to be true for the hydrogen atom too because the potential is spherically symmetric. So in any state with spherical symmetry, angular momentum is well defined, and the $\left(Y_l^m\right)$ constitutes the angular part of the wavefunction.

In this section we have tackled the solution of the hydrogen atom problem in quantum mechanics. We showed that the wavefunction can be written as a product of an angular and radial part. Now we can turn to studying the radial part $R(r)$ for this particular Coulomb potential.

4.7.3 The Radial Wavefunction of the Hydrogen Atom

Returning to face the solution of the radial part, we first note that a more convenient way of writing this equation is to transform:

$$u(r) = rR(r) \tag{4.109}$$

$$\frac{d^2u(r)}{dr^2} + \left[E + \frac{2}{r} - \frac{l(l+1)}{r^2}\right]u(r) = 0 \tag{4.110}$$

Now we note that differential equations involve the angular momentum integers l, so it follows that the eigenstates $u(r)$ must also have the label l, $u = u_l$, but there is also an energy variable E. So what happens to the energy E? Are all values allowed? It turns out not surprisingly that the answer is no! Again the mathematicians saw that long before the physicist used these solutions for the hydrogen atom. Mathematicians found that in order to have bounded and differentiable solutions, only discrete values of E were allowed. These carry the label n, and we have E_n as eigenvalues of energy and thus $u_{nl}(r)$, as eigenstates. The solution of this class of differential equation is a nontrivial exercise in mathematics, so we will only give the final answer here. The normalized solutions can be written as:

$$u_{n,l} = \sqrt{\frac{2r}{n^3}}\Lambda_{n-l-1}^{2l+1}\left(\frac{2r}{n}\right) \tag{4.111}$$

so that the complete solution is:

$$\Psi_{n,l,m} = \frac{1}{r} u_{n,l} Y_l^m(\cos\theta) \tag{4.112}$$

with energy eigenvalues:

$$E_n = -\frac{mq^4}{2n^2(4\pi\varepsilon_0)^2\hbar^2} \tag{4.113}$$

The functions Λ are related to the so-called Laguerre functions where with the variable $t = 2r/n$, we have:

$$\Lambda_k^\alpha(t) = \left[\Gamma(\alpha+1)\binom{k+\alpha}{k}\right]^{-1/2} e^{-t^2/2} t^{\alpha/2} L_k^\alpha(t) \tag{4.114}$$

where now L_k^α is a solution of Laguerre's differential equation:

$$t\frac{d^2L_k^\alpha}{dt^2} + (\alpha+1-t)\frac{dL_k^\alpha}{dt} + kL_k^\alpha = 0 \tag{4.115}$$

where α is a constant and Γ is the Gauss gamma-function with:

$$\binom{k+\alpha}{k} = \frac{\Gamma(k+\alpha+1)}{\Gamma(k+1)\Gamma(\alpha+1)} \tag{4.116}$$

The first few radial functions in atomic units are given by:

$$u_{10} = 2re^{-r} \tag{4.117}$$

$$u_{20} = \frac{1}{\sqrt{8}} e^{-r/2} r(2-r) \tag{4.118}$$

$$u_{21} = \frac{1}{\sqrt{24}} e^{-r/2} r^2 \tag{4.119}$$

$$u_{30} = \frac{2}{81\sqrt{3}} e^{-r/3} r\left(27 - 18r + 2r^2\right) \tag{4.120}$$

In real units the ground-state radial part is $R(r)_{10} = u_{10}/r = \frac{1}{\sqrt{8\pi}}\left(\frac{2}{a_B}\right)^{3/2} e^{-r/a_B}$ where a_B is the Bohr radius. The first few angular functions are (Fig. 4.14):

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \tag{4.121}$$

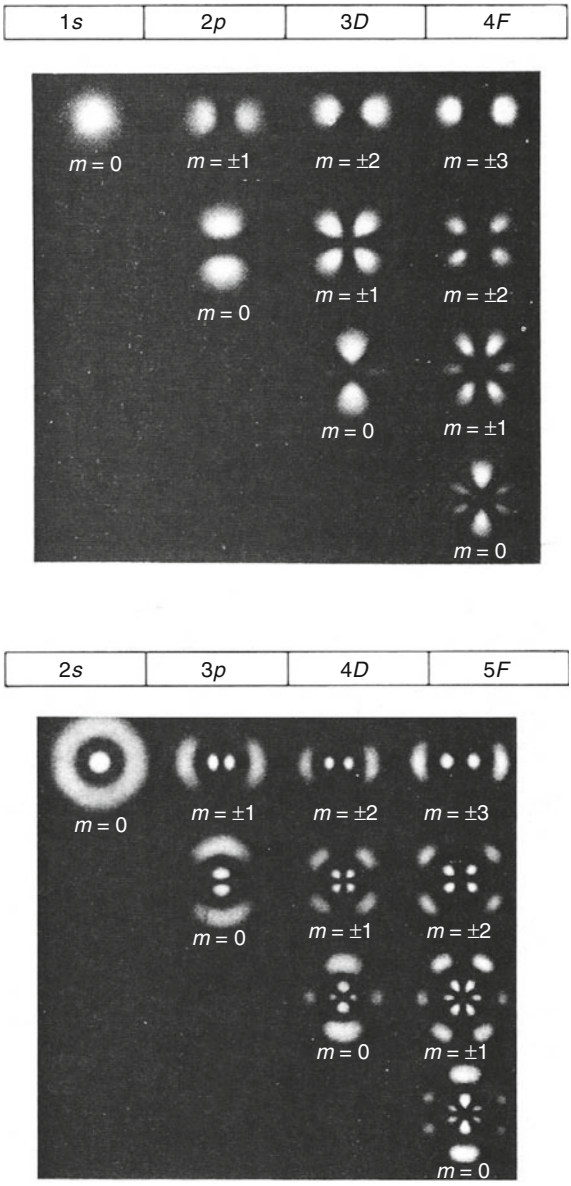


Fig. 4.14 Illustrates the particle density in the first few levels of the hydrogen atom. These are the 2S ($l = 0$), 2P ($l = 1$) and 3D($l = 2$) and 4F ($l = 3$) orbitals to the with the m, projections along the z-axis

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{4.122}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right) \tag{4.123}$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\sin\theta\exp i\varphi \tag{4.124}$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\exp[i\varphi] \tag{4.125}$$

4.7.4 The Unbound States

The above solutions encompass the region $E < 0$, i.e., where the electron is bound to the nucleus. One can also solve for the wavefunctions and energies of eigenstates which are free particle-like (only energies) in the region $E > 0$. The reader is referred to the book by *L*. Chuang in the references for a complete analytical description.

4.7.5 The Two-Dimensional Hydrogen Atom

Another interesting limit is the two-dimensional hydrogen atom which, even though it strictly speaking does not exist, is almost realizable using quantum well technology (see Chap. 15). One can, with atom-by-atom deposition techniques, molecular beam epitaxy (MBE), for example, place a hydrogenic atom in a thin atomic layer sandwiched between barrier layers so that the electronic motion is free in the plane and highly confined in the direction perpendicular to the plane. The analytical solution for the two-dimensional hydrogen atom problem is known mathematically, and the bound states are given by (Chuang 1995):

$$E_n = -\frac{R_y}{(n-1/2)^2}; n = 1, 2, 3\ldots. \tag{4.126}$$

$$R_y = \text{Rydberg} = \frac{mq^4}{2(4\pi\varepsilon_0)^2\hbar^2} \tag{4.127}$$

Comparing with the 3D solution Eq. (4.113), it is interesting to note that the binding energy is stronger in 2D than in 3D, a factor of 4 for the ground state. The wavefunctions only depend on one angle and have the simpler structure:

$$\Psi_{nm}\left(\vec{r}\right) = R_{nm}(r)\frac{e^{im\varphi}}{\sqrt{2\pi}} \tag{4.128}$$

Again we refer the reader to the book by *L.* Chuang in the references for the complete analytical formulae of the radial part and a discussion of the unbound solutions.

4.7.6 The Electron Spin

It was pointed out at the beginning of this chapter that in order to explain the structure of the atom, very early on after the discovery of quantum physics, W. Pauli introduced the concept of the electron spin. He observed that if he assumed that an electron had an extra quantum number which he called spin and if he assumed that the spin is like an angular momentum and can have two values "up or down" with values $\pm\frac{1}{2}\hbar$ and, further, assumed that two electrons cannot be in exactly the same eigenstate, then he could account for the so-called Aufbau principle i.e., explain the structure of the atoms with quantum mechanics.

So we have learned already that the electron must have a quantum number called spin, which is like an angular momentum and can have two values of its projection in the z-direction $S_z = \pm 1/2$. In other words if we make a measurement of the electron spin in a given direction which we call z, then we will find the values $S_z = \pm 1/2$ with equal probability. Once the electron has been prepared in a given spin state, it will stay in it unless disturbed. The electron spin is like an angular momentum in the sense that it carries also a magnetic moment as a classical rotating charge would do in principle. The magnitude of the magnetic moment was postulated and then measured by Stern and Gerlach to be $\mu_B = \frac{q\hbar}{m_0}$ (m_0 is the rest mass) which is called the Bohr magneton. The projection along the z-axis is $m_z = \pm 1/2\mu_B$.

Now the next question that arises is: where does the spin come from? Is it really due to a kind of zero point rotation of the electron in space, a rotating charge as one would think classically? Zero point meaning that according to Heisenberg's uncertainty principle, and as shown explicitly for the harmonic oscillator, when a degree of freedom is allowed, it has to have a "minimum value" associated with it. Otherwise one would know the position of a point on the surface with certainty. However classical rotation, it turns out, cannot be the reason for the electron spin and magnetic moment, because if one calculates the speed at which the charge would have to rotate to give this value of magnetic moment, one would find that the speed of rotation would be greater than the speed of light and therefore contrary to the rules of special relativity.

4.8 Relativity and Quantum Mechanics

The explanation for the electron spin came much later and was given by Paul A. M. Dirac in 1927. Dirac set himself the task of including special relativity into quantum mechanics and used the classical correspondence principle. Using Einstein's formula, gives the energy of the particle as:

$$E = c\sqrt{p^2 + m_0^2 c^2} \tag{4.129}$$

where m_0 is the rest mass and c the velocity of light. In this form, substituting in the Schrödinger momentum, operators would lead to a Hamiltonian which depends on the square root of differential operators. This is awkward to handle and is not evidently Lorentz invariant. Invariance under a Lorentz transformation is essential for special relativity to be satisfied. Of course one can develop the square root using the Taylor expansion assuming that the kinetic energy is small compared to the rest mass. The first two terms then together give back the usual result with a constant rest mass as first term. One can also write down the entire series, as an expansion in p^2:

$$H = m_0 c^2 + \frac{p^2}{2m_0} - \frac{1}{8}\frac{p^4}{m_0^3 c^2} + \ldots \tag{4.130}$$

Then using the quantum mechanical operators, assume that the eigenfunctions are plane waves as free particles and then every term in the series is a simple number with $p^2 \rightarrow (\hbar k)^2$. Resuming the series then gives the energy levels:

$$E_k = c\left[(\hbar k)^2 + m_0^2 c^2\right]^{1/2} \tag{4.131}$$

with a group velocity:

$$v_k = \frac{1}{\hbar}\frac{\partial E_k}{\partial k} = \frac{(\hbar k)c}{\left[m_0^2 c^2 + (\hbar k)^2\right]^{1/2}} \tag{4.132}$$

which saturates at the speed of light when the momentum becomes infinite. But this solution is not complete, and in order to ensure Lorentz invariance, Klein-Gordon and Dirac noted that one should consider the square of the operator and then replace the momentum and energy using the corresponding Schrödinger operators to find:

$$\left\{\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right\}\Psi = \left(\frac{m_0 c^2}{\hbar^2}\right)\Psi \tag{4.133}$$

This equation is known as the Klein-Gordon equation. It is second order in the time derivative as is Maxwell's equation (ME) and indeed is a wave equation as ME, when the particle has zero rest mass. The important observation is that this equation as is ME is relativistically invariant, i.e., it satisfies the Lorentz transformation

symmetry. This by the way also shows that special relativity is naturally true for electromagnetism and is thus an experimental law. Going back to Eq. (4.133), we note that we had to take the square or complex conjugate to arrive at Eq. (4.133), and therefore it will have more solutions than we may need. However it will certainly have all the solutions that we need. The energy operator is now as one can see quadratic in structure and no longer linear as in the nonrelativistic Schrödinger theory. The Klein-Gordon equation for free particles will also have the plane wave solutions discussed in the square expansion form, with the same energy-momentum relations, as can be easily verified by substituting:

$$\Psi\left(\vec{r},t\right) = A\exp\left\{i\,\vec{k}\cdot\vec{r}\,-iEt/\hbar\right) \tag{4.134}$$

Dirac's brilliant observation, which is the starting point of all modern quantum field theories and elementary particle descriptions until today, was to note that maybe one could go back to a linear form in terms of time and write this equation as the product of two linear differential equations. Let us write (Dirac PAM 1967):

$$\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = \left(A\frac{\partial}{\partial x} + B\frac{\partial}{\partial y} + C\frac{\partial}{\partial z} + \frac{i}{c}D\frac{\partial}{\partial t}\right)\left(A\frac{\partial}{\partial x} + B\frac{\partial}{\partial y} + C\frac{\partial}{\partial z} + \frac{i}{c}D\frac{\partial}{\partial t}\right) \tag{4.135}$$

In order for this differential operator relation to be satisfied, we need:

$$\begin{aligned} AB + BA &= 0 \\ AC + CA &= 0 \\ AD + DA &= 0 \\ BC + CB &= 0 \\ BD + DB &= 0 \\ CD + DC &= 0 \end{aligned} \tag{4.136}$$

$$A^2 = B^2 = C^2 = D^2 = 1 \tag{4.137}$$

Dirac observed that this decomposition is possible provided that we do not look at these $\{A,B,C,D\}$ quantities as simple numbers but as matrices. He then solved the matrix problem to find:

$$(A,B,C) = i\beta\alpha_k \tag{4.138}$$

$$D = \beta \tag{4.139}$$

$$\beta = \begin{pmatrix} I, 0 \\ 0, -I \end{pmatrix} \tag{4.140}$$

$$\alpha_k = \begin{pmatrix} 0, \sigma_k \\ \sigma_k, 0 \end{pmatrix} \tag{4.141}$$

$$\sigma_k = \begin{pmatrix} 0, 1 \\ 1, 0 \end{pmatrix}; \begin{pmatrix} 0, -i \\ i, 0 \end{pmatrix}; \begin{pmatrix} 1, 0 \\ 0, -1 \end{pmatrix} \tag{4.142}$$

where I is the unit matrix. Note that A, B, and C are 4×4 matrices. With the above matrix form, the Klein-Gordon equation can be rewritten:

$$\left(A\frac{\partial}{\partial x} + B\frac{\partial}{\partial y} + C\frac{\partial}{\partial z} + \frac{i}{c}D\frac{\partial}{\partial t}\right)\left(A\frac{\partial}{\partial x} + B\frac{\partial}{\partial y} + C\frac{\partial}{\partial z} + \frac{i}{c}D\frac{\partial}{\partial t}\right) - \frac{m_0^2c^2}{\hbar^2}I = 0 \tag{4.143}$$

The linearized form is thus:

$$\left(A\frac{\partial}{\partial x} + B\frac{\partial}{\partial y} + C\frac{\partial}{\partial z} + \frac{i}{c}D\frac{\partial}{\partial t}\right) - \frac{m_0c}{\hbar}I = 0 \tag{4.144}$$

One can also rewrite these equations as the Dirac equation pair:

$$\begin{pmatrix} m_0c^2, c\,\vec{\sigma}\cdot\vec{p} \\ c\,\vec{\sigma}\cdot\vec{p}\,, -m_0c^2 \end{pmatrix}\begin{pmatrix} \phi^+ \\ \phi^- \end{pmatrix} = i\hbar\frac{\partial}{\partial t}\begin{pmatrix} \phi^+ \\ \phi^- \end{pmatrix}. \tag{4.145}$$

Note that these are two distinct coupled 2×2 differential equations. One has positive, the other negative energy solutions. Each component is itself a 2×2 matrix. The $\varphi+$ component is connected to the $\varphi-$ component by a relativistic coupling. In the nonrelativistic limit, the two are not coupled anymore, but the 2×2 matrix structure of each remains. The 2×2 matrix form implies that the particle, apart from its usual spatial degrees of freedom, must also have acquired an additional two-valued degree of freedom. This new degree of freedom is exactly the spin which had been earlier postulated by Pauli to also have exactly this matrix representation. What it means is that the wavefunction of a particle which satisfies the linear Dirac equation has two components, a component with an internal degree of freedom which can be called spin up and the other one spin down. This internal degree of freedom turns out to have the same properties as an angular momentum with the two possible values $\pm\frac{1}{2}\hbar$ as discussed earlier.

This is a remarkable achievement indeed and shows that the symmetry associated with special relativity in quantum mechanics has important consequences on the structure of the basis states of space, on the "fabric of space time," (Wilczek 2006) making the wavefunction 4 component with an extra two-valued degree of freedom. In relativity, space and time are connected, but the time derivative still measures the energy. So to be in an eigenstate of energy, has implications for the spatial coordinates. But this is not all; Dirac's equation implies that along with positive energy solutions, there are also negative energy solutions which at first seems absurd

and artificial until further examination shows that the negative energy solutions can be interpreted as "antiparticles." So Dirac's discovery also leads to the discovery of antiparticles. A further consequence is that the vacuum is not empty but that for short times, when, according to Heisenberg, energy does not have to be conserved, there can be fluctuations in which particles and antiparticles spontaneously emerge out of the vacuum and recombine again. The "pair production" can become long lived and real when a photon of sufficient energy, a gamma ray, decomposes into an electron-positron pair. This is indeed observed experimentally. The photon energy needed twice the rest mass energies and the kinetic energies of decomposition. So the logic seems to make sense: Maxwell's equations satisfy the relativity principle by themselves, without further assumptions, but light can break up into matter and form particle-antiparticle pairs; this is also an experimental observation. But these particles must therefore necessarily also obey the relativity principle, which means they must obey the Dirac equation, when they have spin ½.

So what does this have to do with spin? It means that as the particle moves, it can for short times follow paths which are different to the normal space trajectories that we are used to. The particle can merge into an antiparticle which was spontaneously created as a quantum fluctuation and reappear as the particle component of that pair in another location. Indeed it has to do that, since for short enough time intervals, the particle still exists, but the vacuum it moves through has structure fluctuates, breaks up into matter and antimatter and reforms. Thus new pathways or "points" or space-time realizations are created and can and indeed must be passed through. For very short time intervals, the particle can visit antimatter points and form closed loops, i.e., come back again to where it was having visited antimatter points. The new "vacuum paths" look as if they are orbits and have spin angular momentum. The solutions of the Dirac equation are called fermions and have spin ½ as we have seen. The remarkable property is that even though energy corrections can disappear in the nonrelativistic limit, the spin remains, which shows that the matter-antimatter property of the vacuum still has an effect on the electron which it cannot escape. This new fabric of space time discovered by Dirac exists whether the particle has a low- or high-average velocity. In the short enough time evolution, the new space-time configurations can and are always visited. Dirac showed that the velocity of the particle is actually indeterminate; the instantaneous velocity of the particle is actually the speed of light! Then he found the reason for this strange and novel behavior by calculating the time dependence of the velocity. He discovered that the particle is undergoing an ultrafast, order of speed of light, trembling like motion with frequency $>2m_0c^2/h$, which is more than twice the rest mass frequency, and with spatial amplitude of order $\hbar/m_0c \sim 10^{-15}$ cm. We tentatively interpret these trembling motions as precisely the visits and returns into and from antiparticle space.

The solution of the Klein-Gordon equation in the simple form has apparently no spin. But it turns out that they can, and indeed, and must also have spin. They too move in a vacuum which, as Dirac showed, is not just empty space. In particular they have solutions of integer spin, the so-called bosons, for which there is no Pauli principle, but the proof which has to do with "quantum field theory" is not the subject of this book spin as an internal fabric of space time was just the beginning

elementary particle physics. Other symmetries, combined with special relativity, some intuitive others not, turn out to have similar consequences in quantum mechanics. Particles now have spin, color, charm, etc. This is the subject of the modern field of quantum chromodynamics and string theory which strive to explain the origin of mass and of gravitation in terms of the vibrational excitations of zero mass vacuum entities and then the coupling of these excitations in vacuum.

The positive energy free particle solutions to Dirac's equation are given by:

$$\Psi = \exp\left(-iEt/\hbar + i\,\vec{p}\cdot\vec{r}\right)\begin{pmatrix}1\\0\\\dfrac{cp}{E+m_0c^2}\\0\end{pmatrix} \tag{4.146}$$

$$\Psi = \exp\left(-iEt/\hbar + i\,\vec{p}\cdot\vec{r}\right)\begin{pmatrix}0\\1\\0\\-\dfrac{cp}{E+m_0c^2}\end{pmatrix} \tag{4.147}$$

$$E = \left\{m_0^2c^4 + \vec{p}\cdot\vec{p}\right\}^{1/2} \tag{4.148}$$

Note that the Pauli spin matrix form survives the nonrelativistic limit. Note also the fascinating fact that despite the time linearization, the time oscillations of the velocity, the overall wavefunction time is again only a phase! The particle once in an eigenstate stays there until disturbed. The density is again as in the nonrelativistic Schrödinger equation time independent. The connection to antiparticle space is reduced to just another angular momentum like quantum number the "spin."

4.8.1 The Electron Spin Operator

Now we know where the spin of the electron comes from, we can proceed to formulate the Pauli Dirac spin operators. The wavefunction of a fermion, i.e., a particle which obeys the Dirac equation, can be treated as a vector in a two-dimensional space so that in addition to its spatial component it also has a spin component, so that:

$$\begin{aligned}\Psi_\mu(\vec{r})|\uparrow\rangle &= \phi_\mu(\vec{r})\begin{bmatrix}1\\0\end{bmatrix}\\ \Psi_\mu(\vec{r})|\downarrow\rangle &= \phi_\mu(\vec{r})\begin{bmatrix}0\\1\end{bmatrix}\end{aligned} \tag{4.149}$$

Top one has spin up, and lower one has spin down. The operator which measures the z-component of the spin is:

$$s_z = \frac{\hbar}{2}\begin{pmatrix} 1, 0 \\ 0, -1 \end{pmatrix}. \tag{4.150}$$

The x and y components are:

$$s_x = \frac{\hbar}{2}\begin{pmatrix} 0, 1 \\ 1, 0 \end{pmatrix} \tag{4.151}$$

$$s_y = \frac{\hbar}{2}\begin{pmatrix} 0, -i \\ i, 0 \end{pmatrix} \tag{4.152}$$

The quantities in the matrix bracket are called the Pauli spin matrices.

Experimentally it was discovered that an electron also has a spin magnetic moment. The Dirac equation knows nothing about charge, so it cannot give a magnetic moment. But if we include the charge and let it move in an electromagnetic field, then one also obtains the spin magnetic moment, so that a measurement of magnetic moment corresponds to the operator:

$$m_z = \frac{q}{m_0} s_z \tag{4.153}$$

giving the values $m_z = \pm\frac{q\hbar}{2m_0}$ in MKS units. The energy of a spin in magnetic field B is the spin Zeeman coupling and is described by the term:

$$H_Z = -\underset{s}{\vec{m}}.\vec{B} \tag{4.154}$$

where:

$$m_z = \pm\frac{q\hbar}{2m_0} = \pm\frac{1}{2}\mu_B \tag{4.155}$$

The quantity μ_B is, as mentioned already, called the Bohr magneton.

4.9 The Addition of Angular Momentum

Consider an electron, in, for example, a state of angular momentum l, in an atomic orbit $n > 1$. The spin also has an effective angular momentum, so the electron now has a total angular momentum $\boldsymbol{J}$ where we can write:

$$\vec{J} = \vec{L} + \vec{s} \tag{4.156}$$

In order to see how to add angular momentum, let us consider the addition of the angular momentum of two particles with magnitudes l_1 and l_2. We write $l = l_1 + l_2$:

$$\begin{aligned}\vec{L} &= \vec{L}_1 + \vec{L}_2 \\ \vec{L} \cdot \vec{L} &= L^2 \rightarrow \hbar l(l+1)\end{aligned} \tag{4.157}$$

The allowed values of total angular momentum are given by:

$$l = |l_1 + l_2|, |l_1 + l_2 - 1|, \ldots\ldots |l_1 - l_2|. \tag{4.158}$$

So, for example, with $l_1 = 1$ and $l_2 = 2$, the allowed values are $l = 3$, $l = 2$, and $l = 1$. Each total angular momentum state has (2 l + 1) projections along the z-axis. Thus the combination $l = 3$ has the projections:

$$l_z = 3, 2, 1, 0, -1, -2, -3 \tag{4.159}$$

The same rule applies to the spin, with $l = 1$ and $s = 1/2$; the possible states of total angular momentum are $J = 3/2$, $1/2$ with projections, $Jz = 3/2, 1/2, -1/2, -3/2$ and $J = 1/2$ which gives $Jz = 1/2, -1/2$.

The addition of spins follows a similar rule. For example, two electron spins s_1 and s_2 can combine to form $S = s_1 + s_2$ with possible total spin states $S = 1$ and $S = 0$. The former is called the triplet combination and the latter the singlet. The triplet has three projections along the z-axis with $Sz = (1,0,-1)$.

4.10 The Pauli Principle Applied to Many-Electron Systems: The Slater Determinant

We have seen what the Pauli principle implies in terms of filling the energy levels of many-electron atoms and solids, but now let us consider the formal mathematical representation. The Pauli principle requires that whenever two electrons occupy the same spatial and spin eigenvalues, then the wavefunction cannot exist, i.e., it must vanish. In order to implement this rule, and in all cases where the many-electron system is not interacting, and thus wavefunctions of many electrons can be written as products of single-particle states, there is a simple and elegant representation that satisfies this condition. This representation is called the Slater determinant. The Slater determinant representation ensures that the wavefunction is antisymmetric under exchange of electron coordinates, and this in turn ensures that it vanishes when two electrons are in the same eigenstate. So let an eigenstate, for example, for the free particle system, be written as $\phi_k(r_n)\alpha(n)$ for particle r_n with spin up (α) and $\phi_k(r_n)\beta(n)$ particle r_n with spin down (β). Then a pair in k_1 and k_2 can be represented by the linear combination of eigenstates: (i) both particles have the same spin:

$$\Psi_{1,1}\left(\vec{r}_1, \vec{r}_2\right) = \frac{1}{\sqrt{2}}\left\{\phi_{k_1}(r_1)\phi_{k_2}(r_2) - \phi_{k_2}(r_1)\phi_{k_1}(r_2)\right\}\alpha(1)\alpha(2). \tag{4.160}$$

As one can see, the wavefunction has total spin = 1, i.e., is in a triplet state with $S_z = 1$ and vanishes if the spatial quantum numbers are identical. A similar state exists with both spins down corresponding to $S_z = -1$.

When the spins are opposite, we have two possible antisymmetric combinations: the state with $S = 1$, $S_z = 0$ is:

$$\Psi_{1,0}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\{\phi_{k_1}(r_1)\phi_{k_2}(r_2) - \phi_{k_2}(r_1)\phi_{k_1}(r_2)[\alpha(1)\beta(2) + \alpha(1)\beta(2)] \tag{4.161}$$

and the state with $S = 0$, $S_z = 0$ is:

$$\Psi_{0,0}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\{\phi_{k_1}(r_1)\phi_{k_2}(r_2) + \phi_{k_2}(r_1)\phi_{k_1}(r_2)[\alpha(1)\beta(2) - \alpha(1)\beta(2)] \tag{4.162}$$

All these four combinations are antisymmetric under exchange of coordinates. We can extend this rule for any number of electrons, and if we combine the spin (γ) and spatial quantum number k_n for particle r_n into one, and call it $q_n = (k_n, \gamma)$, we can write for an N-particle system the determinant:

$$\Psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\vec{q}_1), \phi_2(\vec{q}_1) \ldots\ldots\ldots\ldots \phi_N(\vec{q}_1) \\ \phi_1(\vec{q}_2) \ldots \\ \\ \phi_1(\vec{q}_N) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \phi_N(\vec{q}_N) \end{vmatrix} \tag{4.163}$$

When we use Slater determinants instead of simple product of wavefunctions, we include the fact that even though the electrons are to this order strictly speaking not interacting, there is an implicit correlation in their spatial distribution which is caused by the Pauli principle. For example, same-spin electrons cannot penetrate each other; opposite spins can. This spatial correlation, in conjunction with perturbations on the system, gives rise to the so-called exchange corrections.

4.11 Summary

This completes the chapter on the principles of quantum mechanics. We have visited some of the most important and practical application of the Schrödinger equation (SE) to real physical systems. We have shown how to solve the SE for the hydrogen atom which forms the basis for the understanding the structure of all atoms. It is an amazingly powerful result even though it involves a one-electron theory. It turns out that one can use these solutions for many electrons as well, provided one allows for the screening of the nuclear charge by the presence of the other charges in some averaged way. This is the so-called mean field or self-consistent field approach, and one can and must include the antisymmetric nature of the many-electron wavefunction as expressed by the Slater determinant of Eq. (4.163). We saw how spherical symmetry gives rise to the conservation of angular momentum and how this evolves naturally out of the hydrogen atom solutions. We discussed the origin of

the electron spin and showed how that is an internal coordinate which results from the requirement of special relativity when applied to quantum mechanics. The spin quantum number brilliantly follows from the Dirac equation or what is the linearized form of the Klein-Gordon equation, a manifestation of the fact that the "empty vacuum" is only a time averaged concept. That the vacuum can, for short times, spontaneously break up into matter and antimatter and thus allow nonintuitive quantum or quantized pathways of propagation through four-dimensional space time. The "nonintuitive" pathways, symmetries, and quantum numbers are far more numerous today in modern elementary particle physics.

4.12 The Electron in a Magnetic Field

Consider what happens to the motion of an electron in a magnetic field. We will only consider the orbital motion because in the absence of spin-orbit coupling, spin and orbit motion can be treated independently. Classically the charge is subject to the electric (E) and the Lorentz force as given below, which makes the electron follow a curved path in an electric and magnetic field (B):

$$\vec{F} = -q\left(\vec{E} + \vec{v} \times \vec{B}\right) \tag{4.164}$$

where v is the velocity. Quantum mechanically we first have to derive the new Hamiltonian. We make the following observation. A classical charged particle in an electromagnetic field obeys the Hamiltonian:

$$H = \frac{1}{2m}\left(\vec{p} + q\vec{A}\right)^2 \tag{4.165}$$

where $\boldsymbol{A}$ is the vector potential. For a magnetic field $\boldsymbol{B}$, the vector potential is:

$$\vec{B} = \vec{\nabla} \times \vec{A} \tag{4.166}$$

and

$$\vec{A} = (-yB, 0, 0) \tag{4.167}$$

Giving a field in z-direction:

$$\vec{B} = (0, 0, B). \tag{4.168}$$

In quantum mechanics we generate the correct Hamiltonian simply by using the corresponding momentum operators to obtain:

$$H = \left\{ \frac{1}{2m}(p_x + qyB)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \right\} \Psi = E\Psi \tag{4.169}$$

The momenta in x- and z-direction are not coupled, so they have plane wave solutions which allow us to simplify the Schrödinger equation to the form:

$$\Psi_n(k_x, k_z) = e^{i\left(k_x x + k_y y\right)} \varphi_n(y) \tag{4.170}$$

where:

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \phi_n(y)}{\partial y^2} + \left(\frac{(qB)^2}{2m} \right) (y - y_0)^2 \phi_n = \left(E - \frac{\hbar^2 k_z^2}{2m} \right) \phi_n \tag{4.171}$$

$$y_0 = -\frac{\hbar k_x}{qB} \tag{4.172}$$

We call:

$$\omega_c = \frac{eB}{m} \tag{4.173}$$

the cyclotron frequency and note that Eq. (4.171) is an equation describing a one-dimensional harmonic oscillator with the origin shifted by y_0 and for which the eigenvalues and wavefunctions are known from Sect. 4.6. The energy levels of the electron in a magnetic field are:

$$E_n = \hbar\omega_c (n + 1/2) + \frac{\hbar^2 k_z^2}{2m} \tag{4.174}$$

The magnetic levels classified under the quantum number n are called the Landau levels. The corresponding eigenstates are:

$$\Psi_n(k_x, k_z) = A_n H_n \left[\sqrt{\frac{m\omega_c}{\hbar}} (y - y_0) \right] \exp\left[-\frac{1}{2} \sqrt{\frac{m\omega_c}{\hbar}} (y - y_0)^2 + i(k_x x + k_z z) \right] \tag{4.175}$$

where the H_n as before in Sect. 4.6 are the Hermite polynomials and the A_n the normalization factors. Consider now the question of the degeneracy of each Landau level.

* *Note that if we defined the new velocity operator in the presence of a magnetic field* via *the Heisenberg equation of motion and with the Hamiltonian* Eq. (4.169), *which is the right way to define the new operator, then we would get the result*:

$$p_x = -i\hbar\frac{\partial}{\partial x} \rightarrow -ih\frac{\partial}{\partial x} + qBy \tag{4.176}$$

which shows that the correct velocity operator is now B-field dependent. This has no classical analogue. The acceleration operator can similarly be obtained by applying the Heisenberg equation of motion with the velocity operator instead of the position operator.

4.12.1 Degeneracy of the Landau Levels

We note that the energies Eq. (4.174) do not depend on the value of k_x. This implies that to every Landau level, there are many values of k_x momentum eigenstates which give the same energy. How many are there? In order to count the degeneracy, it is convenient to assume that the system is in a cubic box of size L, with periodic boundary conditions such that $\Psi(x + L, y + L, z + L) = \Psi(x, y, z)$. This condition gives rise to the momenta $k_x$which are quantized according to the rule $k_x = \frac{2\pi n_x}{L}, n_x = 0, \pm 1, \pm 2, \ldots$. Going back to Eq. (4.171), we note that the coordinate y_0 is now also limited to be in the range [0, L]. This in turn implies that the range of values:

$$y_0 = \frac{\hbar k_x}{qB_z} = \frac{\hbar n_x}{qBL} = L \tag{4.177}$$

so that the number of values of k_x with the same energy or degeneracy of the Landau level is g_L:

$$g_L = L^2\frac{qB}{\hbar} \tag{4.178}$$

In a two-dimensional x, y system with B in z-direction, we will see that for $B_z = 0$, the density of states is a constant (see Chap. 14). The crossover from the two-dimensional $B_z = 0$ spectrum to the discrete and g_L fold degenerate Landau spectrum is shown in Fig. 4.15.

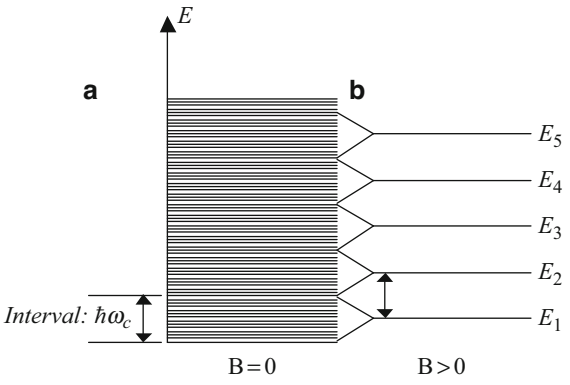


Fig. 4.15 Shows the level structure of a two-dimensional free electron system in a magnetic field. The constant density of states becomes discrete Landau levels. As the B-field increases, the degeneracy of the levels increases, and the Fermi level for a fixed electron number moves down

4.13 Discussion

In the above sections, we have considered situations where the Schrödinger equation (SE) is exactly solvable. We solved the SE in a magnetic field for spinless electrons. Let us now consider examples where an exact solution is not easily derivable analytically and where one has to resort to approximation methods. We start by formulating the very powerful Wentzel Kramer Brillouin (WKB) method.

4.14 The Wentzel Kramer Brillouin Approximation

Consider the situation where the electron moves over an arbitrary potential form $V(x)$ in the x-direction, but the motion in z and y is nearly free electron like. The wavefunction will be as:

$$\Psi(x,y,z) = A\phi(x)\exp\left[i\left(k_y y + k_z z\right)\right] \tag{4.179}$$

where A is the normalization constant and φ satisfies the one-dimensional Schrödinger equation:

$$\frac{d^2\phi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\phi = 0 \tag{4.180}$$

$$\frac{d^2\phi(x)}{dx^2} + \frac{p^2}{\hbar^2}\phi = 0 \tag{4.181}$$

$$p = \sqrt{2m(E - V(x))} \tag{4.182}$$

where the general solution is of the form:

$$\begin{aligned}\phi(x) &= s(x)\exp\left\{\pm\frac{i}{\hbar}\int^{x} dx' p\left(x'\right)\right\} \\ &= s(x)\exp\left\{\pm\frac{i\sqrt{2m}}{\hbar}\int^{x} dx' \sqrt{E - V(x')}\right\}\end{aligned} \tag{4.183}$$

$$s(x) = Kp^{-1/2} \rightarrow K = \text{const.} \rightarrow \text{normalisation} \tag{4.184}$$

The above is called the Wentzel Kramer Brillouin (WKB) approximation and is valid when:

$$\left|\frac{h\frac{\partial p}{\partial x}}{p^2}\right| << 1 \tag{4.185}$$

$$p = \sqrt{2m[E - V(x)]} \tag{4.186}$$

In other words, when the variation of $p(x)$ or $V(x)$ is slow enough to satisfy the above condition (which is true for most situations of interest in engineering applications). In order to construct the entire solution, one considers the solution piecewise over regions of space. The most general solution in each region is of the form:

$$\phi(x) = A\frac{1}{p^{1/2}}\exp\left\{+\frac{i}{\hbar}\int^{x} p\left(x^{'}\right)dx^{'}\right\} + B\frac{1}{p^{1/2}}\exp\left\{-\frac{i}{\hbar}\int^{x} p\left(x^{'}\right)dx^{'}\right\} \tag{4.187}$$

The singular behavior at turning points when $p(E,x) = 0$ is of no serious consequence because the singularity is integrable so the wavefunction is normalizable in a finite interval.

Now one looks at a particular interval and notes that in regions where the energy E of the particle is $E > V(x)$, the function $p(x)$ is real, and the solution is a linear combination of two oscillatory waves, one going to the right and the other to the left. In regions where $E < V(x)$, $p(x)$ is complex, and the wavefunction is exponentially decaying in space in the direction against the potential barrier. The wavefunctions are multiplied by arbitrary constants A, B which have to be determined by the boundary conditions. In order to get the full solutions, one connects the different regions defined above by requiring the continuity of the wavefunction and its derivative. Consider, for example, the potential $V(x)$ in Fig. 4.16; the energy E is shown by the solid line. In region II, the energy of the particle is smaller than the potential barrier, so the wavefunction must decay exponentially as a function of $(x–x_1)$ and behave as:

$$\phi(x) = A_2\frac{1}{|p|^{1/2}}\exp\left\{+\frac{1}{\hbar}\int_{x_1}^{x_2} |p\left(x^{'}\right)|dx^{'}\right\}\} \tag{4.188}$$

In region I, between 0 and x_1, the energy E is larger than $V(x)$, so $p(x)$ is real, the phase oscillatory, and the wavefunction is of the form Eq. (4.187). In the region III, for $x > x_2$, here $E > V(x)$, and the wave has again an oscillatory structure as in Eq. (4.187):

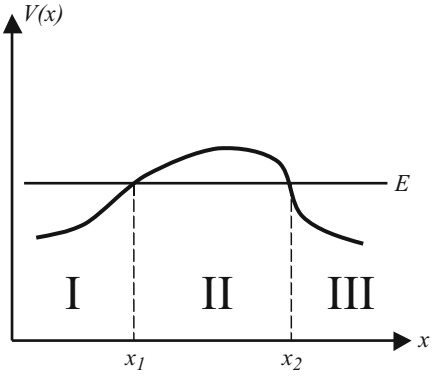


Fig. 4.16 illustrates the example treated in the text. Region II is the quantum mechanical tunneling region

$$\phi(x) = A\frac{1}{p^{1/2}}\exp\left\{+\frac{i}{\hbar}\int_{x_2}^{x} p\left(x'\right)dx'\right\} + B\frac{1}{p^{1/2}}\exp\left\{-\frac{i}{\hbar}\int_{x_2}^{x} p\left(x'\right)dx'\right\} \quad (4.189)$$

The constants A, B, A_2, can be determined by using the boundary conditions as explained above. One can in principle also determine the eigenvalues using the Wentzel Kramer Brillouin (WKB) method which is also a piecewise solution of the one-dimensional Schrödinger equation. The approximate eigenvalues can be generated by using the Bohr Sommerfeld condition which requires that the integral of $p(x)$ over the classical domain where $p(x, E)$ is real and satisfies the quantization condition:

$$\int_{p(x)>0} dx\sqrt{2m\left(E - V(x)\right)} = \left(n + \frac{1}{2}\right)\hbar \quad (4.190)$$

Though useful for finding the approximate eigenvalues of electrons confined between barriers higher than their energies, with unusual potential wells, for example, this is not the main application of WKB. The main application is when one knows the energy and one wants to know how the particle behaves in a given potential region. For example, consider the tunnel barrier as in Fig. 4.17, which is a rectangular barrier lowered by an applied field. The particle is assumed to have energy E; the question is what is the amplitude lowering when the particle has tunneled to the right to the point $p = 0$, after which it becomes an oscillatory function again. The potential in the tunnel region is $\{V(x) = V_0 - qFx\}$, so we have:

$$\phi(x) = A_3\frac{1}{|V_0 - qFx - E|^{1/2}}\exp\left\{-\left(\frac{2m^*}{\hbar^2}\right)^{1/2}\int_{x_2}^{x}\left[V_0 - qFx' - E\right]^{1/2}dx'\right\} \quad (4.191)$$

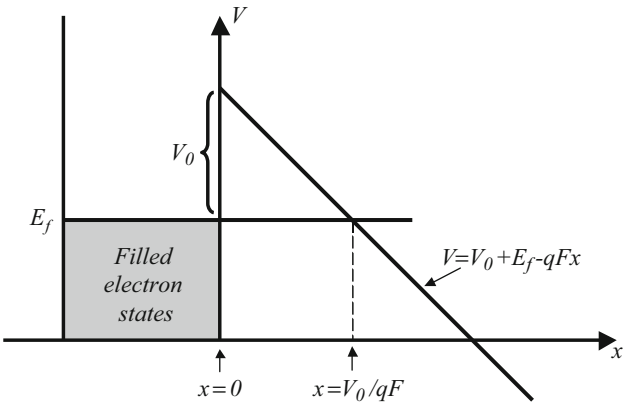


Fig. 4.17 illustrates the constant barrier in the presence of an electric field: the Fowler-Nordheim limit

The upper limit of the integral is set by the condition $E = V_0 - qFx'$, so that the decay in amplitude from the starting point of the barrier at the point x to the critical turning point is:

$$|\phi(x_c)|^2 \sim |\phi(x=0)|^2 \exp\left\{-\frac{4}{3}\left(\frac{2m^*}{\hbar^2}\right)^{1/2}\frac{(V_0-E)^{3/2}}{qF}\right\} \tag{4.192}$$

This then also gives us a measure of the transmission coefficient into the free carrier region beyond the critical point $x_c = (V_0 - E)/qF$:

$$T(E) = T_0 \exp\left\{-\frac{4}{3}\left(\frac{2m^*}{\hbar^2}\right)^{1/2}\frac{(V_0-E)^{3/2}}{qF}\right\} \tag{4.193}$$

This is called the Fowler-Nordheim tunneling structure and is encountered whenever a constant barrier is lowered by an applied electric field.

4.15 Quantum Mechanical Perturbation Theory

4.15.1 Time-Independent Perturbation

One of the most powerful results and methods of quantum mechanics is Perturbation theory. Very often one is confronted with a situation where a system is subject to an interaction or several interactions for which the complete Hamiltonian has no analytic solutions. Very frequently these interactions are also small compared to the main effect which determines the system properties. Consider, for example, a hydrogen atom in an electric field. An applied electric field of even as high as 10^7 $V \cdot cm^{-1}$ represents a tiny effect when compared to the electric field of the proton

nucleus. It is therefore very important to be able to include the effect of such new interactions, at least to some degree, and study what they do to the wavefunctions and energy levels of the system.

The procedure is as follows. We consider a starting Hamiltonian H_0 of which we assume we have the normalized eigenfunctions Φ_n and energy levels E_n. Now consider the full Hamiltonian in the presence of a perturbation V, given by $H = H_0 + V$, and we generate the solutions of this new Hamiltonian as a power series expansion, both for the energies and the wavefunctions. The expansion of energy levels and wavefunctions can be usually stopped in second order, giving us a powerful way of estimating changes in energies and wavefunctions and of course of all the relevant physical properties.

4.15.2 Nondegenerate Perturbation Theory

We first consider the situation where no two energies of the unperturbed system have the same value. Or in this particular application, we assume that the ground state is nondegenerate. In many situations of interest such as, for example, treating the effect of static electric fields on the electronic system, we can work with the time-independent Schrödinger equation and perturbation theory. The time-dependent perturbation expansion is considered in Chap. 10. We write for the new ground-state wavefunction energy the perturbation expansion:

$$\begin{aligned} \Phi_g &= \Phi_g^0 + \Phi_g^1 + \Phi_g^{(2)} \\ E_g &= E_g^0 + E_g^{(1)} + E_g^{(2)} \end{aligned} \tag{4.194}$$

The admixtures are as before linear combinations of the unperturbed eigenstates, in this case excited states, so that:

$$\Phi_g^{(n)} = \sum_{l \neq g} a_{\mathrm{lg}}^{(n)} \Phi_l^0 \tag{4.195}$$

and where the time-independent Schrödinger equation with perturbation V is given by:

$$(H_0 + V)\Phi_g = E_g \Phi_g \tag{4.196}$$

Substituting Eq. (4.194) in Eq. (4.196), and comparing coefficients of the same order, then gives to the zeroth order the obvious result:

$$H_0 \Phi_g^0 = E_g^0 \Phi_g^0 \tag{4.197}$$

First order we have:

$$H_0\Phi_g^1 + V\Phi_g^0 = E_g^0\Phi_g^1 + E_g^1\Phi_g^0 \tag{4.198}$$

In second order we have:

$$H_0\Phi_g^{(2)} + V\Phi_g^1 = E_g^0\Phi_g^{(2)} + E_g^1\Phi_g^1 + E_g^{(2)}\Phi_g^0 \tag{4.199}$$

In order to obtain the zeroth order solution, we substitute the expansion Eq. (4.195) into the first-order equation Eq. (4.198), multiply the left hand on both side by $\left(\Phi_g^0\right)*$ and integrate over all space, and use the orthogonality condition:

$$\int d\ \vec{r}\ \Phi*_n\Phi_m = \delta_{mn} \tag{4.200}$$

to find:

$$E_g^1 = \int d\ \vec{r}\ \left(\Phi_g^0\right)*V\left(\vec{r}\right)\Phi_g^0 \tag{4.201}$$

We carry on the procedure to calculate the first-order change in the wavefunction by multiplying Eq. (4.199) this time on both sides with $\left(\Phi_l^0\right)*$ and integrating while using the orthogonality again and the relation:

$$H_0\Phi_m^0 = E_m^0\Phi_m^0 \tag{4.202}$$

to find the coefficient:

$$a_{\mathrm{lg}}^{(1)} = \frac{V_{\mathrm{lg}}}{E_g - E_l} \tag{4.203}$$

and after multiplying and integrating again with $\left(\Phi_g^0\right)*$ on the second-order Eq. (4.199) and some algebra, we find the second-order energy shift:

$$E_g^{(2)} = \sum_{l\neq g}\frac{V_{gl}V_{\mathrm{lg}}}{E_g - E_l} \tag{4.204}$$

With the wavefunction given to first order by:

$$\Phi_g = \Phi_g^0 + \sum_{l\neq g}\frac{V_{\mathrm{lg}}}{E_g - E_l}\Phi_l^0 \tag{4.205}$$

whereas before the matrix element of the potential is defined by:

$$V_{ls} = \int \Phi*_s^0 V\left(\vec{r}\right)\Phi_l^0 d\ \vec{r} \tag{4.206}$$

Knowing the unperturbed wavefunctions and energy levels allows us to compute the perturbed ones. Equation (4.201), Eq. (4.204), and Eq. (4.205) are, though simple, some of the most useful results of quantum mechanics.

If, for example, we consider the particle in the one-dimensional box problem of Sect. 4.4.3, with confinement in z-direction, and we apply a perturbation which is due to an applied electric field in the z-direction, then $V = -qzE_0^z$, and we can compute the energy's shift to a good approximation with the box wavefunctions given by Eq. (4.46). If the origin is chosen as $z = L/2$ so that the box extends in the range $[-L/2 < z < L/2]$, it follows by symmetry that the first-order shift $V_{gg} = 0$, and we have only the second-order term given by:

$$E_g^{(2)} = \sum_{l \neq g} \left(qE_{0z}\right)^2 \frac{\left|z_{gl}\right|^2}{E_g - E_l} \tag{4.207}$$

If on the other hand we choose the origin to be at $z = 0$ so that the range is $[0 < z < L]$, then the expansion to second order is:

$$E_g = E_g^0 + \int_0^L dz \frac{2}{L} Sin^2\left(\frac{\pi z}{L}\right)\left(-qzE_0^z\right) + \sum_{l \neq g} \frac{\int_0^L dz \frac{2}{L} \sin\left(\frac{\pi z}{L}\right)\left(-qE_0^z z\right) \sin\left(\frac{l\pi z}{L}\right)}{E_g - E_l} \tag{4.208}$$

In summary, we have shown that to second order, the new perturbed energy levels for general perturbation V is given as:

$$E_g = E_g^0 + \int d\,\vec{r}\;\Phi_g^* V \Phi_g + \sum_{l \neq g} \frac{\left|V_{gl}\right|^2}{E_g - E_l} \tag{4.209}$$

where V_{ls} is defined by Eq. (4.206). It is interesting to note that the second-order term is for the ground-state energy, always an energy lowering term irrespective of the nature of the perturbation.

4.15.3 Degenerate-State Perturbation Theory to Second Order

When two or more energies states of the unperturbed system can have the same value, we may bypass the difficulty by using the renormalized or so-called Brillouin Wigner expansion, which to second order is the same as Eq. (4.204) except that the energy denominator contains the exact final energy and not the unperturbed ground state:

$$E_g = E_g^0 + \int d\,\vec{r}\;\Phi_g^* V \Phi_g + \sum_{l \neq g} \frac{|V_{gl}|^2}{E_g - E_l} \tag{4.210}$$

If the dominant term is due to coupling with the degenerate level $E_{g_1}^0 = E_g^0$ then to second order, the sum can be separated into the degenerate term with $l = g_1$, and the rest can stay un-renormalized to second order to give:

$$E_g = E_g^0 + V_{gg} + \frac{|V_{gg_1}|^2}{E_g - E_{g_1}^0} + \sum_{l \neq g,\, g_1} \frac{|V_{gl}|^2}{E_g^0 - E_l^0} \tag{4.211}$$

where $V_{gg} = \int d\,\vec{r}\;\Phi_g^* V \Phi_g$ and we have a simple quadratic equation to solve. Putting $E_g^0 = E_{g_1}^0$ by definition of degeneracy:

$$\left(E_g - E_g^0\right)^2 - V_t \left(E_g - E_g^0\right) - |V_{gg_1}|^2 = 0 \tag{4.212}$$

$$V_t = V_{gg} + \sum_{l \neq g,\, g_1} \frac{|V_{gl}|^2}{E_g^0 - E_l^0} \tag{4.213}$$

The quadratic has two distinct roots, and the degeneracy of the ground state is now lifted by the perturbation. The two roots are:

$$E_g = E_g^0 + \frac{1}{2}\left\{ V_t \pm \left[V_t^2 + 4V_{gg_1}^2 \right]^{1/2} \right\} \tag{4.214}$$

$$V_{gg_1} = \int d\,\vec{r}\;\Phi_g^* V(\vec{r}) \Phi_{g_1} \tag{4.215}$$

$$V_{gl} = \int d\bar{r} \Phi_g^* V(\vec{r}) \Phi_l \tag{4.216}$$

The result is very simple if we can neglect the admixture to the nondegenerate excited level or $V_{gl} = 0$; $l \neq g, g_1$.

The time-dependent perturbation method is treated in Chap. 10, in the context of optical properties, but the method presented in Chap. 10 is quite general and can be used for any time-dependent perturbation.

4.16 Final Summary

In the first part of this chapter, we introduced the principles of quantum mechanics. Then we applied the method to a number of exactly solvable problems of great physical significance: the particle in the box, the harmonic oscillator, and the hydrogen atom. We encountered angular momentum and spin. In the final parts of the chapter, we considered simple Hamiltonians which are not exactly solvable analytically and which need approximate treatments. We introduced the so-called Wentzel Kramer Brillouin (WKB) method which is a powerful method by which one can estimate the wavefunction in quasi-one-dimensional irregular potentials. We applied it to a simple but very important example with many applications: the constant potential barrier in an electric field.

In the last part of this chapter, we demonstrated how one can calculate the effect of small perturbations on quantum mechanical systems. The energy corrections were evaluated up to second order in powers of the disturbance Hamiltonian for the energy, and the corrections to the wavefunction were developed up to first order. The method was formulated for the case when the ground state is nondegenerate, and it was shown how to extend it to the case when the ground state is degenerate.

Problems

1. According to the quantum mechanics, electromagnetic radiation of frequency ν can be regarded as consisting of photons of energy $h\nu$ where $h = 6.626 \times 10^{-34}$ J·s is the Planck's constant.
   (a) What is the frequency range of visible photons (400 nm to 700 nm)? What is the energy range of visible photons (both in J and in eV)?
   (b) How many photons per second does a low power (1 mW) He-Ne laser ($336 = \lambda$ nm) emit? A cell phone that emits 0.4 W of 850 MHz radiation? A microwave oven operating at 2.45 GHz generating a microwave power of 750 W? How many photons of the latter frequency have to be absorbed to heat up a glass of water (0.2 L, heat capacity of water 4.18 $kJ \cdot kg^{-1} \cdot K^{-1}$) by 10 °C?

   At a given power of an electromagnetic wave, do you expect a classical wave description to work better for radio frequencies or X-rays? Why? At what He-Ne laser power do you expect quantum effects to become important?
2. An adapted human eye (person that has spent 30 min in the dark) can see 1 ms flashes of power 4×10^{-14} W at 510 nm with 60% reliability. Assuming that 10% of the incident power reaches the retina, how many photons at the receptors generate the signal that the test person recognizes as flash of light?
3. (a) The thermal energy scale is k_bT, where $k_b = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant and T is the absolute temperature. What energy does room temperature correspond to? What would be the frequency and wavelength

of the corresponding photons? Is it reasonable that a hot body starts to glow around 1000 °C?

(b) What is the photon flux (rate of arriving photons per unit area) at 1 m distance from a 60 W light bulb, if you assume that the bulb conversion efficiency (electrical power to light bulb) is 10% and take the photon wavelength as 500 nm?

(c) A photodiode measures light power by converting incident photons into electron-hole pairs, such that the electron current is proportional to the incident light power. The quantum efficiency is defined as the probability that an incident photon generates an electron. If a typical photodiode has a responsivity of 0.5 A/W for infrared light at 850 nm, what is the quantum efficiency of the device? If the quantum efficiency is independent of frequency, what responsivity do you expect for blue light at 400 nm?

Student can find a simulation of black body radiation and related topics (Planck's law, Wien's law) at http://csep10.phys.utk.edu/guidry/java/planck/planck.html.

4. From the expression of the distribution of energy radiated by a blackbody, Eq. (4.2c) shows that the product $\lambda_M T$ is a constant, where λ_M is the wavelength of the peak of distribution at the temperature T (see Fig. 1.3).
5. Ultraviolet light of wavelength 350 nm falls on a potassium surface. The maximum energy of the photoelectrons is 1.6 eV. What is the work function of potassium? Above what wavelength will no photoemission be observed?
6. What is the deBroglie wavelength of an automobile (2000 kg) traveling at 25 miles per hour? A dust of radius 1 μm and density 200 kg·m^{-3} being jostled by air molecules at room temperature ($T = 300$ K)? An 87Rb atom that has been laser cooled to a temperature of $T = 100$ μK? An electron and a proton accelerated to 100 eV?

   Assume that the kinetic energy of the particle is given by $(3/2)k_bT$.
7. Reflection high-energy electron diffraction (RHEED) has become a commonplace technique for probing the atomic surface structures of materials. Under vacuum conditions an electron beam is made to strike the surface of the sample under test at a glancing angle ($\theta < 10°$). The beam reflects off the surface of the material and subsequently strikes a phosphorescent screen. Because of the wave-like nature of the electrons, a diffraction pattern characteristic of the first few atomic layers is observed on the screen if the surface is flat and the material is crystalline. With a distance between atomic planes of $d = 5$ Å, a glancing angle of 1°, and an operating de Broglie wavelength for the electrons of $2d\sin\theta$, compute the electron energy employed in the technique.
8. (a) Confirm, as pointed out in the text, that $<p_x> = 0$ for all energy states of a particle in a l-D box.

   (b) Verify that the normalization factor for wavefunctions describing a particle in a l-D box is $A_n = (2/a)^{1/2}$.
9. A particle with mass 6.65×10^{-27} kg is confined to an infinite square well of width L. The energy of the third level is 2.00×10^{-24} J. Calculate the value of L.

10. A particle of mass m is prepared in the ground state of an infinite-potential box of size a extending from $x = 0$ to $x = a$. Suddenly, the wall at $x = a$ is moved to $x = 2a$ within a time Δt doubling the box size. You may assume that the wavefunction is the same immediately after the change, if the change happens fast enough.
    (a) How fast is fast enough?
    (b) What is the probability that the particle is in the second ($n = 2$) state of the new well, immediately after the change? Note that the wavelength within the well, and hence the energy, for this state is the same as for the initial state in the old well. Make sure that you properly normalized wavefunctions for your calculations.
    (c) What is the probability that the particle would be found in the ground state of the sudden expansion?
    (d) What is the expectation value of the energy of the particle before and after the sudden expansion?
11. An electron is confined to a 1 micron layer of silicon. Assuming that the semiconductor can be adequately described by a one-dimensional quantum well with infinite walls, calculate the lowest possible energy within the material in units of electron volt. If the energy is interpreted as the kinetic energy of the electron, what is the corresponding electron velocity? The effective mass of electrons in silicon is 0.26 m_0, where $m_0 = 9.11 \times 10^{-31}$ kg is the free electron rest mass.
12. In examining the finite potential well solution, suppose we restrict our interest to energies where $\zeta = E/U_o < 0.01$ and permit "a" to become very large such that in Eq. (3.61), $\alpha_0 a \zeta_{max}^{1/2} >> \pi$. Present an argument which concludes that the energy states of interest will be very closely approximated by those of the infinitely deep potential well.
13. In this exercise, we will apply the material in Sect. 4.4.4 (page144) to calculate the factor of confinement of a particle in a finite well. For convenience we consider symmetric case, we will translate the x-axis so that the potential equals to 0 in the region: $-a/2 < x < a/2$.
    (a) Rewrite the Eq. (4.57) in this new coordinate system. Use the boundary condition to eliminate some trivial constants. By symmetry, we search for solutions in two families of functions: even and odd function. Show that the even solutions satisfy two equations:

$$\begin{cases} \tan\left(\dfrac{ka}{2}\right) = \dfrac{\alpha}{k} \\ k^2 + \alpha^2 = \dfrac{2mU_0}{\hbar^2} \end{cases}$$

while the odd solutions satisfy:

$$\begin{cases} -\cot\left(\dfrac{ka}{2}\right) = \dfrac{\alpha}{k} \\ k^2 + \alpha^2 = \dfrac{2mE}{\hbar^2} \end{cases}$$

How can you resolve these equations graphically?

(b) The particle is in the ground state, which is even, of energy E. Find the probability for the particle to stay in the well. This quantity is defined as the confinement factor (or coefficient of confinement).

Student can find a simulation of this problem at http://www.sgi.com/fun/java/john/wave-sim.html.

14. Consider a particle of mass m moving in the potential:

$$V(x) = -\frac{\hbar^2 a^2}{m}\frac{1}{\cosh^2(ax)}$$

(a) Show that this potential has a bound eigenstate described by the wavefunction:

$$\psi_0(x) = \frac{A}{\cosh(ax)}$$

and find the corresponding eigenenergy. Normalize ψ_0 and sketch it. This turns out to be the only bound state for this potential.

(b) Show that the wavefunction is:

$$\psi_k(x) = B\left(\frac{ik - a\tanh(ax)}{ik + a}\right)e^{ikx}$$

where $\hbar k = \sqrt{2mE}$, solves the Schrödinger equation for any positive energy E and near $\pm\infty$ the asymptotic of $\psi_k(x)$ has the plane wave form. Determine the transmission coefficient if it is defined as the square of the ratio between the amplitude of the coming wave (at $-\infty$) and that of the going out wave (at $+\infty$). What physical situation does ψ_k represents?

Student can find a simulation of this problem at http://www.kfunigraz.ac.at/imawww/thaller/visualization/vis.html.

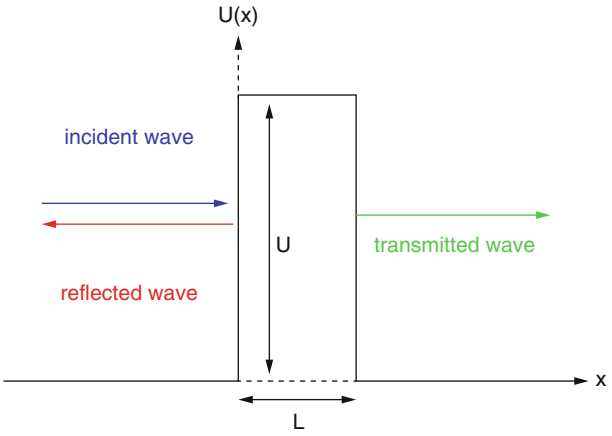
15. Using the Heisenberg equation of motion Eq. (4.30) and the Hamiltonian of a free particle in a magnetic field given by Eq. (4.171), evaluate the velocity operators vx, vy, and vz. Note how the magnetic field has modified one of the velocities. How does the presence of an electric field, if at all, modify the velocity operators?

As a consequence of relativity, the spin magnetic moment of an electron is coupled to its own orbit via the interaction:

$$H_{so} = \frac{\hbar}{4m^2c^2}\left[\vec{\nabla}\, V(\vec{r}) \times \vec{p}\right] \cdot \vec{s}$$

where $V(\vec{r})$ is the total potential seen by the electron and $\vec{s}$ is the spin operator. What is the effect of the spin-orbit interaction on the quantum mechanical definition of the velocity operator (use the Heisenberg equation of motion Eq. (4.30)). What is the dependence of the spin-orbit coupling on the orbital angular momentum L, if $V(\vec{r})$ is the Coulomb potential of the hydrogen atom?

16. A particle of energy E traveling from the left hits a barrier of height $U > E$ and thickness L. Calculate the transmission coefficient.



Student can find a simulation of this problem at http://www.kfunigraz.ac.at/imawww/thaller/visualization/vis.html http://www.sgi.com/fun/java/john/wave-sim.html.

17. The one-dimensional harmonic oscillator Eq. (4.62) is subject to an electric field F which produces an extra term qFx in the Hamiltonian. Calculate the new wavefunctions and energy levels using the zero field solutions. How does the field affect the symmetry of the charge distribution in the ground state?
18. Explain the Wentzel Kramer Brillouin (WKB) approximation. Why is it important and when would you use it? Using Eq.(4.183) verify the estimate of Eq. (4.185).
19. We have seen that in a magnetic field, the magnetic moment of an electron couples to an external magnetic field B to give the so-called Zeeman term $H_Z = -g\mu_B . B_z s_z$ where for free electrons the factor g we have introduced is called the g-value and is given without quantum field corrections by $g = -2$ and with corrections by $g = -2.0023$. In a medium the spin-orbit coupling can change the effective value of g called also the Lande's g-value. In an electron spin resonance experiment (ESR), the spins of electrons in a magnetic field can

be flipped by photon absorption. Calculate the energy of a photon needed to change the spin direction of an electron from down to up in a magnetic field of 0.3 T and a g-value of 2.35.

20. Calculate the first-order correction to the energy of an electron in electron volts eV, in the ground state of hydrogen due to the gravitational potential of the nucleus given by $V_G = -\frac{m_1 m_2 G}{r}$ where m_1 and m_2 are electron and proton masses, respectively, and G is the gravitational constant given by $G = 6.672.10^{-11}\mathrm{N{\cdot}m^2{\cdot}kg^{-2}}$.

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