

Chapter 2

Introduction to Quantum Physics

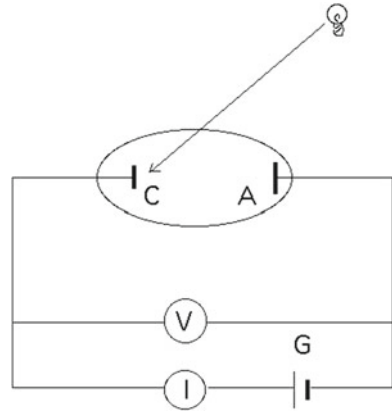
The gestation of Quantum Physics has been very long and its phenomenological foundations were various. Historically, the original idea came from the analysis of the black body spectrum. This is not surprising since the black body, in fact an oven in thermal equilibrium with the electromagnetic radiation, is a simple and fundamental system once the law of electrodynamics are established. As a matter of fact many properties of the spectrum can be deduced starting from the general laws of electrodynamics and thermodynamics; the crisis came from the violation of the equipartition of energy. That suggested to Planck the idea of *quantum*, from which everything originated. Of course a long sequence of different discoveries, first of all the photoelectric effect, the line spectra for atomic emission/absorption, the Compton effect and so on, gave a compelling evidence for the new theory.

Due to the particular limits of the present notes, an exhaustive analysis of the whole phenomenology is impossible. Even a clear discussion of the black body problem needs an exceeding amount of space. Therefore we have chosen a particular line, putting major emphasis on the photoelectric effect and on the inadequacy of a classical approach based on Thomson's model of the atom, followed by Bohr's analysis of the quantized structure of Rutherford's atom and by the construction of Schrödinger's theory. This does not mean that we have completely overlooked the remaining phenomenology; we have just presented it in the light of the established quantum theory. Thus, for example, Chap. 3 deals with the analysis of the black body spectrum in the light of quantum theory.

2.1 The Photoelectric Effect

The photoelectric effect was discovered by H. Hertz in 1887. As sketched in Fig. 2.1, two electrodes are placed in a vacuum cell; one of them (C) is hit by monochromatic light of variable frequency, while the second (A) is set to a negative potential with respect to the first, as determined by a generator G and measured by a voltmeter V.

Fig. 2.1 A sketch of Hertz's photoelectric effect apparatus



By measuring the electric current going through the amperometer I, one observes that, if the light frequency is higher than a given threshold ν_V , determined by the potential difference V between the two electrodes, the amperometer reveals a flux of current i going from A to C which is proportional to the flux of luminous energy hitting C. The threshold ν_V is a linear function of the potential difference V

$$\nu_V = a + bV . \quad (2.1)$$

The reaction time of the apparatus to light is substantially determined by the (RC) time constant of the circuit and can be reduced down to values of the order of 10^{-8} s. The theoretical interpretation of this phenomenon remained an open issue for about 14 years, because of the following reasons.

The direction of the current and the possibility to stop it by increasing the potential difference clearly show that the electric flux is made up of electrons pulled out from the atoms of electrode C by the luminous radiation.

A reasonable model for this process, which was inspired by Thomson's atomic model, assumed that electrons, which are particles of mass $m = 9 \times 10^{-31}$ kg and electric charge $-e \simeq -1.6 \times 10^{-19}$ C, were elastically bound to atoms of size $R_A \sim 3 \times 10^{-10}$ m and subject to a viscous force of constant η . The value of η is determined as a function of the atomic relaxation time, $\tau = 2m/\eta$, that is the time needed by the atom to release its energy through radiation or collisions, which is of the order of 10^{-8} s. Let us confine ourselves to considering the problem in one dimension and write the equation of motion for an electron

$$m\ddot{x} = -kx - \eta\dot{x} - eE , \quad (2.2)$$

where E is an applied electric field and k is determined on the basis of atomic frequencies. In particular we suppose the presence of many atoms with different frequencies continuously distributed around

$$\sqrt{\frac{k}{m}} = \omega_0 = 2\pi\nu_0 \sim 10^{15} \text{ s}^{-1}. \quad (2.3)$$

If we assume an oscillating electric field $E = E_0 \cos(\omega t)$ with $\omega \sim 10^{15} \text{ s}^{-1}$, corresponding to visible light, then a general solution to (2.2) is given by

$$x = x_0 \cos(\omega t + \phi) + A_1 e^{-\alpha_1 t} + A_2 e^{-\alpha_2 t}, \quad (2.4)$$

where the second and third term satisfy the homogeneous equation associated with (2.2), so that $\alpha_{1/2}$ are the solutions of the following equation

$$m\alpha^2 - \eta\alpha + k = 0, \\ \alpha = \frac{\eta \pm \sqrt{\eta^2 - 4km}}{2m} = \frac{1}{\tau} \pm \sqrt{\frac{1}{\tau^2} - \omega_0^2} \simeq \frac{1}{\tau} \pm i \omega_0, \quad (2.5)$$

where last approximation is due to the assumption $\tau \gg \omega_0^{-1}$.

Regarding the particular solution $x_0 \cos(\omega t + \phi)$, we obtain by substitution:

$$-m\omega^2 x_0 \cos(\omega t + \phi) = -kx_0 \cos(\omega t + \phi) + \eta\omega x_0 \sin(\omega t + \phi) - eE_0 \cos(\omega t) \quad (2.6)$$

hence

$$(k - m\omega^2)x_0 (\cos(\omega t) \cos \phi - \sin(\omega t) \sin \phi) \\ = \eta\omega x_0 (\sin(\omega t) \cos \phi + \cos(\omega t) \sin \phi) - eE_0 \cos(\omega t)$$

from which, by taking alternatively $\omega t = 0, \pi/2$, we obtain the following system

$$\left(m \left(\omega_0^2 - \omega^2 \right) \cos \phi - \eta\omega \sin \phi \right) x_0 = -eE_0, \\ m \left(\omega_0^2 - \omega^2 \right) x_0 \sin \phi + \eta\omega x_0 \cos \phi = 0 \quad (2.7)$$

which can be solved for ϕ

$$\tan \phi = \frac{2\omega}{\tau (\omega^2 - \omega_0^2)}, \\ \cos \phi = \frac{\omega^2 - \omega_0^2}{\sqrt{(\omega_0^2 - \omega^2)^2 + \frac{4\omega^2}{\tau^2}}}, \quad \sin \phi = \frac{(2\omega/\tau)}{\sqrt{(\omega_0^2 - \omega^2)^2 + \frac{4\omega^2}{\tau^2}}} \quad (2.8)$$

and finally for x_0 , for which we obtain the well known resonant form

$$x_0 = \frac{eE_0/m}{\sqrt{(\omega_0^2 - \omega^2)^2 + \frac{4\omega^2}{\tau^2}}} . \quad (2.9)$$

To complete our computation, we must determine A_1 and A_2 . On the other hand, taking into account (2.5) and the fact that x is real, we can rewrite the general solution in the following equivalent form:

$$x = x_0 \cos(\omega t + \phi) + Ae^{-t/\tau} \cos(\omega_0 t + \phi_0) . \quad (2.10)$$

If we assume that the electron is initially at rest, we can determine A and ϕ_0 by taking $x = \dot{x} = 0$ for $t = 0$, i.e.

$$x_0 \cos \phi + A \cos \phi_0 = 0 , \quad (2.11)$$

$$x_0 \omega \sin \phi = -A \left(\frac{\cos \phi_0}{\tau} + \omega_0 \sin \phi_0 \right) , \quad (2.12)$$

hence in particular

$$\tan \phi_0 = \frac{\omega}{\omega_0} \tan \phi - \frac{1}{\omega_0 \tau} . \quad (2.13)$$

These equations give us enough information to discuss the photoelectric effect without explicitly substituting A in (2.10).

Indeed in our simplified model the effect, i.e. the liberation of the electron from the atomic bond, happens as the amplitude of the electron displacement x is greater than the atomic radius. In Eq. (2.10) x is the sum of two parts, the first corresponding to stationary oscillations, the second to a transient decaying with time constant τ . In principle, the maximum amplitude could take place during the transient or later: to decide which is the case we must compare the value of A with that of x_0 . It is apparent from (2.11) that the magnitude of A is of the same order as x_0 unless $\cos \phi_0$ is much less than $\cos \phi$. On the other hand, Eq. (2.13) tells us that, if $\tan \phi_0$ is large, then $\tan \phi$ is large as well, since $(\omega_0 \tau)^{-1} \sim 10^{-7}$ and $\omega/\omega_0 \sim 1$. Therefore, the order of magnitude of the maximum displacement is given by x_0 , and can be sensitive to the electric field frequency. That happens in the resonant regime, where ω differs from ω_0 by less than $2\sqrt{\omega/\tau}$.

Let us consider separately the generic case from the resonant one. In the first case the displacement is of the order of $eE_0/(\omega^2 m)$, since the square root of the denominator in (2.9) has the same order of magnitude as ω^2 . In order to induce the photoelectric effect it is therefore necessary that

$$\frac{eE_0}{\omega^2 m} \sim R_A ,$$

from which we can compute the power density needed for the luminous beam which hits electrode C:

$$P = c\epsilon_0 E_0^2 \sim c\epsilon_0 \left(\frac{R_A \omega^2 m}{e} \right)^2 ,$$

where c is the speed of light and ϵ_0 is the vacuum dielectric constant. P comes out to be of the order of 10^{15} W/m², a power density which is difficult to realize in practice and which would anyway be enough to vaporize any kind of electrode. We must conclude that our model cannot explain the photoelectric effect if ω is far from resonance. Let us consider therefore the resonant case and set $\omega = \omega_0$. On the basis of (2.9), (2.11) and (2.13), that implies:

$$\phi = \phi_0 = \frac{\pi}{2} , \quad A = -x_0 ,$$

hence

$$x = \frac{-eE_0\tau}{2m\omega_0} (1 - e^{-t/\tau}) \sin(\omega_0 t) . \quad (2.14)$$

In order for the photoelectric effect to take place, the oscillation amplitude must be greater than the atomic radius:

$$\frac{eE_0\tau}{2m\omega_0} (1 - e^{-t/\tau}) \geq R_A .$$

That sets the threshold field to $2m\omega_0 R_A/(e\tau)$ and the power density of the beam to

$$P = c\epsilon_0 \left(\frac{4\omega_0 m R_A}{\tau e} \right)^2 \sim 100 \text{ W/m}^2 ,$$

while the time required to reach the escape amplitude is of the order of τ .

In conclusion, our model predicts a threshold for the power of the beam, but not for its frequency, which however must be tuned to the resonance frequency: the photoelectric effect would cease both below and above the typical resonance frequencies of the atoms in the electrode. Moreover the expectation is that the electron does not gain any further appreciable energy from the electric field once it escapes the atomic bond: hence the emission from the electrode could be strong, but made up of electrons of energy equal to that gained during the last atomic oscillation. Equation (2.14) shows that, during the transient ($t \ll \tau$), the oscillation amplitude grows roughly by $eE_0/(m\omega_0^2)$ in one period, so that the energy of the escaped electron would be of the order of magnitude of $kR_A eE_0/(m\omega_0^2) = eE_0 R_A$, corresponding also to the energy acquired by the electron from the electric field E_0 when crossing the atom. It is easily computed that for a power density of the order of $10 - 100$ W/m², the electric field E_0 is roughly 100 V/m, so that the final kinetic energy of the electron would be 10^{-8} eV $\sim 10^{-27}$ J: this value is much smaller than the typical thermal energy at room temperature ($3kT/2 \sim 10^{-1}$ eV).

The prediction of the model is therefore in clear contradiction with the experimental results described above. In particular, the very small energy of the emitted electrons implies that the electric current I should vanish even for small negative potential differences.

Einstein proposed a description of the effect based on the hypothesis that the energy be transferred from the luminous radiation to the electron in a single *elementary* (i.e. no further separable) process, instead than through a gradual excitation. Moreover, he proposed that the transferred energy be equal to $h\nu = h\omega/(2\pi) \equiv \hbar\omega$, a quantity called *quantum* by Einstein himself. The constant h had been introduced by Planck several years before to describe the radiation emitted by an oven and its value is 6.63×10^{-34} J s.

If the quantum of energy is enough for electron liberation, i.e. according to our model if it is larger than $E_t \equiv kR_A^2/2 = \omega_0^2 R_A^2 m/2 \sim 10^{-19}$ J ~ 1 eV, and the frequency exceeds 1.6×10^{14} Hz (corresponding to ω in our model), then the electron is emitted keeping the energy exceeding the threshold in the form of kinetic energy. The number of emitted electrons, hence the intensity of the process, is proportional to the flux of luminous energy, i.e. to the number of quanta hitting the electrode.

Since $E = h\nu$ is the energy gained by the electron, which spends a part E_t to get free from the atom, the final electron kinetic energy is $T = h\nu - E_t$, so that the electric current can be interrupted by placing the second electrode at a negative potential

$$V = \frac{h\nu - E_t}{e},$$

thus reproducing (2.1).

The most important point in Einstein's proposal, which was already noticed by Planck, is that a physical system of typical frequency ν can exchange only quanta of energy equal to $h\nu$. The order of magnitude in the atomic case is $\omega \sim 10^{15}$ s $^{-1}$, hence $\hbar\omega \equiv (h/2\pi) \omega \sim 1$ eV.

2.2 Bohr's Quantum Theory

After the introduction of the concept of a quantum of energy, *quantum theory* was developed by N. Bohr in 1913 and then perfected by A. Sommerfeld in 1916: they gave a precise proposal for multi-periodic systems, i.e. systems which can be described in terms of periodic components.

The main purpose of their studies was that of explaining, in the framework of Rutherford's atomic model, the light spectra emitted by gases (in particular mono-atomic ones) excited by electric discharges. The most simple and renowned case is that of the mono-atomic hydrogen gas (which can be prepared with some difficulties since hydrogen tends to form diatomic molecules). It has a discrete spectrum, i.e. the emitted frequencies can assume only some discrete values, in particular:

$$\nu_{n,m} = R \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \quad (2.15)$$

for all possible positive integer pairs with $m > n$: this formula was first proposed by J. Balmer in 1885 for the case $n = 2, m \geq 3$, and then generalized by J. Rydberg in 1888 for all possible pairs (n, m) . The emission is particularly strong for $m = n + 1$.

Rutherford had shown that the positive charge in an atom is localized in a practically point-like nucleus, which also contains most of the atomic mass. In particular the hydrogen atom can be described as a two-body system: a heavy and positively charged particle, which nowadays is called proton, bound by Coulomb forces to a light and negatively charged particle, the electron.

We will confine our discussion to the case of circular orbits of radius r , covered with uniform angular velocity ω , and will consider the proton as if it were infinitely heavy (its mass is about 2×10^3 times that of the electron). In this case we have

$$m\omega^2 r = \frac{e^2}{4\pi\epsilon_0 r^2},$$

where m is the electron mass. Hence the orbital frequencies, which in classical physics correspond to those of the emitted radiation, are continuously distributed as a function of the radius

$$\nu = \frac{\omega}{2\pi} = \frac{e}{\sqrt{16\pi^3\epsilon_0 m r^3}}; \quad (2.16)$$

this is in clear contradiction with (2.15). Based on Einstein's theory of the photoelectric effect, Bohr proposed to interpret (2.15) by assuming that only certain orbits be allowed in the atom, which are called *levels*, and that the frequency $\nu_{n,m}$ correspond to the transition from the m -th level to n -th one. In that case

$$h\nu_{n,m} = E_m - E_n, \quad (2.17)$$

where the atomic energies (which are negative since the atom is a bound system) would be given by

$$E_n = -\frac{hR}{n^2}. \quad (2.18)$$

Since, according to classical physics for the circular orbit case, the atomic energy is given by

$$E_{\text{circ}} = -\frac{e^2}{8\pi\epsilon_0 r},$$

Bohr's hypothesis is equivalent to the assumption that the admitted orbital radii be

$$r_n = \frac{e^2 n^2}{8\pi\epsilon_0 h R}. \quad (2.19)$$

It is clear that Bohr's hypothesis seems simply aimed at reproducing the observed experimental data; it does not permit any particular further development, unless further conditions are introduced. The most natural, which is called *correspondence principle*, is that the classical law, given in (2.16), be reproduced by (2.15) for large values of r , hence of n , and at least for the strongest emissions, i.e. those with $m = n + 1$, for which we can write

$$\nu_{n,n+1} = R \frac{2n+1}{n^2(n+1)^2} \rightarrow \frac{2R}{n^3}, \quad (2.20)$$

these frequencies should be identified in the above mentioned limit with what resulting from the combination of (2.16) and (2.19):

$$\nu = \frac{e}{\sqrt{16\pi^3\epsilon_0 m r_n^3}} = \frac{\epsilon_0 \sqrt{32(hR)^3}}{e^2 \sqrt{mn^3}}. \quad (2.21)$$

By comparing last two equations we get the value of the coefficient R in (2.15), which is called *Rydberg constant*:

$$R = \frac{me^4}{8\epsilon_0^2 h^3}$$

and is in excellent agreement with experimental determinations. We have then the following *quantized* atomic energies

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2 n^2}, \quad n = 1, 2, \dots$$

while the quantized orbital radii are

$$r_n = \frac{\epsilon_0 h^2 n^2}{\pi m e^2}. \quad (2.22)$$

In order to give a numerical estimate of our results, it is convenient to introduce the ratio $e^2/(2\epsilon_0 hc) \equiv \alpha \simeq 1/137$, which is dimensionless and is known as the *fine structure constant*. The energy of the state with $n = 1$, which is called the *ground state*, is

$$E_1 = -hR = -\frac{mc^2}{2}\alpha^2;$$

noticing that $mc^2 \sim 0.51$ MeV, we have $E_1 \simeq -13.6$ eV. The corresponding atomic radius (Bohr radius) is $r_1 \simeq 0.53 \times 10^{-10}$ m.

Notwithstanding the excellent agreement with experimental data, the starting hypothesis, to be identified with (2.18), looks still quite conditioned by the particular form of Balmer law given in (2.15). For that reason Bohr tried to identify a

physical observable to be quantized according to a simpler and more fundamental law. He proceeded according to the idea that such observable should have the same dimensions of the Planck constant, i.e. those of an action, or equivalently of an angular momentum. In the particular case of quantized circular orbits this last quantity reads:

$$L = pr = m\omega r^2 = \frac{e}{\sqrt{4\pi\epsilon_0}} \sqrt{mr_n} = \frac{h}{2\pi} n \equiv n\hbar, \quad n = 1, 2, \dots \quad (2.23)$$

2.3 de Broglie's Interpretation

In this picture of partial results, even if quite convincing from the point of view of the phenomenological comparison, the real progress towards understanding quantum physics came as L. de Broglie suggested the existence of a *universal wave-like behavior* of material particles and of energy quanta associated to force fields. As we have seen in the case of electromagnetic waves, when discussing the Doppler effect, a phase can always be associated with a wave-like process, which is variable both in space and in time (e.g. given by $2\pi(x/\lambda - \nu t)$ in the case of waves moving parallel to the x axis). The assumption that quanta can be interpreted as real particles and that Einstein's law $E = h\nu$ be universally valid, would correspond to identifying the wave phase with $2\pi(x/\lambda - Et/h)$. If we further assume the phase to be relativistically invariant, then it must be expressed in the form $(px - Et)/\hbar$, where E and p are identified with relativistic energy and momentum, i.e. in the case of material particles:

$$E = \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}}, \quad p = \frac{mv}{\sqrt{1 - \frac{v^2}{c^2}}}.$$

In order to simplify the discussion as much as possible, we will consider here and in most of the following a one-dimensional motion (parallel to the x axis). In conclusion, by comparing last two expressions given for the phase, we obtain de Broglie's equation:

$$p = \frac{h}{\lambda},$$

which is complementary to Einstein's law, $E = h\nu$.

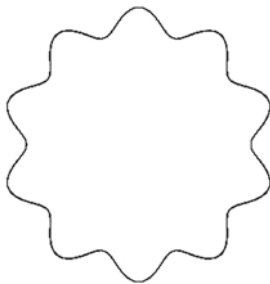
These formulae give an idea of the scale at which quantum effects are visible. For an electron having kinetic energy $E_k = 10^2 \text{ eV} \simeq 1.6 \times 10^{-17} \text{ J}$, quantum effects show up at distances of the order of $\lambda = h/p = h/\sqrt{2mE_k} \sim 10^{-10} \text{ m}$, corresponding to atomic or slightly subatomic distances; that confirms the importance of quantum effects for electrons in condensed matter and in particular in solids, where typical energies are of the order of a few electron-volts. For a gas of light atoms in equilibrium at temperature T , the kinetic energy predicted by the equipartition

theorem is $3 kT/2$, where k is Boltzmann's constant. At a temperature $T = 300^\circ\text{K}$ (room temperature) the kinetic energy is roughly 2.5×10^{-2} eV, corresponding to wavelengths of about 10^{-10} m for atom masses of the order of 10^{-26} kg. However at those distances the picture of a non-interacting (perfect) gas does not apply because of strong repulsive forces coming into play: in order to gain a factor ten over distances, it is necessary to reduce the temperature by a factor 100, going down to a few Kelvin degrees, at which quantum effects are manifest. For a macroscopic body of mass 1 kg and kinetic energy 1 J, quantum effects would show up at distances roughly equal to 3×10^{-34} m, hence completely negligible with respect to the thermal oscillation amplitudes of atoms, which are proportional to the square root of the absolute temperature, and are in particular of the order of a few nanometers at $T = 10^3$ °K, where the solid melts.

On the other hand, Einstein's formula gives us information about the scale of times involved in quantum processes, which is of the order of $\hbar/\Delta E$, where ΔE corresponds to the amount of exchanged energy. For $\Delta E \sim 1$ eV, times are roughly 4×10^{-15} s, while for thermal interactions at room temperature time intervals increase by a factor 40.

In conclusion, in the light of de Broglie's formula, quantum effects are not visible for macroscopic bodies and at macroscopic energies. For atoms in matter they show up after condensation, or anyway at very low temperatures, while electrons in solids or in atoms are fully in the quantum regime.

In Rutherford's atomic model illustrated in the previous Section, the circular motion of the electron around the proton must be associated, according to de Broglie, with a wave closed around a circular orbit. That resembles wave-like phenomena analogous to the oscillations of a ring-shaped elastic string or to air pressure waves in a toroidal reed pipe. That implies well tuned wavelengths, as in the case of musical instruments (which are not ring-shaped for obvious practical reasons). The need for tuned wavelength can be easily understood in the case of the toroidal reed pipe: a complete round of the ring must bring the phase back to its initial value, so that the total length of the pipe must be an integer multiple of the wavelength.



Taking into account previous equations regarding circular atomic orbits, we have the following electron wavelength:

$$\lambda = \frac{h}{p} = \frac{h}{e} \sqrt{\frac{4\pi\epsilon_0 r}{m}},$$

so that the tuning condition reads

$$2\pi r = n\lambda = \frac{nh}{e} \sqrt{\frac{4\pi\epsilon_0 r}{m}}$$

giving

$$r = \frac{n^2 h^2 \epsilon_0}{\pi e^2 m},$$

which confirms (2.22) and gives support to the picture proposed by Bohr and Sommerfeld. De Broglie's hypothesis, which was formulated in 1924, was confirmed in 1926 by Davisson and Gerner by measuring the intensity of an electron beam reflected by a nickel crystal. The apparatus used in the experiment is sketched in Fig. 2.2. The angular distribution of the electrons, reflected in conditions of normal incidence, shows a strongly anisotropic behavior with a marked dependence on the beam accelerating potential. In particular, an accelerating potential equal to 48 V leads to a quite pronounced peak at a reflection angle $\phi = 55.3^\circ$. An analogous X-ray diffraction experiment permits to interpret the nickel crystal as an atomic lattice of spacing 0.215×10^{-9} m. The comparison between the angular distributions obtained for X-rays and for electrons shows relevant analogies, suggesting a diffractive interpretation also in the case of electrons. Bragg's law, giving the n -th maximum in the diffraction figure, is $d \sin \phi_n = n\lambda$.

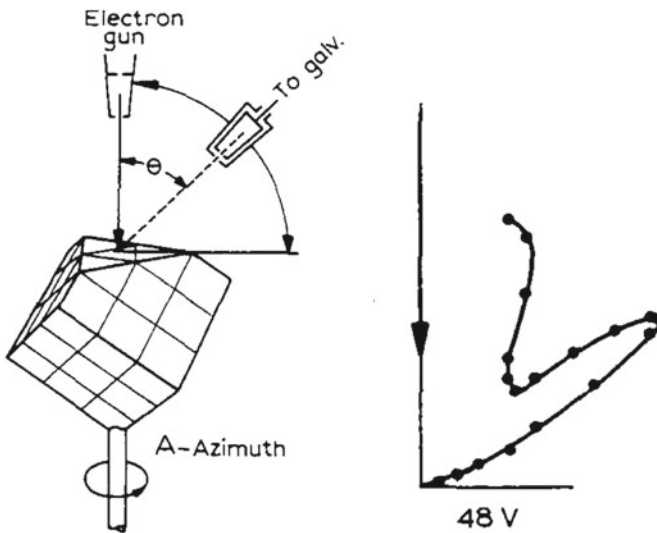


Fig. 2.2 A schematic description of Davisson-Gerner apparatus and a polar coordinate representation of the results obtained at 48 V electron energy, as they appear in Davisson's Noble Price Lecture, from *Nobel Lectures, Physics 1922–1941* (Elsevier Publishing Company, Amsterdam 1965)

For the peak corresponding to the principal maximum at 55.3° we have

$$d \sin \phi = \lambda \simeq 0.175 \times 10^{-9} \text{ m} .$$

On the other hand the electrons in the beam have a kinetic energy

$$E_k \simeq 7.68 \times 10^{-18} \text{ J} ,$$

hence a momentum $p \simeq 3.7 \times 10^{-24} \text{ N s}$, in excellent agreement with de Broglie's formula $p = h/\lambda$. In the following years analogous experiments were repeated using different kinds of material particles, in particular neutrons.

Once established the wave-like behavior of propagating material particles, it must be clarified what is the physical quantity the phenomenon refers to, i.e. what is the physical meaning of the oscillating quantity (or quantities) usually called *wave function*, for which a *linear* propagating equation will be supposed, in analogy with mechanical or electromagnetic waves. It is known that, in the case of electromagnetic waves, the quantities measuring the amplitude are electric and magnetic fields. Our question regards exactly the analogous of those fields in the case of de Broglie's waves. The experiment by Davisson and Gerner gives an answer to this question. Indeed, as illustrated in Fig. 2.2, the detector reveals the presence of one or more electrons at a given angle; if we imagine to repeat the experiment several times, with a single electron in the beam at each time, and if we measure the frequency at which electrons are detected at the various angles, we get the *probability* of having the electron in a given site covered by the detector.

In the case of an optical measure, what is observed is the interference effect in the energy deposited on a plate; that is proportional to the square of the electric field on the plate. Notice that the linearity in the wave equation and the quadratic relation between the measured quantity and the wave amplitude are essential conditions for the existence of interference and diffractive phenomena. We must conclude that also in the case of material particles some *positive quadratic form* of the de Broglie wave function gives the probability of having the electron in a given point.

We have quite generically mentioned a quadratic form, since at the moment it is still not clear if the wave function has one or more components, i.e. if it corresponds to one or more real functions. By a positive quadratic form we mean a homogeneous second order polynomial in the wave function components, which is positive for real and non-vanishing values of its arguments. In the case of a single component, we can say without loss of generality that the probability density is the wave function squared, while in the case of two or more components it is always possible, by suitable linear transformations, to reduce the quadratic form to a sum of squares.

We are now going to show that the hypothesis of a single component must be discarded. Let us indicate by $\rho(\mathbf{r}, t)d^3r$ the probability of the particle being in a region of size d^3r around \mathbf{r} at time t , and by $\psi(\mathbf{r}, t)$ the wave function, which for the moment is considered as a real valued function, defined so that

$$\rho(\mathbf{r}, t) = \psi^2(\mathbf{r}, t) . \quad (2.24)$$

If Ω indicates the whole region accessible to the particle, the probability density must satisfy the natural constraint:

$$\int_{\Omega} d^3r \rho(\mathbf{r}, t) = 1, \quad (2.25)$$

which implies the condition:

$$\int_{\Omega} d^3r \dot{\rho}(\mathbf{r}, t) \equiv \int_{\Omega} d^3r \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = 0. \quad (2.26)$$

This expresses the fact that, if the particle cannot escape Ω , the probability of finding it in that region must always be one. This condition can be given in mathematical terms analogous to those used to express electric charge conservation: the charge contained in a given volume, i.e. the integral of the charge density, may change only if the charge flows through the boundary surface. The charge flux through the boundaries is expressed in terms of the current density flow and can be rewritten as the integral of the divergence of the current density itself by using Gauss–Green theorem

$$\int_{\Omega} \dot{\rho} = -\Phi_{\partial\Omega}(J) = -\int_{\Omega} \nabla \cdot \mathbf{J}.$$

Finally, by reducing the equation from an integral form to a differential one, we can set the temporal derivative of the charge density equal to minus the divergence of the current density. Based on this analogy, let us introduce the *probability current* density \mathbf{J} and write

$$\dot{\rho}(\mathbf{r}, t) = -\frac{\partial J_x(\mathbf{r}, t)}{\partial x} - \frac{\partial J_y(\mathbf{r}, t)}{\partial y} - \frac{\partial J_z(\mathbf{r}, t)}{\partial z} \equiv -\nabla \cdot \mathbf{J}(\mathbf{r}, t). \quad (2.27)$$

The conservation equation must be automatically satisfied as a consequence of the propagation equation of de Broglie's waves, which we write in the form:

$$\dot{\psi} = L\left(\psi, \nabla\psi, \nabla^2\psi, \dots\right), \quad (2.28)$$

where L indicates a generic linear function of ψ and its derivatives like:

$$L\left(\psi, \nabla\psi, \nabla^2\psi, \dots\right) = \alpha\psi + \beta\nabla^2\psi. \quad (2.29)$$

Notice that if L were not linear the interference mechanism upon which quantization is founded would soon or later fail. Furthermore we assume invariance under the reflection of the coordinates, at least in the free case, so that terms proportional to first derivatives are excluded.

From Eq. (2.24) we have $\dot{\rho} = 2\psi\dot{\psi}$, which can be rewritten, using (2.28), as:

$$\dot{\rho} = 2\psi L \left(\psi, \nabla\psi, \nabla^2\psi, \dots \right). \quad (2.30)$$

The right-hand side of last equation must be identified with $-\nabla \cdot \mathbf{J}(\mathbf{r}, t)$. Moreover \mathbf{J} must necessarily be a bilinear function of ψ and its derivatives, exactly like $\dot{\rho}$. Therefore, since \mathbf{J} is a vector-like quantity, it must be expressible as

$$\mathbf{J} = c \psi \nabla\psi + d \nabla\psi \nabla^2\psi + \dots$$

from which it appears that $\nabla \cdot \mathbf{J}(\mathbf{r}, t)$ must necessarily contain bilinear terms in which both functions are derived, like $\nabla\psi \cdot \nabla\psi$. However, such terms are clearly missing in (2.30).

We come to the conclusion that the description of de Broglie's waves requires at least two wave functions ψ_1 and ψ_2 , defined so that $\rho = \psi_1^2 + \psi_2^2$. In an analogous way we can introduce the complex valued function:

$$\psi = \psi_1 + i\psi_2, \quad (2.31)$$

defined so that

$$\rho = |\psi|^2; \quad (2.32)$$

this choice implies:

$$\dot{\rho} = \psi^* \dot{\psi} + \psi \dot{\psi}^*.$$

If we assume, for instance, the wave equation corresponding to (2.29):

$$\dot{\psi} = \alpha\psi + \beta\nabla^2\psi, \quad (2.33)$$

we obtain:

$$\dot{\rho} = \psi^* \left(\alpha\psi + \beta\nabla^2\psi \right) + \psi \left(\alpha^*\psi^* + \beta^*\nabla^2\psi^* \right).$$

If we also assume that the probability current density be

$$\mathbf{J} = ik \left(\psi^* \nabla\psi - \psi \nabla\psi^* \right), \quad (2.34)$$

with k real so as to make \mathbf{J} real as well, we easily derive

$$\nabla \cdot \mathbf{J} = ik \left(\psi^* \nabla^2\psi - \psi \nabla^2\psi^* \right).$$

It can be easily verified that the continuity equation (2.27) is satisfied if

$$\alpha + \alpha^* = 0, \quad \beta = -ik. \quad (2.35)$$

It is of great physical interest to consider the case in which the wave function has more than two real components. In particular, the wave function of electrons has four components or, equivalently, two complex components. In general, the multiplicity of the complex components is linked to the existence of an intrinsic angular momentum, which is called *spin*. The various complex components are associated with the different possible spin orientations. In the case of particles with non-vanishing mass, the number of components is $2S + 1$, where S is the spin of the particle. In the case of the electron, $S = 1/2$.

For several particles, as for the electron, spin is associated with a magnetic moment which is inherent to the particle: it behaves as a microscopic magnet with various possible orientations, corresponding to those of the spin, which can be selected by placing the particle in a non-uniform magnetic field and measuring the force acting on the particle.

2.4 Schrödinger's Equation

The simplest case to which our considerations can be applied is that of a non-relativistic free particle of mass m . To simplify notations and computations, we will confine ourselves to a one-dimensional motion, parallel, for instance, to the x axis; if the particle is not free, forces will be parallel to the same axis as well. The obtained results will be extensible to three dimensions by exploiting the vector formalism. In practice, we will systematically replace ∇ by its component $\nabla_x = \partial/\partial x \equiv \partial_x$ and the Laplacian operator $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ by $\partial^2/\partial x^2 \equiv \partial_x^2$; the probability current density \mathbf{J} will be replaced by J_x (J) as well. The inverse replacement will suffice to get back to three dimensions.

The energy of a non-relativistic free particle is

$$E = c\sqrt{m^2c^2 + p^2} \simeq mc^2 + \frac{p^2}{2m} + O\left(\frac{p^4}{m^3c^2}\right),$$

where we have explicitly declared our intention to neglect terms of the order of $p^4/(m^3c^2)$. Assuming de Broglie's interpretation, we write the wave function:

$$\psi_P(x, t) \sim e^{2\pi i(x/\lambda - \nu t)} = e^{i(px - Et)/\hbar} \quad (2.36)$$

(we are considering a motion in the positive x direction). Our choice implies the following wave equation

$$\dot{\psi}_P = -\frac{iE}{\hbar}\psi_P = -\frac{i}{\hbar}\left(mc^2 + \frac{1}{2m}p^2\right)\psi_P. \quad (2.37)$$

We have also

$$\partial_x \psi_P = \frac{i}{\hbar} p \psi_P, \quad (2.38)$$

from which we deduce

$$i \hbar \dot{\psi}_P = mc^2 \psi_P - \frac{\hbar^2}{2m} \partial_x^2 \psi_P. \quad (2.39)$$

Our construction can be simplified by multiplying the initial wave function by the phase factor $e^{imc^2 t/\hbar}$, i.e. defining

$$\psi \equiv e^{imc^2 t/\hbar} \psi_P \sim \exp \left(\frac{i}{\hbar} \left(px - \frac{p^2}{2m} t \right) \right). \quad (2.40)$$

Since the dependence on x is unchanged, ψ still satisfies (2.38) and has the same probabilistic interpretation as ψ_P . Indeed both ρ and J are unchanged. The wave equation instead changes:

$$i \hbar \dot{\psi} = -\frac{\hbar^2}{2m} \partial_x^2 \psi \equiv T \psi. \quad (2.41)$$

This is the *Schrödinger equation* for a free (non-relativistic) particle, in which the right-hand side has a natural interpretation in terms of the particle energy, which in the free case is only of kinetic type.

In the case of particles under the influence of a force field corresponding to a potential energy $V(x)$, the equation can be generalized by adding $V(x)$ to the kinetic energy:

$$i \hbar \dot{\psi} = -\frac{\hbar^2}{2m} \partial_x^2 \psi + V(x) \psi. \quad (2.42)$$

This is the one-dimensional Schrödinger equation that we shall apply to various cases of physical interest.

Equations (2.34) and (2.35) show that the probability density current does not depend on V and is given by:

$$J = -\frac{i \hbar}{2m} (\psi^* \partial_x \psi - \psi \partial_x \psi^*). \quad (2.43)$$

Going back to the free case and considering the *plane* wave function given in (2.36), it is interesting to notice that the corresponding probability density, $\rho = |\psi|^2$, is a constant function. This result is paradoxical since, by reducing (2.25) to one dimension, we obtain

$$\int_{-\infty}^{\infty} dx \rho(x, t) = \int_{-\infty}^{\infty} dx |\psi(x, t)|^2 = 1, \quad (2.44)$$

which cannot be satisfied in the examined case since the integral of a constant function is divergent. We must conclude that our interpretation excludes the possibility that a particle has a well defined momentum.

We are left with the hope that this difficulty may be overcome by admitting some (small) uncertainty on the knowledge of momentum. This possibility can be easily analyzed thanks to the linearity of the Schrödinger equation. Indeed Eq. (2.41) admits other different solutions besides the simple plane wave, in particular the *wave packet* solution, which is constructed as a linear superposition of many plane waves according to the following integral:

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \tilde{\psi}(p) \exp\left(\frac{i}{\hbar} \left(px - \frac{p^2}{2m}t\right)\right). \quad (2.45)$$

Considering the expression for $\psi(x, 0)$ it is easy to deduce the expression¹:

$$\tilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx \psi(x, 0) \exp\left(-\frac{i}{\hbar} px\right). \quad (2.46)$$

The squared modulus of the superposition coefficients, $|\tilde{\psi}(p)|^2$, can be naturally interpreted as the probability density in terms of momentum, exactly in the same way as $\rho(x)$ is interpreted as a probability density in terms of position.

Let us choose in particular a Gaussian distribution:

$$\tilde{\psi}(p) = \frac{1}{\sqrt{\sqrt{2\pi}\Delta}} e^{-(p-p_0)^2/(4\Delta^2)}, \quad (2.47)$$

corresponding to

$$\psi_{\Delta}(x, t) = \frac{1}{\sqrt{\sqrt{(2\pi)^3}\Delta\hbar}} \int_{-\infty}^{\infty} dp e^{-(p-p_0)^2/(4\Delta^2)} e^{i(px - p^2t/2m)/\hbar} \quad (2.48)$$

where the coefficients in (2.45) and (2.47) are determined in such a way that

$$\int_{-\infty}^{\infty} dx |\psi_{\Delta}(x, t)|^2 = 1. \quad (2.49)$$

¹Using the following formulae it is easy to verify (2.45) and (2.46) in the case of Gaussian wave packets. By linearity this proves the validity of the same equations in the case of fast decreasing, infinitely differentiable (C^{∞}) functions. A further extension of the validity is shown in the framework of distribution theory. In our analysis the restriction to fast decreasing C^{∞} functions is understood.

The integral in (2.48) can be computed by recalling that, if α is a complex number with positive real part ($\text{Re}(\alpha) > 0$), then

$$\int_{-\infty}^{\infty} dp e^{-\alpha p^2} = \sqrt{\frac{\pi}{\alpha}}$$

and that the Riemann integral measure dp is left invariant by translations in the complex plane,

$$\begin{aligned} \int_{-\infty}^{\infty} dp e^{-\alpha p^2} &\equiv \int_{-\infty}^{\infty} d(p + \gamma) e^{-\alpha(p+\gamma)^2} \\ &= \int_{-\infty}^{\infty} dp e^{-\alpha(p+\gamma)^2} = e^{-\alpha\gamma^2} \int_{-\infty}^{\infty} dp e^{-\alpha p^2} e^{-2\alpha\gamma p}, \end{aligned}$$

for every complex number γ . Therefore we have

$$\int_{-\infty}^{\infty} dp e^{-\alpha p^2} e^{\beta p} = \sqrt{\frac{\pi}{\alpha}} e^{\beta^2/4\alpha}. \quad (2.50)$$

Developing (2.48) with the help of (2.50) we can write

$$\begin{aligned} \psi_{\Delta}(x, t) &= \frac{1}{\sqrt{\sqrt{(2\pi)^3 \Delta \hbar}}} e^{-\frac{p_0^2}{4\Delta^2}} \int_{-\infty}^{\infty} dp e^{-\left[\frac{1}{4\Delta^2} + \frac{it}{2m\hbar}\right] p^2} e^{\left[\frac{p_0}{2\Delta^2} + \frac{ix}{\hbar}\right] p} \\ &= \sqrt{\frac{1}{\sqrt{2\pi}\left(\frac{\hbar}{2\Delta} + \frac{i\Delta t}{m}\right)}} \exp\left(\frac{\left[\frac{p_0}{2\Delta^2} + \frac{ix}{\hbar}\right]^2}{\frac{1}{\Delta^2} + \frac{2it}{m\hbar}} - \frac{p_0^2}{4\Delta^2}\right). \end{aligned} \quad (2.51)$$

We are interested in particular in the x dependence of the probability density $\rho(x)$: that is solely related to the real part of the exponent of the rightmost term in (2.51), which can be expanded as follows:

$$\frac{\frac{p_0^2}{4\Delta^4} + \frac{ip_0x}{\Delta^2\hbar} - \frac{x^2}{\hbar^2}}{\frac{1}{\Delta^2} + \frac{2it}{m\hbar}} - \frac{p_0^2}{4\Delta^2} = -\frac{p_0^2}{4\Delta^2} \frac{\frac{4t^2\Delta^4}{m^2\hbar^2} + \frac{2it\Delta^2}{m\hbar}}{1 + \frac{4t^2\Delta^4}{m^2\hbar^2}} - \left(\frac{\Delta^2 x^2}{\hbar^2} - \frac{ip_0x}{\hbar}\right) \frac{1 - \frac{2it\Delta^2}{m\hbar}}{1 + \frac{4t^2\Delta^4}{m^2\hbar^2}}$$

the real part being

$$-\frac{\Delta^2 \left(x - \frac{p_0 t}{m}\right)^2}{\hbar^2 \left(1 + \frac{4t^2\Delta^4}{m^2\hbar^2}\right)} \equiv -\frac{\Delta^2 (x - v_0 t)^2}{\hbar^2 \left(1 + \frac{4t^2\Delta^4}{m^2\hbar^2}\right)}.$$

Since p_0 is clearly the average momentum of the particle, we have introduced the corresponding average velocity $v_0 = p_0/m$. Recalling the definition of ρ as well as its normalization constraint, we finally find

$$\rho(x, t) = \frac{\Delta}{\hbar} \sqrt{\frac{2}{\pi \left(1 + \frac{4t^2 \Delta^4}{m^2 \hbar^2}\right)}} \exp\left(-\frac{2\Delta^2}{\hbar^2} \frac{(x - v_0 t)^2}{1 + \frac{4t^2 \Delta^4}{m^2 \hbar^2}}\right), \quad (2.52)$$

while the probability distribution in terms of momentum reads

$$\tilde{\rho}(p) = \frac{1}{\sqrt{2\pi}\Delta} e^{-(p-p_0)^2/(2\Delta^2)}. \quad (2.53)$$

Given a Gaussian distribution $\rho(x) = 1/(\sqrt{2\pi}\sigma)e^{-(x-x_0)^2/(2\sigma^2)}$, it is a well known fact, which anyway can be easily derived from previous formulae, that the mean value \bar{x} is x_0 while the mean quadratic deviation $\overline{(x - \bar{x})^2}$ is equal to σ^2 . Hence, in the examined case, we have an average position $\bar{x} = v_0 t$ with a mean quadratic deviation equal to $\hbar^2/(4\Delta^2) + t^2 \Delta^2/m^2$, while the average momentum is p_0 with a mean quadratic deviation Δ^2 . The mean values represent the kinematic variables of a free particle, while the mean quadratic deviations are roughly inversely proportional to each other: if we improve the definition of one observable, the other becomes automatically less defined.

The distributions given in (2.52) and (2.53), even if derived in the context of a particular example, permit us to reach important general conclusions which, for the sake of clarity, are listed in the following as distinct points.

2.4.1 The Uncertainty Principle

While the mean quadratic deviation relative to the momentum distribution

$$\overline{(p - \bar{p})^2} = \Delta^2$$

has been fixed a priori, by choosing $\tilde{\psi}(p)$, and is independent of time, thus confirming that momentum is a constant of motion for a free particle, that relative to the position

$$\overline{(x - \bar{x})^2} = \left(1 + \frac{4t^2 \Delta^4}{m^2 \hbar^2}\right) \frac{\hbar^2}{4\Delta^2}$$

does not contain further free parameters and does depend on time. Indeed, Δ_x grows significantly for $2t\Delta^2/(m\hbar) > 1$, hence for times greater than $t_s = m\hbar/(2\Delta^2)$. Notice that t_s is nothing but the time needed for a particle of momentum Δ to cover a distance $\hbar/(2\Delta)$, therefore this spreading has a natural interpretation also from a

classical point of view: a set of independent particles having momenta distributed according to a width Δ_p , spreads with velocity $\Delta_p/m = v_s$; if the particles are statistically distributed in a region of size initially equal to Δ_x , the same size will grow significantly after times of the order of Δ_x/v_s .

What is new in our results is, first of all, that they refer to a single particle, meaning that uncertainties in position and momentum are not avoidable; secondly, these uncertainties are strictly interrelated. Without considering the spreading in time, it is evident that the uncertainty in one variable can be diminished only as the other uncertainty grows. Indeed, Δ can be eliminated from our equations by writing the inequality:

$$\Delta_x \Delta_p \equiv \sqrt{(x - \bar{x})^2 (p - \bar{p})^2} \geq \frac{\hbar}{2}, \quad (2.54)$$

which is known as the *Heisenberg uncertainty principle*. The case of a real Gaussian packet corresponds to the minimal possible value $\Delta_x \Delta_p = \hbar/2$.

We have discussed Heisenberg's uncertainty principle using Gaussian wave packets and understanding that the results have general validity. It is not difficult to prove this generality. Indeed, let us consider a generic wave packet $\psi(x)$ satisfying the normalization condition (2.49), and let us denote by \bar{x} the average value of the particle position

$$\bar{x} = \int_{-\infty}^{\infty} dx x |\psi(x)|^2. \quad (2.55)$$

The mean quadratic deviation in position can be easily computed by:

$$\Delta_x^2 = \int_{-\infty}^{\infty} dx (x - \bar{x})^2 |\psi(x)|^2 = \int_{-\infty}^{\infty} dx x^2 |\psi(x + \bar{x})|^2. \quad (2.56)$$

Completely analogous formulae in terms of $\tilde{\psi}$ hold true for \bar{p} and Δ_p . However, using (2.45) and (2.46), it is possible to compute \bar{p} and Δ_p directly from ψ . Indeed one has:

$$\begin{aligned} \bar{p} &= \int_{-\infty}^{\infty} dp \tilde{\psi}^*(p) p \tilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \tilde{\psi}^*(p) \int_{-\infty}^{\infty} dx \psi(x) i\hbar \frac{d}{dx} e^{-\frac{ipx}{\hbar}} \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \tilde{\psi}^*(p) e^{-\frac{ipx}{\hbar}} (-i\hbar) \frac{d}{dx} \psi(x) \\ &= \int_{-\infty}^{\infty} dx \psi^*(x) (-i\hbar) \frac{d}{dx} \psi(x). \end{aligned} \quad (2.57)$$

This shows that the same results are obtained replacing at the same time $\tilde{\psi}$ by ψ and the multiplication of $\tilde{\psi}$ by p by the action of $(-i\hbar) \frac{d}{dx}$ on ψ . Both the multiplication by the variable, be it x or p , and the action of the derivative on the wave packets, in much the same way as the Laplacian, are operations which transform linearly wave packets of a certain class (e.g. with a certain number of continuous derivatives)

into wave packets of another class. They are called linear *operators* since they act linearly on the space of wave functions.² Linear operators can be combined into linear combinations and ordered *products*. A product of operators represents the combined action on the wave function of the factors of the operator product, beginning from the first operator on the right and ending with the last one on the left. The resulting action depends on the order of the factors, for this reason one says that linear operators form a *non-commutative algebra*. In general the above mentioned properties allow defining functions of operators. We shall use operators in Sects. 2.7 and 2.9.

Based on this comment, we can write a formula for the mean quadratic deviation in momentum. For this it is convenient to introduce the modified wave packet:

$$\hat{\psi}(x) \equiv e^{-\frac{i\bar{p}x}{\hbar}} \psi(x + \bar{x}) . \quad (2.58)$$

Notice that

$$(\tilde{\psi})(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx \psi(x + \bar{x}) e^{-\frac{i(p+\bar{p})x}{\hbar}} = \tilde{\psi}(p + \bar{p}) e^{-\frac{i(p+\bar{p})\bar{x}}{\hbar}} . \quad (2.59)$$

Therefore, using (2.46) and (2.56) we have:

$$\Delta_x^2 = \int_{-\infty}^{\infty} dx |x \hat{\psi}(x)|^2, \quad \Delta_p^2 = \hbar^2 \int_{-\infty}^{\infty} dx \left| \frac{d}{dx} \hat{\psi}(x) \right|^2, \quad (2.60)$$

indeed, the first equation is identical to Eq. (2.56), while the second one is the same equation written in terms of the variable p .

Now we can consider the product $\Delta_x^2 \Delta_p^2$. Before that, let us introduce a general inequality called Cauchy-Schwarz inequality. Consider two wave packets ψ_1 and ψ_2 not satisfying the normalization constraint (2.49), one has the inequality:

$$\int_{-\infty}^{\infty} dx_1 |\psi_1(x_1)|^2 \int_{-\infty}^{\infty} dx_2 |\psi_2(x_2)|^2 \geq \left| \int_{-\infty}^{\infty} dx \psi_1^*(x) \psi_2(x) \right|^2, \quad (2.61)$$

which is analogous to the triangular inequality: the square scalar product of two vectors cannot exceed the product of the square lengths of the same vectors. The product of the integrals on the left-hand side of the inequality corresponds to that of the square lengths of the vectors. The integral on the right-hand side corresponds to the scalar product. This analogy justifies the general validity of the inequality.

Let us now replace into Eq. (2.61) $\psi_1(x)$ by $x \psi(x)$ and $\psi_2(x)$ by $\hbar \frac{d}{dx} \psi(x)$. Taking into account Eq. (2.60), we have

²In general, given a normalized wave function, e.g. $\psi(x)$, and an operator O acting on it, $\int dx \psi^*(x) O \psi(x) \equiv \langle O \rangle$ is the average value of the physical quantity associated with O in the state described by the wave function $\psi(x)$.

$$\begin{aligned}
\Delta_x^2 \Delta_p^2 &\geq \hbar^2 \left| \int_{-\infty}^{\infty} dx \, x \psi^*(x) \frac{d}{dx} \psi(x) \right|^2 \\
&\geq \frac{\hbar^2}{4} \left| \int_{-\infty}^{\infty} dx \left(x \psi^*(x) \frac{d}{dx} \psi(x) + x \psi(x) \frac{d}{dx} \psi^*(x) \right) \right|^2 \\
&= \frac{\hbar^2}{4} \left| \int_{-\infty}^{\infty} dx \, \psi^*(x) \left(x \frac{d}{dx} - \frac{d}{dx} x \right) \psi(x) \right|^2 = \frac{\hbar^2}{4}. \quad (2.62)
\end{aligned}$$

It appears clearly that the uncertainty relation (2.54) holds true for any wave packet, and that it is due to the lack of commutativity of the operators corresponding to multiplication by x and to x -derivative. In more physical terms, the origin of the uncertainty relation is due to the lack of commutativity of the operators associated with position (x) and momentum ($-i\hbar \frac{d}{dx}$).

This result obviously generalizes to any pair of quantities (observables) whose corresponding operators do not commute. We shall use this generalization in Sect. 2.9, considering pairs of components of the angular momentum.

From a phenomenological point of view this principle originates from the universality of diffractive phenomena. Indeed, diffractive effects are those which prevent the possibility of a simultaneous measurement of position and momentum with arbitrarily good precision for both quantities. Let us consider for instance the case in which the measurement is performed through optical instruments; in order to improve the resolution it is necessary to make use of radiation of shorter wavelength, thus increasing the momenta of photons, which hitting the object under observation change its momentum in an unpredictable way. If instead position is determined through mechanical instruments, like slits, then the uncertainty in momentum is caused by diffractive phenomena.

It is important to evaluate the order of magnitude of quantum uncertainty in cases of practical interest. Let us consider for instance a beam of electrons emitted by a cathode at a temperature $T = 1000^\circ\text{K}$ and accelerated through a potential difference equal to 10^4 V. The order of magnitude of the kinetic energy uncertainty Δ_E is kT , where $k = 1.381 \times 10^{-23}$ J/ $^\circ\text{K}$ is the Boltzmann constant (alternatively one can use $k = 8.617 \times 10^{-5}$ eV/ $^\circ\text{K}$). Therefore $\Delta_E = 1.38 \times 10^{-20}$ J while $E = 1.6 \times 10^{-15}$ J, corresponding to a quite precise determination of the beam energy ($\Delta_E/E \sim 10^{-5}$). We can easily compute the momentum uncertainty by using error propagation ($\Delta_p/p = \frac{1}{2} \Delta_E/E$) and computing $p = \sqrt{2m_e E} = 5.6 \times 10^{-23}$ N s; we thus obtain $\Delta_p = 2.8 \times 10^{-28}$ N s, hence, making use of (2.54), $\Delta_x \geq 2 \times 10^{-7}$ m. It is clear that the uncertainty principle does not place significant constraints in the case of particle beams.

A macroscopic body of mass $M = 1$ kg placed at room temperature ($T \simeq 300^\circ\text{K}$) has an average thermal momentum, caused by collisions with air molecules, which is equal to $\Delta_p \sim \sqrt{2M 3kT/2} \simeq 9 \times 10^{-11}$ N s, so that the minimal quantum uncertainty on its position is $\Delta_x \sim 10^{-24}$ m, hence not appreciable.

The uncertainty principle is instead quite relevant at the atomic level, where it is the stabilizing mechanism which prevents the electron from collapsing onto the nucleus. We can think of the electron orbital radius as a rough estimate of its position uncertainty ($\Delta_x \sim r$) and evaluate the kinetic energy deriving from the momentum uncertainty; we have $E_k \sim \Delta_p^2/(2m) \sim \hbar^2/(2mr^2)$. Taking into account the binding Coulomb energy, the total energy is

$$E(r) \sim \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$

We infer that the system is stable, since the total energy $E(r)$ has an absolute minimum. The stable radius r_m corresponding to this minimum can be computed through the equation

$$\frac{e^2}{4\pi\epsilon_0 r_m^2} - \frac{\hbar^2}{mr_m^3} = 0,$$

hence

$$r_m \sim \frac{4\pi\epsilon_0 \hbar^2}{me^2},$$

which nicely reproduces the value of the atomic radius for the ground level in Bohr's model, see (2.22).

2.4.2 The Speed of Waves

It is known that electromagnetic waves move without distortion at a speed $c = 1/\sqrt{\epsilon_0\mu_0}$ and that, for a harmonic wave, c is given by the wavelength multiplied by the frequency.

In the case of de Broglie's waves introduced in (2.40), we have $\nu = p^2/(2mh)$ and $\lambda = h/p$; therefore the velocity of harmonic waves is given by $v_F \equiv \lambda\nu = p/(2m)$. If we consider instead the wave packet given in (2.51) and its corresponding probability density given in (2.52), we clearly see that it moves with a velocity $v_G \equiv p_0/m$, which is equal to the classical velocity of a particle with momentum p_0 . We have used different symbols to distinguish the velocity of plane waves v_F , which is called *phase velocity*, from v_G , which is the speed of the packet and is called *group velocity*. Previous equations lead to the result that, contrary to what happens for electromagnetic waves propagating in vacuum, the two velocities are different for de Broglie's waves, and in particular the group velocity does not coincide with the average value of the phase velocities of the different plane waves making up the packet. Moreover, the phase velocity depends on the wavelength ($v_F = h/(2m\lambda)$). The relation between frequency and wavelength is given by $\nu = c/\lambda$ for electromagnetic waves, while for de Broglie's waves it is $\nu = h/(2m\lambda^2)$.

There is a very large number of examples of wave-like propagation in physics: electromagnetic waves, elastic waves, gravity waves in liquids and several other ones. In each case the frequency presents a characteristic dependence on the wavelength, $\nu(\lambda)$. Considering as above the propagation of gaussian wave packets, it is always possible to define the phase velocity, $v_F = \lambda \nu(\lambda)$, and the group velocity, which in general is defined by the relation:

$$v_G = -\lambda^2 \frac{d\nu(\lambda)}{d\lambda} . \quad (2.63)$$

Last equation can be verified by considering that, for a generic dependence of the wave phase on the wave number $\exp(ikx - i\omega(k)t)$ and for a generic wave packet described by superposition coefficients strongly peaked around a given value $k = k_0$, the resulting wave function

$$\psi(x) \propto \int_{-\infty}^{\infty} dk f(k - k_0) e^{i(kx - \omega(k)t)}$$

will be peaked around an x_0 such that the phase factor is stationary, hence almost constant, for $k \sim k_0$, leading to $x_0 \sim \omega'(k_0)t$.

In the case of de Broglie's waves, Eq. (2.63) reproduces the result found previously. Media where the frequency is inversely proportional to the wavelength, as for electromagnetic waves in vacuum, are called *non-dispersive media*, and in that case the two velocities coincide.

It may be interesting to notice that, if we adopt the relativistic form for the plane wave, we have $\nu(\lambda) = \sqrt{m^2 c^4 / h^2 + c^2 / \lambda^2}$, hence

$$v_F = \lambda \sqrt{\frac{m^2 c^4}{h^2} + \frac{c^2}{\lambda^2}} = \frac{E}{p} > c ,$$

$$v_G = \frac{c^2}{\lambda} \left(\frac{m^2 c^4}{h^2} + \frac{c^2}{\lambda^2} \right)^{-1/2} = \frac{pc^2}{E} < c .$$

In particular v_G , which describes the motion of wave packets, satisfies the constraint of being less than c and coincides with the relativistic expression for the speed of a particle in terms of momentum and energy given in Chap. 1.

2.4.3 The Collective Interpretation of de Broglie's Waves

The description of single particles as wave packets is at the basis of a rigorous formulation of Schrödinger's theory. There is however an alternative interpretation

of the wave function, which is of much simpler use and can be particularly useful to describe average properties, like a particle flow in the free case.

Let us consider the plane wave in (2.40): $\psi = \exp(i(p x - p^2 t/(2m))/\hbar)$ and compute the corresponding current density J :

$$J = -\frac{i\hbar}{2m} (\psi^* \partial_x \psi - \psi \partial_x \psi^*) = -\frac{i\hbar}{2m} \left(\psi^* \frac{ip}{\hbar} \psi - \psi \frac{-ip}{\hbar} \psi^* \right) = \frac{p}{m}, \quad (2.64)$$

while $\rho = \psi^* \psi = 1$. On the other hand we notice that given a distribution of classical particles with density ρ and moving with velocity v , the corresponding current density is $J = \rho v$.

That suggests to go beyond the problem of normalizing the probability distribution in (2.44), relating instead the wave function in (2.40) not to a single particle, as we have done till now, but to a stationary flux of independent particles, which are uniformly distributed with unitary density and move with the same velocity v .

It should be clear that in this way we are a priori giving up the idea of particle localization, however we obtain in a much simpler way information about the group velocity and the flux. We will thus be able, in the following Section, to easily and clearly interpret the effects of a potential barrier on a particle flux.

2.5 The Potential Barrier

The most interesting physical situation is that in which particles are not free, but subject to forces corresponding to a potential energy $V(x)$. In these conditions the Schrödinger equation in the form given in (2.42) has to be used. Since the equation is linear, the study can be limited, without loss of generality, to solutions which are periodic in time, like:

$$\psi(x, t) = e^{-iEt/\hbar} \psi_E(x). \quad (2.65)$$

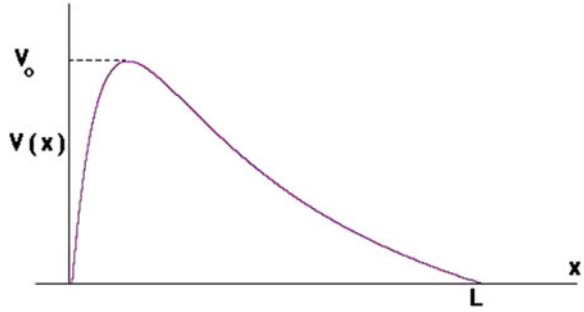
Indeed the general time dependent solution can always be decomposed in periodic components through a Fourier expansion, so that its knowledge is equivalent to that of $\psi_E(x)$ plus the expansion coefficients.

Furthermore, according to the collective interpretation of de Broglie waves presented in the last section, the wave function in (2.65) describes either a stationary flow or a *stationary state* of particles. In particular we shall begin studying a stationary flow hitting a potential barrier.

The function $\psi_E(x)$ is a solution of the equation obtained by replacing (2.65) into (2.42), i.e.

$$i\hbar \partial_t e^{-iEt/\hbar} \psi_E(x) = E e^{-iEt/\hbar} \psi_E(x) = e^{-iEt/\hbar} \left[-\frac{\hbar^2}{2m} \partial_x^2 \psi_E + V(x) \psi_E \right]$$

Fig. 2.3 A typical example of a potential barrier, referring in particular to that due to Coulomb repulsion that will be used when discussing Gamow's theory of nuclear α -emission



hence

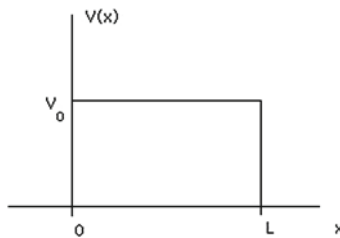
$$E\psi_E(x) = -\frac{\hbar^2}{2m}\partial_x^2\psi_E(x) + V(x)\psi_E(x), \quad (2.66)$$

which is known as the *time-independent* or *stationary* Schrödinger equation.

We shall consider at first the case of a *potential barrier*, in which $V(x)$ vanishes for $x < 0$ and $x > L$, and is positive in the segment $[0, L]$, as shown in Fig. 2.3. A flux of classical particles hitting the barrier from the left will experience slowing forces as $x > 0$. If the starting kinetic energy, corresponding in this case to the total energy E in (2.66), is greater than the barrier height V_0 , the particles will reach the point where V has a maximum, being accelerated from there forward till they pass point $x = L$, where the motion gets free again. Therefore the flux is completely transmitted, the effect of the barrier being simply a slowing down in the segment $[0, L]$. If instead the kinetic energy is less than V_0 , the particles will stop before they reach the point where V has a maximum, reversing their motion afterwards: the flux is completely reflected in this case. Quantum Mechanics gives a completely different result.

In order to analyze the differences from a qualitative point of view, it is convenient to choose a barrier which makes the solution of (2.66) easier: that is the case of a potential which is piecewise constant, like the square given below. The choice is motivated by the fact that, if V is constant, then (2.66) can be rewritten as follows:

$$\partial_x^2\psi_E(x) + \frac{2m}{\hbar^2}(E - V)\psi_E(x) = 0, \quad (2.67)$$



and has the general solution:

$$\psi_E(x) = a_+ \exp\left(i \frac{\sqrt{2m(E-V)}}{\hbar} x\right) + a_- \exp\left(-i \frac{\sqrt{2m(E-V)}}{\hbar} x\right), \quad (2.68)$$

if $E > V$, while

$$\psi_E(x) = a_+ \exp\left(\frac{\sqrt{2m(V-E)}}{\hbar} x\right) + a_- \exp\left(-\frac{\sqrt{2m(V-E)}}{\hbar} x\right), \quad (2.69)$$

in the opposite case. The problem is then to establish how the solution found in a definite region can be connected to those found in the nearby regions. In order to solve this kind of problem we must be able to manage differential equations in the presence of discontinuities in their coefficients, and that requires a brief *mathematical interlude*.

2.5.1 Mathematical Interlude: Differential Equations with Discontinuous Coefficients

Differential equations with discontinuous coefficients can be treated by smoothing the discontinuities, then solving the equations in terms of functions which are derivable several times, and finally reproducing the correct solutions in the presence of discontinuities through a limit process. In order to do so, let us introduce the function $\varphi_\epsilon(x)$, which is defined as

$$\varphi_\epsilon(x) = 0 \quad \text{if } |x| > \epsilon,$$

$$\varphi_\epsilon(x) = \frac{\epsilon^2 + x^2}{2(\epsilon^2 - x^2)^2} \frac{1}{\cosh^2(x/(\epsilon^2 - x^2))} \quad \text{if } |x| < \epsilon.$$

This function, as well as all of its derivatives, is continuous and it can be easily shown that

$$\int_{-\infty}^{\infty} \varphi_\epsilon(x) dx = 1.$$

Based on this property we conclude that if $f(x)$ is locally integrable, i.e. if it admits at most isolated singularities where the function may diverge with a degree less than one, like for instance $1/|x|^{1-\delta}$ when $\delta > 0$, then the integral

$$\int_{-\infty}^{\infty} \varphi_\epsilon(x-y) f(y) dy \equiv f_\epsilon(x)$$

defines a function which can be derived in x an infinite number of times; the derivatives of f_ϵ tend to those of f in the limit $\epsilon \rightarrow 0$ and in all points where the latter are defined. We have in particular, by part integration,

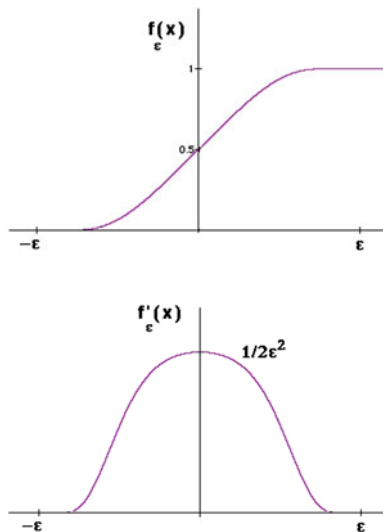
$$\frac{d^n}{dx^n} f_\epsilon(x) = \int_{-\infty}^{\infty} \varphi_\epsilon(x-y) \frac{d^n}{dy^n} f(y) dy; \quad (2.70)$$

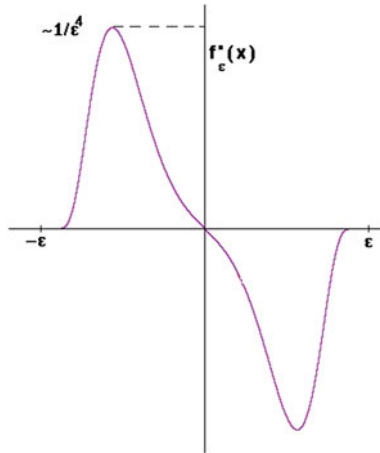
f_ϵ is called *regularized function*. If for instance we consider the case in which f is the step function in the origin, i.e. $f(x) = 0$ for $x < 0$ and $f(x) = 1$ for $x > 0$, we have for $f_\epsilon(x)$, $\partial_x f_\epsilon(x) = f'_\epsilon(x)$ and $\partial_x^2 f_\epsilon(x) = f''_\epsilon(x)$ the behaviors showed in the figures given below. Notice in particular that since

$$f_\epsilon(x) = \int_0^\infty \varphi_\epsilon(x-y) dy = \int_{-\infty}^x \varphi_\epsilon(z) dz$$

we have $\partial_x f_\epsilon(x) = \varphi_\epsilon(x)$. By looking at the three figures it is clear that $f_\epsilon(x)$ continuously interpolates between the two values, zero and one, which the function assumes respectively to the left of $-\epsilon$ and to the right of ϵ , staying less than 1 for every value of x . It is important to notice that instead the second figure, showing $\partial_x f_\epsilon(x)$, i.e. $\varphi_\epsilon(x)$, has a maximum of height proportional to $1/\epsilon^2$, hence diverging as $\epsilon \rightarrow 0$.

The third figure, showing the second derivative $\partial_x^2 f_\epsilon(x)$, has an oscillation of amplitude proportional to $1/\epsilon^4$ around the discontinuity point. Since, for small ϵ , the regularized function depends, close to the discontinuity, on the nearby values of the original function, it is clear that the qualitative behaviors showed in the figures are valid, close to discontinuities of the first kind (i.e. where the function itself has a discontinuous gap), for every starting function f .





Let us now consider (2.67) close to a discontinuity point of the first kind (step function) for V , and suppose we regularize both terms on the left hand side. Assuming that the wave function does not present discontinuities worse than first kind, the second term in the equation may present only steps so that, once regularized, it is limited independently of ϵ . However the first term may present oscillations of amplitude $\sim 1/\epsilon^4$ if ψ_E has a first kind discontinuity, or a peak of height $\sim \pm 1/\epsilon^2$ if ψ_E is continuous but its first derivative has such discontinuity: in each case the modulus of the first regularized term would diverge faster than the second in the limit $\epsilon \rightarrow 0$. That shows that in the presence of a first kind discontinuity in V , both the wave function ψ_E and its derivative must be continuous.

In order to simply deal with barriers of length L much smaller than the typical wavelengths of the problem, it is useful to introduce infinitely thin barriers: that can be done by choosing a potential energy which, once regularized, is equal to $V_\epsilon(x) = \mathcal{V} \varphi_\epsilon(x)$, i.e.

$$V(x) = \mathcal{V} \lim_{\epsilon \rightarrow 0} \varphi_\epsilon(x) \equiv \mathcal{V} \delta(x). \quad (2.71)$$

Equation (2.71) defines the so-called *Dirac's delta function* as a limit of φ_ϵ .

When studying Schrödinger equation regularized as done above, it is possible to show, by integrating the differential equation between $-\epsilon$ and ϵ , that in the presence of a potential barrier proportional to the Dirac delta function the wave function stays continuous, but its derivative has a first kind discontinuity of amplitude

$$\lim_{\epsilon \rightarrow 0} (\psi'_E(\epsilon) - \psi'_E(-\epsilon)) = \frac{2m}{\hbar^2} \mathcal{V} \psi_E(0). \quad (2.72)$$

Notice that a potential barrier proportional to the Dirac delta function can be represented equally well by a square barrier of height \mathcal{V}/L and width L , in the limit as $L \rightarrow 0$ with $\int_{-\infty}^{\infty} dx V(x) = \mathcal{V}$ kept constant.

2.5.2 The Square Barrier

Let us consider the stationary Schrödinger equation (2.66) with a potential corresponding to the square barrier described above, that is $V(x) = V$ for $0 < x < L$ and vanishing elsewhere. As in the classical case we can distinguish two different regimes:

- (a) the case $E > V$, in which classically the flux would be entirely transmitted;
- (b) the opposite case, $E < V$, in which classically the flux would be entirely reflected.

Let us start with case (a) and distinguish three different regions:

- (1) the region $x < 0$, in which the general solution is

$$\psi_E(x) = a_+ e^{i\sqrt{2mE} x/\hbar} + a_- e^{-i\sqrt{2mE} x/\hbar}; \quad (2.73)$$

this wave function corresponds to two opposite fluxes, the first moving rightwards and equal to $|a_+|^2 \sqrt{2E/m}$, the other opposite to the first and equal to $-|a_-|^2 \sqrt{2E/m}$. Since we want to study a quantum process analogous to that described classically, we arbitrarily choose $a_+ = 1$, thus fixing the incident flux to $\sqrt{2E/m}$, hence

$$\psi_E(x) = e^{i\sqrt{2mE} x/\hbar} + a e^{-i\sqrt{2mE} x/\hbar}; \quad (2.74)$$

a takes into account the possible reflected flux, $|a|^2 \sqrt{2E/m}$. The physically interesting quantity is the fraction of the incident flux which is reflected, which is called the *reflection coefficient* of the barrier and, with our normalization for the incident flux, is $R = |a|^2$;

- (2) the region $0 < x < L$, where the general solution is

$$\psi_E(x) = b e^{i\sqrt{2m(E-V)} x/\hbar} + c e^{-i\sqrt{2m(E-V)} x/\hbar}; \quad (2.75)$$

(3) the region $x > L$, where the general solution is given again by (2.73). However, since we want to study reflection and transmission through the barrier, we exclude the possibility of a backward flux, i.e. coming from $x = \infty$, thus assuming that the only particles present in this region are those going rightwards after crossing the barrier. Therefore in this region we write

$$\psi_E(x) = d e^{i\sqrt{2mE} x/\hbar}. \quad (2.76)$$

The potential has two discontinuities in $x = 0$ and $x = L$, therefore we have the following conditions for the continuity of the wave function and its derivative:

$$\begin{aligned}
1 + a &= b + c, \\
1 - a &= \sqrt{\frac{E - V}{E}} (b - c), \\
b e^{i\sqrt{2m(E-V)}L/\hbar} + c e^{-i\sqrt{2m(E-V)}L/\hbar} &= d e^{i\sqrt{2mE}L/\hbar}, \\
\sqrt{\frac{E - V}{E}} \left[b e^{i\sqrt{2m(E-V)}L/\hbar} - c e^{-i\sqrt{2m(E-V)}L/\hbar} \right] &= d e^{i\sqrt{2mE}L/\hbar}.
\end{aligned} \tag{2.77}$$

We have thus a linear system of 4 equations with 4 unknown variables which, for a generic choice of parameters, should univocally identify the solution. However our main interest is the determination of $|a|^2$. Dividing side by side the first two as well as the last two equations, we obtain after simple algebra:

$$\begin{aligned}
\frac{1 - a}{1 + a} &= \sqrt{\frac{E - V}{E}} \frac{\frac{b}{c} - 1}{\frac{b}{c} + 1}, \\
\frac{\frac{b}{c} - e^{-2i\sqrt{2m(E-V)}L/\hbar}}{\frac{b}{c} + e^{-2i\sqrt{2m(E-V)}L/\hbar}} &= \sqrt{\frac{E}{E - V}}.
\end{aligned} \tag{2.78}$$

Solving the second equation for b/c and the first for a we obtain:

$$\begin{aligned}
\frac{b}{c} &= e^{-2i\sqrt{2m(E-V)}L/\hbar} \frac{\sqrt{\frac{E-V}{E}} + 1}{\sqrt{\frac{E-V}{E}} - 1}, \\
a &= \frac{1 + \sqrt{\frac{E-V}{E}} + \frac{b}{c} \left(1 - \sqrt{\frac{E-V}{E}} \right)}{1 - \sqrt{\frac{E-V}{E}} + \frac{b}{c} \left(1 + \sqrt{\frac{E-V}{E}} \right)}
\end{aligned} \tag{2.79}$$

and finally, by substitution:

$$a = \frac{\left(1 - \frac{E-V}{E} \right) \left(e^{i\sqrt{2m(E-V)}L/\hbar} - e^{-i\sqrt{2m(E-V)}L/\hbar} \right)}{\left(1 - \sqrt{\frac{E-V}{E}} \right)^2 e^{i\sqrt{2m(E-V)}L/\hbar} - \left(1 + \sqrt{\frac{E-V}{E}} \right)^2 e^{-i\sqrt{2m(E-V)}L/\hbar}},$$

so that

$$a = \frac{V}{E} \frac{\sin \left(\frac{\sqrt{2m(E-V)}}{\hbar} L \right)}{\frac{2E-V}{E} \sin \left(\frac{\sqrt{2m(E-V)}}{\hbar} L \right) + 2i \sqrt{\frac{E-V}{E}} \cos \left(\frac{\sqrt{2m(E-V)}}{\hbar} L \right)}, \tag{2.80}$$

which clearly shows that $0 \leq |a| < 1$ and that, for $V > 0$, a vanishes only when $\sqrt{(2m(E - V))}L/\hbar = n\pi$.

This is a clear interference effect, showing that reflection by the barrier is a wave-like phenomenon. For those knowing the physics of coaxial cables there should be a clear analogy between our result and the reflection happening at the junction of two cables having mismatching impedances: television set technicians well known that as a possible origin of failure.

The quantum behavior in case (b), i.e. when $E < V$, is more interesting and important for its application to microscopic physics. In this case the wave functions in regions 1 and 3 do not change, while for $0 < x < L$ the general solution is:

$$\psi_E(x) = b e^{\sqrt{2m(V-E)} x/\hbar} + c e^{-\sqrt{2m(V-E)} x/\hbar}, \quad (2.81)$$

so that the continuity conditions become:

$$\begin{aligned} 1 + a &= b + c, \\ 1 - a &= -i \sqrt{\frac{V-E}{E}} (b - c), \\ b e^{\sqrt{2m(V-E)}L/\hbar} + c e^{-\sqrt{2m(V-E)}L/\hbar} &= d e^{i\sqrt{2mE}L/\hbar}, \\ -i \sqrt{\frac{V-E}{E}} \left[b e^{\sqrt{2m(V-E)}L/\hbar} - c e^{-\sqrt{2m(V-E)}L/\hbar} \right] &= d e^{i\sqrt{2mE}L/\hbar}. \end{aligned} \quad (2.82)$$

Dividing again side by side we have:

$$\begin{aligned} \frac{\frac{b}{c} - e^{-2\sqrt{2m(V-E)}L/\hbar}}{\frac{b}{c} + e^{-2\sqrt{2m(V-E)}L/\hbar}} &= i \sqrt{\frac{E}{V-E}}, \\ \frac{1-a}{1+a} &= i \sqrt{\frac{V-E}{E}} \frac{1 - \frac{b}{c}}{1 + \frac{b}{c}}, \end{aligned} \quad (2.83)$$

which can be solved as follows:

$$\begin{aligned} a &= -\frac{1 - \frac{b}{c} + i \sqrt{\frac{E}{V-E}} \left(1 + \frac{b}{c}\right)}{1 - \frac{b}{c} - i \sqrt{\frac{E}{V-E}} \left(1 + \frac{b}{c}\right)}, \\ \frac{b}{c} &= e^{-2\sqrt{2m(V-E)}L/\hbar} \frac{1 + i \sqrt{\frac{E}{V-E}}}{1 - i \sqrt{\frac{E}{V-E}}}. \end{aligned} \quad (2.84)$$

We can get the expression for a , hence the reflection coefficient $R \equiv |a|^2$, by replacing b/c in the first equation. The novelty is that R is not equal to one since, as it is clear from (2.84), b/c is a complex number. Therefore a fraction $1 - R \equiv T$ of the

incident flux is transmitted through the barrier, in spite of the fact that, classically, the particles do not have enough energy to reach the top of it. That is known as *tunnel effect* and plays a very important role in several branches of modern physics, from radioactivity to electronics.

Instead of giving a complete solution for a , hence for the *transmission coefficient* T , and in order to avoid too complex and unreadable formulae, we will confine the discussion to two extreme cases, which however have a great phenomenological interest. We consider in particular:

- (a) the case in which $e^{-2\sqrt{2m(V-E)}L/\hbar} \ll 1$, with a generic value for $\frac{E}{V-E}$, i.e. $L \gg \hbar/\sqrt{2m(V-E)}$, which is known as the thick barrier case;
- (b) the case in which the barrier is thin, corresponding in particular to the limit $L \rightarrow 0$ with $VL \equiv \mathcal{V}$ kept constant.

The thick barrier

In this case $|b/c|$ is small, so that it could be neglected in a first approximation, however it is clear from (2.84) that if $b/c = 0$ then $|a| = 1$, so that there is actually no tunnel effect. For this reason we must compute the Taylor expansion in the expression of a as a function of b/c up to the first order:

$$\begin{aligned}
 a &= -\frac{1+i\sqrt{\frac{E}{V-E}}}{1-i\sqrt{\frac{E}{V-E}}} \frac{1-\frac{b}{c}\frac{1-i\sqrt{E/(V-E)}}{1+i\sqrt{E/(V-E)}}}{1-\frac{b}{c}\frac{1+i\sqrt{E/(V-E)}}{1-i\sqrt{E/(V-E)}}} \\
 &\sim -\frac{1+i\sqrt{\frac{E}{V-E}}}{1-i\sqrt{\frac{E}{V-E}}} \left[1 - \frac{b}{c} \left(\frac{1-i\sqrt{\frac{E}{V-E}}}{1+i\sqrt{\frac{E}{V-E}}} - \frac{1+i\sqrt{\frac{E}{V-E}}}{1-i\sqrt{\frac{E}{V-E}}} \right) \right] \\
 &= -\frac{1+i\sqrt{\frac{E}{V-E}}}{1-i\sqrt{\frac{E}{V-E}}} \left[1 + 4i\frac{b}{c}\frac{\sqrt{E(V-E)}}{V} \right] \\
 &= -\frac{1+i\sqrt{\frac{E}{V-E}}}{1-i\sqrt{\frac{E}{V-E}}} \left[1 + 4i\frac{\sqrt{E(V-E)}}{V} e^{-2\sqrt{2m(V-E)}L/\hbar} \frac{1+i\sqrt{\frac{E}{V-E}}}{1-i\sqrt{\frac{E}{V-E}}} \right].
 \end{aligned} \tag{2.85}$$

In the last line we have replaced b/c by the corresponding expression in (2.84). Neglecting terms of the order of $e^{-4\sqrt{2m(V-E)}L/\hbar}$ or smaller we obtain

$$|a|^2 = R = 1 - 16\frac{E(V-E)}{V^2} e^{-2\sqrt{2m(V-E)}L/\hbar}. \tag{2.86}$$

Therefore the transmission coefficient, which measures the probability for a particle hitting the barrier to cross it, is given by:

$$T \equiv 1 - R = 16\frac{E(V-E)}{V^2} e^{-2\sqrt{2m(V-E)}L/\hbar}. \tag{2.87}$$

Notice that the result seems to vanish for $V = E$, but this is not true since in this case the terms neglected in our approximation come into play.

This formula was first applied in nuclear physics, and more precisely to study α emission, a phenomenon in which a heavy nucleus breaks up into a lighter nucleus plus a particle carrying twice the charge of the proton and roughly four times its mass, which is known as α particle. The decay can be simply described in terms of particles of mass $\sim 0.66 \times 10^{-26}$ kg and energy $E \simeq 4\text{--}8$ MeV $\simeq 10^{-12}$ J, hitting barriers of width roughly equal to 3×10^{-14} m; the difference $V-E$ is of the order of 10 MeV $\simeq 1.6 \times 10^{-12}$ J.

In these conditions we have $2\sqrt{2m(V-E)}L/\hbar \simeq 83$ and therefore $T \sim e^{-2\sqrt{2m(V-E)}L/\hbar} \sim 10^{-36}$. Given the order of magnitude of the energy E and of the mass of the particle, we infer that it moves with a velocity of the order of 10^7 m/s: since the radius R_0 of heavy nuclei is roughly 10^{-14} m, the frequency of collisions against the barrier is $\nu_u \sim 10^{21}$ Hz. That indicates that, on average, the time needed for the α particle to escape the nucleus is of the order of $1/(\nu_u T)$, i.e. about 10^{15} s, equal to 10^8 years. However, if the width of the barrier is only 4 times smaller, the decay time goes down to about 100 years. That shows a great sensitivity of the result to the parameters and justifies the fact that we have neglected the pre-factor in front of the exponential in (2.87). On the other hand that also shows that, for a serious comparison with the actual mean lives of nuclei, an accurate analysis of parameters is needed, but it is also necessary to take into account the fact that we are not dealing with a true square barrier, since the repulsion between the nucleus and the α particle is determined by Coulomb forces, i.e. $V(x) = 2Ze^2/(4\pi\epsilon_0 x)$ for x greater than a given threshold, see Fig. 2.3.

As a consequence, the order of magnitude of the transmission coefficient given in (2.87), i.e.

$$T \simeq e^{-2\sqrt{2m(V-E)}L/\hbar} \quad (2.88)$$

must be replaced by³

$$T \simeq \exp\left(-2 \int_{R_0}^{R_1} dx \frac{\sqrt{2m(V(x) - E)}}{\hbar}\right) \equiv e^{-G}, \quad (2.89)$$

where R_0 is the already mentioned nuclear radius and $R_1 = 2Ze^2/(4\pi E\epsilon_0)$ is the solution of the equation $V(R_1) = E$. We have then

³One can think of a thick, but not square, barrier as a series of thick square barriers of different heights.

$$\begin{aligned}
G &= 2 \frac{\sqrt{2m}}{\hbar} \int_{R_0}^{R_1} dx \sqrt{\frac{2Ze^2}{4\pi\epsilon_0 x} - E} = 2 \frac{\sqrt{2mE}}{\hbar} \int_{R_0}^{R_1} dx \sqrt{\frac{R_1}{x} - 1} \\
&= 2 \frac{\sqrt{2mE} R_1}{\hbar} \int_{\frac{R_0}{R_1}}^1 dy \sqrt{\frac{1}{y} - 1} = 2 \sqrt{\frac{2m}{E}} \frac{Ze^2}{\pi\epsilon_0 \hbar} \int_{\sqrt{\frac{R_0}{R_1}}}^1 dz \sqrt{1 - z^2} \\
&= \sqrt{\frac{2m}{E}} \frac{Ze^2}{\pi\epsilon_0 \hbar} \left[\arccos \sqrt{\frac{R_0}{R_1}} - \sqrt{\frac{R_0}{R_1} - \left(\frac{R_0}{R_1}\right)^2} \right]. \tag{2.90}
\end{aligned}$$

In the approximation $R_0/R_1 \ll 1$ we have

$$G \simeq \frac{2\pi Ze^2}{\epsilon_0 \hbar v}, \tag{2.91}$$

where v is the velocity of the alpha particle. Hence, if we assume like above that the collision frequency be $\nu_u \sim 10^{21}$ Hz, the mean life is

$$\tau = 10^{-21} \exp\left(\frac{2\pi Ze^2}{\epsilon_0 \hbar v}\right). \tag{2.92}$$

If we instead make use of the last expression in (2.90), with $R_0 = 1.1 \times 10^{-14}$ m, we infer for $\ln \tau$ the behavior shown in Fig. 2.4, where the crosses indicate experimental values for the mean lives of various isotopes: ^{232}Th , ^{238}U , ^{230}Th , ^{241}Am , ^{230}U , ^{210}Rn , ^{220}Rn , ^{222}Ac , ^{215}Po , ^{218}Th . Taking into account that the figure covers 23 orders of magnitude, the agreement is surely remarkable. Indeed Gamow's first presentation of these results in 1928 made a great impression.

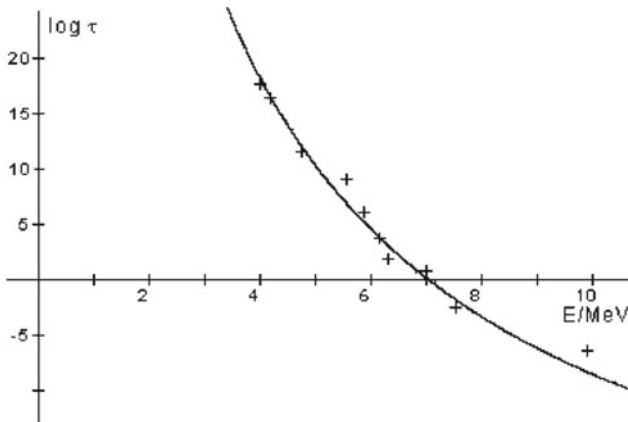


Fig. 2.4 The mean lives of a sample of α -emitting isotopes plotted against the corresponding α -energies. The solid line shows the values predicted by Gamow's theory

The thin barrier

In the case of a thin barrier we can neglect E with respect to V , so that $\sqrt{E/(V-E)} \simeq \sqrt{E/V}$ and $e^{-\sqrt{2m(V-E)}L/\hbar} \simeq 1 - \sqrt{2mV}L/\hbar$. We also remind that $\sqrt{2mV}L/\hbar$ is infinitesimal, since $L \rightarrow 0$ with $VL \equiv \mathcal{V}$ fixed, so that $e^{i\sqrt{2mE}L/\hbar}$ can be put equal to 1. Therefore Eq. (2.83) becomes

$$\begin{aligned} 1 + a &= b + c, \\ 1 - a &= -i\sqrt{\frac{V}{E}}(b - c), \\ b + c + \frac{\sqrt{2mV}}{\hbar}L(b - c) &= d, \\ b - c + \frac{\sqrt{2mV}}{\hbar}L(b + c) &= i\sqrt{\frac{E}{V}}d, \end{aligned} \quad (2.93)$$

and substituting $b \pm c$ we obtain:

$$\begin{aligned} d &= 1 + a + i\sqrt{\frac{E}{V}}\frac{\sqrt{2mV}}{\hbar}L(1 - a) \simeq 1 + a, \\ i\sqrt{\frac{E}{V}}(1 - a) + \frac{\sqrt{2mV}}{\hbar}L(1 + a) &= i\sqrt{\frac{E}{V}}d, \end{aligned} \quad (2.94)$$

in its simplest form. Taking further into account our approximation, the system can be rewritten as

$$\begin{aligned} 1 + a &= d, \\ 1 - a &= \left(i\sqrt{\frac{2m}{E}}\frac{VL}{\hbar} + 1 \right) d \equiv \left(1 + i\sqrt{\frac{2m}{E}}\frac{\mathcal{V}}{\hbar} \right) d. \end{aligned} \quad (2.95)$$

Finally we find, by eliminating a , that

$$d = \frac{1}{1 + i\sqrt{\frac{m}{2E}}\frac{\mathcal{V}}{\hbar}}, \quad (2.96)$$

hence

$$T = \frac{1}{1 + \frac{m}{2E}\frac{\mathcal{V}^2}{\hbar^2}} \quad (2.97)$$

and

$$R = \frac{1}{1 + \frac{2E}{m}\frac{\hbar^2}{\mathcal{V}^2}}. \quad (2.98)$$

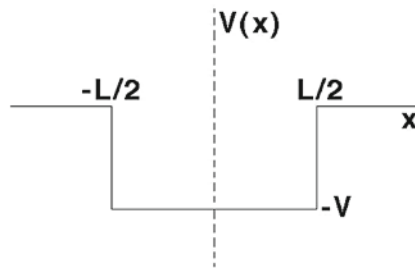
Notice that the system (2.95) confirms what predicted about the continuity conditions for the wave function in the presence of a potential energy equal to $\mathcal{V}\delta(x)$, i.e. that the wave function is continuous ($1 + a = d$) while its derivative has a discontinuity ($i\sqrt{2mE}(1 - a - d)/\hbar$) equal to $2m\mathcal{V}/\hbar^2$ times the value of the wave function (d in our case).

2.6 Quantum Wells and Energy Levels

Having explored the tunnel effect in some details, let us now discuss the solutions of the Schrödinger equation in the case of binding potentials. For bound states, i.e. for solutions with wave functions localized in the neighborhood of a potential well, we expect computations to lead to energy quantization, i.e. to the presence of discrete *energy levels*. Let us start our discussion from the case of a square well

$$V(x) = -V \quad \text{for } |x| < \frac{L}{2}, \quad V(x) = 0 \quad \text{for } |x| > \frac{L}{2}. \quad (2.99)$$

Notice that the origin of the coordinate has been chosen in order to emphasize the *symmetry* of the system, corresponding in this case to the invariance of Schrödinger equation under axis reflection $x \rightarrow -x$. In general, the symmetry of the potential allows us to find new solutions of the equation starting from known solutions, or to simplify the search for solutions by a priori fixing some of their features. In this case it can be noticed that if $\psi_E(x)$ is a solution, $\psi_E(-x)$ is a solution too, so that, by linearity of the differential equation, any linear combination (with complex coefficients) of the two wave functions is a good solution corresponding to the same value of the energy E , in particular the combinations $\psi_E(x) \pm \psi_E(-x)$, which are even/odd under reflection of the x axis. Naturally one of the two solutions may well vanish, but it is clear that all possible solutions can be described in terms of (i.e. they can be written as linear combinations of) functions which are either even or odd under x -reflection.



To better clarify the point, let us notice that, since the Schrödinger equation is linear, the set of all possible solutions having the same energy constitutes what is usually called a *linear space*, which is completely fixed once we know one particular basis for it. What we have learned is that in the present case even/odd functions are

a good basis, so that the search for solutions can be solely limited to them. This is probably the simplest example of the application of a *symmetry principle* asserting that, if the Schrödinger equation is invariant under a coordinate transformation, it is always possible to choose its solutions so that the transformation does not change them but for a constant phase factor, which in the present case is ± 1 .

We will consider in the following only bound solutions which, assuming that the potential energy vanishes for $|x| \rightarrow \infty$, correspond to a negative total energy E and are therefore the analogous of bound states in classical mechanics. Solutions with positive energy, instead, present reflection and transmission phenomena, as in the case of barriers. We notice that, in the case of bound states, the collective interpretation of the wave function does not apply, since these are states involving a single particle: that is in strict relation with the fact that bound state solutions vanish rapidly enough as $|x| \rightarrow \infty$, so that the probability distribution in (2.44) can be properly normalized.

Let us start by considering even solutions: it is clear that we can limit our study to the positive x axis, with the additional constraint of a vanishing first derivative in the origin, as due for an even function (whose derivative is odd). We can divide the positive x axis into two regions where the potential is constant:

(a) that corresponding to $x < L/2$, where the general solution is:

$$\psi_E(x) = a_+ e^{i\sqrt{2m(E+V)}x/\hbar} + a_- e^{-i\sqrt{2m(E+V)}x/\hbar},$$

which is even for $a_+ = a_-$, so that

$$\psi_E(x) = a \cos\left(\frac{\sqrt{2m(E+V)}}{\hbar}x\right); \quad (2.100)$$

(b) that corresponding to $x > L/2$, where the general solution is:

$$\psi_E(x) = b_+ e^{\sqrt{2m|E|}x/\hbar} + b_- e^{-\sqrt{2m|E|}x/\hbar}.$$

The condition that $|\psi|^2$ be an integrable function constrains $b_+ = 0$, otherwise the probability density would unphysically diverge for $|x| \rightarrow \infty$; therefore we can write

$$\psi_E(x) = b e^{-\sqrt{2m|E|}x/\hbar}. \quad (2.101)$$

Notice that we have implicitly excluded the possibility $E < -V$, the reason being that in this case (2.100) would be replaced by

$$\psi_E(x) = a \cosh\left(\frac{\sqrt{2m|E+V|}}{\hbar}x\right)$$

which for $x > 0$ has a positive logarithmic derivative ($\partial_x \psi_E(x)/\psi_E(x)$) which cannot continuously match the negative logarithmic derivative of the solution in the second region given in (2.101). Therefore quantum theory is in agreement with classical

mechanics about the impossibility of having states with total energy less than the minimum of the potential energy.

The solutions to the Schrödinger equation on the whole axis can be found by solving the system:

$$\begin{aligned} a \cos \frac{\sqrt{2m(E+V)}L}{2\hbar} &= b e^{-\sqrt{2m|E|}L/(2\hbar)}, \\ \frac{\sqrt{2m(E+V)}}{\hbar} a \sin \frac{\sqrt{2m(E+V)}L}{2\hbar} &= \frac{\sqrt{2m|E|}}{\hbar} b e^{-\sqrt{2m|E|}L/(2\hbar)} \end{aligned} \quad (2.102)$$

dividing previous equations side by side we obtain the continuity condition for the logarithmic derivative:

$$\tan \frac{\sqrt{2m(E+V)}L}{2\hbar} = \sqrt{\frac{|E|}{E+V}}. \quad (2.103)$$

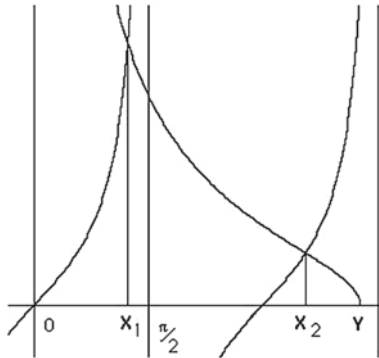
In order to discuss last equation let us introduce the variable

$$x \equiv \frac{\sqrt{2m(E+V)}L}{2\hbar} \quad (2.104)$$

and the parameter

$$y \equiv \sqrt{2mV}L/2\hbar, \quad (2.105)$$

and let us plot together the behavior of the two functions $\tan x$ and $\sqrt{(y^2 - x^2)/x^2} = \sqrt{|E|/(E+V)}$. In the figure we show the case $y^2 = 20$. From a qualitative point of view the figure shows that energy levels, corresponding to the intersection points of the two functions, are quantized, thus confirming also for the case of potential wells the discrete energy spectrum predicted by Bohr's theory. In particular the plot shows two intersections, the first for $x = x_1 < \pi/2$, the second for $\pi < x = x_2 < 3\pi/2$.



Notice that quantization of energy derives from the physical requirement of having a bound state solution which does not diverge but instead vanishes outside the well:

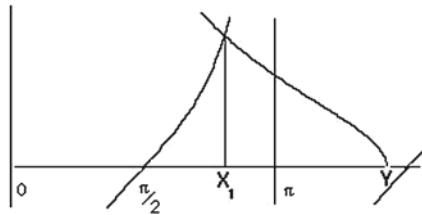
for this reason the external solution is parametrized in terms of only one parameter. The reduced number of available parameters allows for non-trivial solutions of the homogeneous linear system (2.103) only if the energy quantization condition (2.103) is satisfied.

The number of possible solutions increases as y grows and since $y > 0$ it is anyway greater than zero. Therefore the square potential well in one dimension has always at least one bound state corresponding to an even wave function. It can be proved that the same is true for every symmetric well in one dimension (i.e. such that $V(-x) = V(x) \leq 0$). On the contrary, an extension of this analysis (see in particular the discussion about the spherical well in Sect. 2.9) shows that in the three-dimensional case the existence of at least one bound state is not guaranteed any more.

Let us now consider the case of odd solutions: we must choose a wave function which vanishes in the origin, so that the cosine must be replaced by a sine in (2.100). Going along the same lines leading to (2.103) we arrive to the equation

$$\cot \frac{\sqrt{2m(E+V)L}}{2\hbar} = -\sqrt{\frac{|E|}{E+V}}. \quad (2.106)$$

Using the same variables x and y as above, we have the corresponding figure given below, which shows that intersections are present only if $y > \pi/2$, i.e. if $V > \pi^2 \hbar^2 / (2mL^2)$ (which by the way is also the condition for the existence of at least one bound state in three dimensions). Notice that the energy levels found in the odd case are different from those found in the even case. In particular any possible negative energy level can be put in correspondence with only one wave function (identified by neglecting a possible irrelevant constant phase factor): this implies that, in the present case, dealing with solutions having a definite transformation property under the symmetry of the problem (i.e. even or odd) is not a matter of choice, as it is in the general case, but a necessity, since those are the only possible solutions. Indeed a different kind of solution could only be constructed in the presence of two solutions, one even and the other odd, corresponding to the same energy level.



The number of independent solutions corresponding to a given energy level is usually called the *degeneracy* of the level. We have therefore demonstrated that, for the potential square well in one dimension, the discrete energy levels have always degeneracy equal to one or, stated otherwise, that they are *non-degenerate*. This is in fact a general property of bound states in one dimension, which can be demonstrated for any kind of potential well.

It is interesting to apply our analysis to the case of an infinitely deep well. Obviously, if we want to avoid dealing with divergent negative energies as we deepen the well, it is convenient to shift the zero of the energy so that the potential energy vanishes inside the well and is V outside. That is equivalent to replacing in previous formulae $E + V$ by E and $|E|$ by $V - E$; moreover, bound states will now correspond to energies $E < V$. Taking the limit $V \rightarrow \infty$ in the quantization conditions given in (2.103) and (2.106), we obtain respectively $\tan \sqrt{2mE}L/(2\hbar) = +\infty$ and $-\cot \sqrt{2mE}L/(2\hbar) = +\infty$, so that $\sqrt{2mE}L/(2\hbar) = (2n-1)\pi/2$ and $\sqrt{2mE}L/(2\hbar) = n\pi$ with $n = 1, 2, \dots$. Finally, combining odd and even states, we have

$$\frac{\sqrt{2mE}}{\hbar}L = n\pi : \quad n = 1, 2, \dots$$

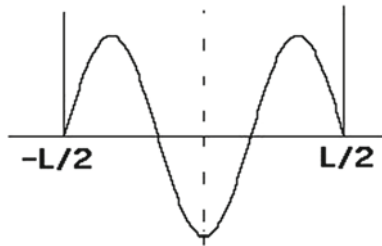
and the following energy levels

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}. \quad (2.107)$$

The corresponding wave functions vanish outside the well while in the region $|x| < L/2$ the even functions are $\sqrt{2/L} \cos(2n-1)\pi x/L$ and the odd ones are $\sqrt{2/L} \sin 2n\pi x/L$, with the coefficients fixed in order to satisfy (2.44). It is also possible to describe all wave functions by a unique formula:

$$\begin{aligned} \psi_{E_n}(x) &= \sqrt{\frac{2}{L}} \sin \frac{n\pi(x + \frac{L}{2})}{L} \quad \text{for } |x| < \frac{L}{2}, \\ \psi_{E_n}(x) &= 0 \quad \text{for } |x| > \frac{L}{2}. \end{aligned} \quad (2.108)$$

While all wave functions are continuous in $|x| = L/2$, their derivatives are not, as in the case of the potential barrier proportional to the Dirac delta function. The generic solution ψ_{E_n} has the behavior showed in the figure, where the analogy with the electric component of an electromagnetic wave reflected between two mirrors clearly appears. Therefore the infinitely deep well can be identified as the region between two reflecting walls.



If the wave amplitude vanishes over the mirrors, the distance between them must necessarily be an integer multiple of half the wavelength; this is the typical tuning

condition for a musical instrument and implies wavelength and energy quantization. The exact result agrees with that of Problem 2.4.

Going back to the analogy with electromagnetic waves, the present situation corresponds to a one-dimensional *resonant cavity*. In the cavity the field can only oscillate according to the permitted wavelengths, which are $\lambda_n = 2L/n$ for $n = 1, 2, \dots$ corresponding to the frequencies $\nu_n = c/\lambda_n = nc/(2L)$, which are all multiple of the *fundamental* frequency of the cavity.

Our results regarding the infinitely deep well can be easily generalized to three dimensions. To that purpose, let us introduce a cubic box of side L with reflecting walls. The condition that the wave function vanishes over the walls is equivalent, inside the box and choosing solutions for which the dependence on x , y and z is factorized, to:

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{L^3}} \sin \frac{n_x \pi (x + \frac{L}{2})}{L} \sin \frac{n_y \pi (y + \frac{L}{2})}{L} \sin \frac{n_z \pi (z + \frac{L}{2})}{L}, \quad (2.109)$$

where we have assumed the origin of the coordinates to be placed in the center of the box. The corresponding energy coincides with the kinetic energy inside the box and can be obtained by writing the Schrödinger equation in three dimensions:

$$-\frac{\hbar^2}{2m} (\partial_x^2 + \partial_y^2 + \partial_z^2) \psi_{n_x, n_y, n_z} = E_{n_x, n_y, n_z} \psi_{n_x, n_y, n_z}, \quad (2.110)$$

leading to

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2mL^2} [n_x^2 + n_y^2 + n_z^2]. \quad (2.111)$$

This result will be useful for studying the properties of a gas of non-interacting particles (perfect gas) contained in a box with reflecting walls. Following the same analogy as above one can study in a similar way the oscillations of an electromagnetic field in a three-dimensional cavity, with proper frequencies given by $\nu_{n_x, n_y, n_z} = (c/2L)\sqrt{n_x^2 + n_y^2 + n_z^2}$.

2.7 The Harmonic Oscillator

The one-dimensional harmonic oscillator can be identified with the mechanical system formed by a particle of mass m bound to a fixed point (taken as the origin of the coordinate) by an ideal spring of elastic constant k and vanishing length at rest. This is equivalent to a potential energy $V(x) = kx^2/2$. In classical mechanics the corresponding equation of motion is

$$m\ddot{x} + kx = 0,$$

whose general solution is

$$x(t) = X \cos(\omega t + \phi),$$

where $\omega = \sqrt{k/m} = 2\pi\nu$ and ν is the proper frequency of the oscillator.

At the quantum level we must solve the following stationary Schrödinger equation:

$$-\frac{\hbar^2}{2m} \partial_x^2 \psi_E(x) + \frac{m\omega^2}{2} x^2 \psi_E(x) = E \psi_E(x). \quad (2.112)$$

In order to solve this equation we can use the identity

$$\begin{aligned} & \left(\sqrt{\frac{m\omega^2}{2}} x - \frac{\hbar}{\sqrt{2m}} \partial_x \right) \left(\sqrt{\frac{m\omega^2}{2}} x + \frac{\hbar}{\sqrt{2m}} \partial_x \right) f(x) \\ &= \frac{m\omega^2}{2} x^2 f(x) + \frac{\hbar\omega}{2} x \partial_x f(x) - \frac{\hbar\omega}{2} \partial_x (x f(x)) - \frac{\hbar^2}{2m} \partial_x^2 f(x) \\ &= -\frac{\hbar^2}{2m} \partial_x^2 f(x) + \frac{m\omega^2}{2} x^2 f(x) - \frac{\hbar\omega}{2} f(x) \\ &= \left(-\frac{\hbar^2}{2m} \partial_x^2 + \frac{m\omega^2}{2} x^2 - \frac{\hbar\omega}{2} \right) f(x), \end{aligned} \quad (2.113)$$

which is true for any function f which is derivable at least two times.

It is important to notice the *operator* notation used in last equation, where we have introduced some specific symbols, $(\sqrt{m\omega^2/2} x \pm (\hbar/\sqrt{2m}) \partial_x)$ or $(-\hbar^2/2m \partial_x^2 + (m\omega^2/2) x^2 - \hbar\omega/2)$, to indicate operations in which derivation and multiplication by some variable are combined together. As already mentioned, these are usually called operators, meaning that they give a correspondence law between functions belonging to some given class (for instance those which can be derived n times) and other functions belonging, in general, to a different class.

In this way, leaving aside the specific function f , Eq. (2.113) can be rewritten as an operator relation

$$\left(\sqrt{\frac{m\omega^2}{2}} x - \frac{\hbar}{\sqrt{2m}} \partial_x \right) \left(\sqrt{\frac{m\omega^2}{2}} x + \frac{\hbar}{\sqrt{2m}} \partial_x \right) = \left(-\frac{\hbar^2}{2m} \partial_x^2 + \frac{m\omega^2}{2} x^2 - \frac{\hbar\omega}{2} \right) \quad (2.114)$$

and equations of similar nature can be introduced, like for instance:

$$\begin{aligned} & \left(\sqrt{\frac{m\omega^2}{2}} x + \frac{\hbar}{\sqrt{2m}} \partial_x \right) \left(\sqrt{\frac{m\omega^2}{2}} x - \frac{\hbar}{\sqrt{2m}} \partial_x \right) \\ & - \left(\sqrt{\frac{m\omega^2}{2}} x - \frac{\hbar}{\sqrt{2m}} \partial_x \right) \left(\sqrt{\frac{m\omega^2}{2}} x + \frac{\hbar}{\sqrt{2m}} \partial_x \right) = \hbar\omega. \end{aligned} \quad (2.115)$$

In order to shorten formulae, it is useful to introduce the two symbols:

$$X_{\pm} \equiv \left(\sqrt{\frac{m\omega^2}{2}}x \pm \frac{\hbar}{\sqrt{2m}}\partial_x \right) = \sqrt{\frac{\hbar\omega}{2}} \left(\alpha x \pm \frac{1}{\alpha} \frac{\partial}{\partial x} \right) \quad (2.116)$$

in which the constant $\alpha \equiv \sqrt{m\omega/\hbar}$ has been defined, corresponding to the inverse of the typical length scale of the system. That allows us to rewrite (2.115) in the simpler form:

$$X_+X_- - X_-X_+ = \hbar\omega. \quad (2.117)$$

If, extending the operator formalism, we define

$$H \equiv -\frac{\hbar^2}{2m}\partial_x^2 + \frac{m\omega^2}{2}x^2, \quad (2.118)$$

we can rewrite (2.114) as:

$$X_-X_+ = H - \frac{\hbar\omega}{2}, \quad (2.119)$$

then obtaining from (2.117):

$$X_+X_- = H + \frac{\hbar\omega}{2}. \quad (2.120)$$

The Schrödinger equation can be finally written as:

$$H\psi_E(x) = E\psi_E(x). \quad (2.121)$$

The operator formalism permits to get quite rapidly a series of results.

(a) The wave function which is solution of the equation

$$X_+\psi_0(x) = \sqrt{\frac{m\omega^2}{2}}x\psi_0(x) + \frac{\hbar}{\sqrt{2m}}\partial_x\psi_0(x) = 0, \quad (2.122)$$

is also a solution of (2.121) with $E = \hbar\omega/2$. In order to compute it we can rewrite (2.122) as:

$$\frac{\partial_x\psi_0(x)}{\psi_0(x)} = -\alpha^2x,$$

hence, integrating both members:

$$\ln \psi_0(x) = c - \frac{\alpha^2}{2}x^2,$$

from which it follows that

$$\psi_0(x) = e^c e^{-\alpha^2 x^2/2},$$

where the constant c can be fixed by the normalization condition given in (2.44), leading finally to

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-m\omega x^2/(2\hbar)}. \quad (2.123)$$

We would like to remind the need for restricting the analysis to the so-called *square integrable* functions, which can be normalized according to (2.44). This is understood in the following.

(b) What we have found is the lowest energy solution, usually called the *ground state* of the system, as can be proved by observing that, for every normalized solution $\psi_E(x)$, the following relations hold:

$$\begin{aligned} \int_{-\infty}^{\infty} dx \psi_E(x)^* \left(\sqrt{\frac{m\omega^2}{2}}x - \frac{\hbar}{\sqrt{2m}}\partial_x \right) \left(\sqrt{\frac{m\omega^2}{2}}x + \frac{\hbar}{\sqrt{2m}}\partial_x \right) \psi_E(x) \\ = \int_{-\infty}^{\infty} dx |X_+ \psi_E(x)|^2 = \int_{-\infty}^{\infty} dx \psi_E(x)^* \left(E - \frac{\hbar\omega}{2} \right) \psi_E(x) \\ = E - \frac{\hbar\omega}{2} \geq 0, \end{aligned} \quad (2.124)$$

where the derivative in X_- has been integrated by parts, exploiting the vanishing of the wave function at $x = \pm\infty$. Last inequality follows from the fact that the integral of the squared modulus of any function cannot be negative. Moreover it must be noticed that if the integral vanishes, i.e. if $E = \hbar\omega/2$, then necessarily $X_+ \psi_E = 0$, so that ψ_E is proportional to ψ_0 . That proves that the ground state is unique.

(c) If ψ_E satisfies (2.112) then $X_{\pm}\psi_E$ satisfies the same equation with E replaced by $E \mp \hbar\omega$, i.e. we have

$$H X_{\pm} \psi_E = (E \mp \hbar\omega) X_{\pm} \psi_E. \quad (2.125)$$

Notice that $X_+ \psi_E$ vanishes if and only if $\psi_E = \psi_0$ while $X_- \psi_E$ never vanishes: one can prove this by verifying that if $X_- \psi_E = 0$ then ψ_E behaves as ψ_0 but with the sign + in the exponent, hence it is not square integrable. In order to prove Eq. (2.125), from (2.119) and (2.120) we infer, for instance:

$$\begin{aligned} X_+ X_- X_+ \psi_E &= X_+ \left(H - \frac{\hbar\omega}{2} \right) \psi_E(x) = \left(H + \frac{\hbar\omega}{2} \right) X_+ \psi_E(x) \\ &= X_+ \left(E - \frac{\hbar\omega}{2} \right) \psi_E(x) = \left(E - \frac{\hbar\omega}{2} \right) X_+ \psi_E(x) \end{aligned} \quad (2.126)$$

from which (2.125) follows in the + case.

Last computations show again that operators combine in a fashion which resembles usual multiplication, however their product is strictly dependent on the order in which they appear. We say that the product is non-commutative; that is also evident from (2.117), which expresses what is usually known as the *commutator* of two operators.

Exchanging X_- and X_+ in previous equations we have:

$$\begin{aligned} X_- X_+ X_- \psi_E &= X_- \left(H + \frac{\hbar\omega}{2} \right) \psi_E(x) = \left(H - \frac{\hbar\omega}{2} \right) X_- \psi_E(x) \\ &= X_- \left(E + \frac{\hbar\omega}{2} \right) \psi_E(x) = \left(E - \frac{\hbar\omega}{2} \right) X_- \psi_E(x) \end{aligned} \quad (2.127)$$

which completes the proof of (2.125).

(d) Finally, combining points (a-c), we can show that the only possible energy levels are:

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega. \quad (2.128)$$

In order to prove that, let us suppose instead that (2.112) admits the level $E = (m + 1/2) \hbar\omega + \delta$, where $0 < \delta < \hbar\omega$, and then repeatedly apply X_+ to ψ_E up to $m + 1$ times. If $X_+^k \psi_E = 0$ with $k \leq m + 1$ and $X_+^{k-1} \psi_E \neq 0$, then we would have $X_+(X_+^{k-1} \psi_E) = 0$ which, as we have already seen, is equivalent to $X_+^{k-1} \psi_E \sim \psi_0$, hence to $H X_+^{k-1} \psi_E = \hbar\omega/2 \psi_E$. However Eq. (2.125) implies $H X_+^{k-1} \psi_E = (E - (k - 1)\hbar\omega) \psi_E$, hence $E = (k - 1/2)\hbar\omega$, which is in contrast with the starting hypothesis ($\delta \neq 0$). On the other hand $X_+^k \psi_E \neq 0$ even for $k = m + 1$ would imply the presence of a solution with energy less than $\hbar\omega/2$, in contrast with (2.124). We have instead no contradiction if $\delta = 0$ and $k = m + 1$.

We have therefore shown that the spectrum of the harmonic oscillator consists of the energy levels $E_n = (n + 1/2) \hbar\omega$. We also know from (2.125) that $\sim X_-^n \psi_0$ is a possible solution with $E = E_n$: we will now show that this is actually the only possible solution.

(e) Any wave function corresponding to the n -th energy level is necessarily proportional to $X_-^n \psi_0$:

$$\psi_{E_n} \sim X_-^n \psi_0. \quad (2.129)$$

We already know that this is true for $n = 0$ (ground state). Now let us suppose the same to be true for $n = k$ and we shall prove it for $n = k + 1$, thus concluding our argument by induction. Let $\psi_{E_{k+1}}$ be a solution corresponding to E_{k+1} , then, by (2.125) and by the uniqueness of ψ_{E_k} , we have

$$X_+ \psi_{E_{k+1}} = a \psi_{E_k} \quad (2.130)$$

for some constant $a \neq 0$, with $\psi_{E_k} \propto X_-^k \psi_0$. By applying X_- to both sides of last equation we obtain

$$\begin{aligned} X_- X_+ \psi_{E_{k+1}} &= \left(H - \frac{\hbar\omega}{2} \right) \psi_{E_{k+1}} = (k+1) \hbar\omega \psi_{E_{k+1}} \\ &= X_- a \psi_{E_k} \propto X_- X_-^k \psi_0 = X_-^{k+1} \psi_0, \end{aligned} \quad (2.131)$$

which proves that also $\psi_{E_{k+1}}$ is proportional to $X_-^{k+1} \psi_0$.

In order to find the correct normalization factor, let us first find it for $\psi_{E_{k+1}}$, assuming that ψ_{E_k} is already correctly normalized. We notice that

$$\begin{aligned} \int_{-\infty}^{\infty} dx |X_- \psi_{E_k}|^2 &= \int_{-\infty}^{\infty} dx \psi_{E_k}^* X_+ X_- \psi_{E_k} = \int_{-\infty}^{\infty} dx \psi_{E_k}^* \left(H + \frac{\hbar\omega}{2} \right) \psi_{E_k} \\ &= \hbar\omega(k+1) \int_{-\infty}^{\infty} dx |\psi_{E_k}|^2 = \hbar\omega(k+1), \end{aligned} \quad (2.132)$$

where in the first equality one of the X_- operators has been integrated by parts and in the second equality Eq.(2.120) has been used. We conclude that $\psi_{E_{k+1}} = (\hbar\omega(k+1))^{-1/2} X_- \psi_{E_k}$, hence, setting for simplicity $\psi_n \equiv \psi_{E_n}$:

$$\psi_n = \sqrt{\frac{1}{n!}} \left(\frac{X_-}{\sqrt{\hbar\omega}} \right)^n \psi_0 \equiv \sqrt{\frac{1}{n!}} (A^\dagger)^n \psi_0 \quad (2.133)$$

where one defines $A^\dagger \equiv X_-/\sqrt{\hbar\omega}$.

That concludes our analysis of the one-dimensional harmonic oscillator, which, based on an algebraic approach, has led us to finding both the possible energy levels, given in (2.128), and the corresponding wave functions, described by (2.123) and (2.129). In particular, confirming a general property of bound states in one dimension, we have found that the energy levels are non-degenerate. The operators X_+ and X_- permit us to transform a given solution into a different one, in particular by rising (X_-) or lowering (X_+) the energy level by one quantum $\hbar\omega$.

Also in this case, as for the square well, solutions have definite transformation properties under axis reflection, $x \rightarrow -x$, which follow from the symmetry of the potential, $V(-x) = V(x)$. In particular they are divided into even and odd functions according to the value of n , $\psi_n(-x) = (-1)^n \psi_n(x)$, as can be proved by noticing that ψ_0 is an even function and that the operator X_- transforms an even (odd) function into an odd (even) one.

Moreover we notice that, according to (2.129), (2.123) and to the expression for X_- given in (2.116), all wave functions are real. This is also a general property of bound states in one dimension, which can be easily proved and has a simple interpretation. Indeed, suppose ψ_E be the solution of the stationary Schrödinger equation (2.66) corresponding to a discrete energy level E ; since obviously both E and the potential energy $V(x)$ are real, it follows, by taking the complex conjugate

of both sides of (2.66), that also ψ_E^* is a good solution corresponding to the same energy. However the non-degeneracy of bound states in one dimension implies that ψ_E must be unique. The only possibility is $\psi_E^* \propto \psi_E$, hence $\psi_E^* = e^{i\phi} \psi_E$, so that, leaving aside an irrelevant overall phase factor, ψ_E is a real function.

On the other hand, recalling the definition of the probability current density J given in (2.43), it can be easily proved that the wave function is real if and only if the current density vanishes everywhere. Since we are considering a stationary problem, the probability density is constant in time by definition and the conservation equation (2.27) implies, in one dimension, that the current density J is a constant in space (the same is not true in more than one dimension, where that translates in \mathbf{J} being a vector field with vanishing divergence, see Problem 2.47). On the other hand, for a bound state J must surely vanish as $|x| \rightarrow \infty$, hence it must vanish everywhere, implying a real wave function: in a one-dimensional bound state there is no current flow at all.

Our results admit various generalizations of great physical interest. First of all, let us consider their extension to the isotropic three-dimensional harmonic oscillator corresponding to the following Schrödinger equation:

$$-\frac{\hbar^2}{2m} (\partial_x^2 + \partial_y^2 + \partial_z^2) \psi_E + \frac{m\omega^2}{2} (x^2 + y^2 + z^2) \psi_E = E \psi_E, \quad (2.134)$$

where $\psi_E = \psi_E(x, y, z)$ is the three-dimensional wave function. This is the typical example of a *separable* Schrödinger equation: if we look for a particular class of solutions, written as the product of three functions depending separately on x , y and z , then Eq. (2.134) becomes equivalent⁴ to three independent equations for three one-dimensional oscillators along x , y and z .

Therefore we conclude that the quantized energy levels are in this case:

$$E_{n_x, n_y, n_z} = \hbar\omega \left(n_x + n_y + n_z + \frac{3}{2} \right), \quad (2.135)$$

and that the corresponding wave functions are

$$\psi_{n_x, n_y, n_z}(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z). \quad (2.136)$$

Notice that, according to (2.135) and (2.136), in three dimensions several degenerate solutions can be found having the same energy, corresponding to all possible integers n_x, n_y, n_z such that $n_x + n_y + n_z = n$ where n is a non-negative integer. The number of such solutions is $(n+1)(n+2)/2$.

Since we have looked for particular solutions, having the dependence on x , y and z factorized, it is natural to ask if in this way we have exhausted the possible solutions of equation (2.134). In some sense this is not true: since the Schrödinger

⁴This is clear if we divide both sides of Eq. (2.134) by ψ_E : the resulting equation requires that the sum of three functions depending separately on x , y and z be a constant, implying that each function must be constant separately.

equation is linear, we can make linear combinations (with complex coefficients) of the $(n+1)(n+2)/2$ degenerate solutions described above, obtaining new solutions having the same energy $E_n = (n+3/2)\hbar\omega$ but not writable, in general, as the product of three functions of x , y and z . However we have exhausted all the possible solutions in some other sense: indeed it is possible to demonstrate that no further solution can be found beyond all the possible linear combinations of the particular solutions in equation (2.136). In other words, all the possible solutions of equation (2.134), which are found for $E = (n+3/2)\hbar\omega$, form a linear space of dimension $(n+1)(n+2)/2$, having the particular solutions in equation (2.136) as an orthonormal basis. We have thus found a possible *complete set* of solutions of equation (2.134): we shall find a different complete set (i.e. a different basis) for the same problem in Sect. 2.9 (see also Problem 2.47).

A further generalization is that regarding small oscillations around equilibrium for a system with N degrees of freedom, whose energy can be separated into the sum of the contributions from N one-dimensional oscillators having, in general, different proper frequencies (ν_i , $i = 1, \dots, N$). In this case the quantization formula reads

$$E_{(n_1, \dots, n_N)} = \sum_{i=1}^N \hbar\omega_i \left(n_i + \frac{1}{2} \right), \quad (2.137)$$

and the corresponding wave function can be written as the product of the wave functions associated with every single oscillator.

Let us now take a short detour by recalling the analysis of the electromagnetic field resonating in one dimension. It can be shown that, from a dynamical point of view, the electromagnetic field can be described as an ensemble of harmonic oscillators, i.e. mechanical systems with definite frequencies. Applying the result of this Section we confirm Einstein's assumption that the electromagnetic field can only exchange quanta of energy equal to $\hbar\omega = h\nu$. That justifies the concept of a photon as a particle carrying an energy equal to $h\nu$. At the quantum level, the possible states of an electromagnetic field oscillating in a cavity can thus be seen as those of a system of photons, corresponding in number to the total quanta of energy present in the cavity, which bounce elastically between the walls.

2.8 Periodic Potentials and Band Spectra

In previous Sections we have encountered and discussed situations in which the energy spectrum is continuous, as for particles free to move far to infinity with or without potential barriers, and other cases presenting a discrete spectrum, like that of bound particles. We will now show that other different interesting situations exist, in particular those characterized by a band spectrum. That is the case for a particle in a periodic potential, like an electron in the atomic lattice of a solid.

An example, which can be treated in a relatively simple way, is that in which the potential energy can be written as the sum of an infinite number of thin barriers (Kronig-Penney model), each proportional to the Dirac delta function, placed at a constant distance a from each other:

$$V(x) = \sum_{n=-\infty}^{\infty} \mathcal{V} \delta(x - na) . \quad (2.138)$$

It is clear that:

$$V(x + a) = V(x) , \quad (2.139)$$

so that we are dealing with a periodic potential. Our analysis will be limited to the case of barriers, i.e. $\mathcal{V} > 0$.

Equation (2.139) expresses a symmetry property of the Schrödinger equation, which is completely analogous to the symmetry under axis reflection discussed for the square well and valid also in the case of the harmonic oscillator. With an argument similar to that used in the square well case, it can be shown that for periodic potentials, i.e. invariant under translations by a , if $\psi_E(x)$ is a solution of the stationary Schrödinger equation then $\psi_E(x + a)$ is a solution too, corresponding to the same energy, so that, by suitable linear combinations, the analysis can be limited to a particular class of functions which are not changed by the symmetry transformation but for an overall multiplicative constant. In the case of reflections that constant must be ± 1 , since a double reflection must bring back to the original configuration. Instead, in the case of translations $x \rightarrow x + a$, solutions can be chosen so as to satisfy the following relation:

$$\psi_E(x + a) = \alpha \psi_E(x) ,$$

where α is in general a complex number. Clearly such functions, like plane waves, are not normalizable, so that we have to make reference to the collective physical interpretation, as in the case of the potential barrier. In this case probability densities which do not vanish in the limit $|x| \rightarrow \infty$ are acceptable, but those diverging in the same limit must be discarded anyway. That constrains α to be a pure phase factor, $\alpha = e^{i\phi}$, so that

$$\psi_E(x + a) = e^{i\phi} \psi_E(x) . \quad (2.140)$$

This is therefore another application of the symmetry principle enunciated in Sect. 2.6.

The wave function $\psi_E(x)$ must satisfy both (2.140) and the free Schrödinger equation in each interval $(n - 1)a < x < na$:

$$-\frac{\hbar^2}{2m} \partial_x^2 \psi_E(x) = E \psi_E(x) ,$$

which has the general solution

$$\psi_E(x) = a_n e^{i\sqrt{2mE}x/\hbar} + b_n e^{-i\sqrt{2mE}x/\hbar}.$$

Finally, at the position of each delta function, the wave function must be continuous while its first derivative must be discontinuous with a gap equal to $(2m\mathcal{V}/\hbar^2)\psi_E(na)$. Since, according to (2.140), the wave function is pseudo-periodic, these conditions will be satisfied in every point $x = na$ if they are satisfied in the origin.

The continuity (discontinuity) conditions in the origin can be written as

$$\begin{aligned} a_0 + b_0 &= a_1 + b_1, \\ i \frac{\sqrt{2mE}}{\hbar} (a_1 - b_1 - a_0 + b_0) &= \frac{2m\mathcal{V}}{\hbar^2} (a_0 + b_0), \end{aligned} \quad (2.141)$$

while (2.140), in the interval $-a < x < 0$, is equivalent to:

$$a_1 e^{i\sqrt{2mE}(x+a)/\hbar} + b_1 e^{-i\sqrt{2mE}(x+a)/\hbar} = e^{i\phi} \left(a_0 e^{i\sqrt{2mE}x/\hbar} + b_0 e^{-i\sqrt{2mE}x/\hbar} \right). \quad (2.142)$$

Last equation implies:

$$a_1 = e^{i(\phi - \sqrt{2mE}a/\hbar)} a_0, \quad b_1 = e^{i(\phi + \sqrt{2mE}a/\hbar)} b_0,$$

which replaced in (2.141) leads to a system of two homogeneous linear equation in two unknown quantities:

$$\begin{aligned} \left(1 - e^{i(\phi - \frac{\sqrt{2mE}}{\hbar}a)} - i\sqrt{\frac{2m}{E}} \frac{\mathcal{V}}{\hbar} \right) a_0 - \left(1 - e^{i(\phi + \frac{\sqrt{2mE}}{\hbar}a)} + i\sqrt{\frac{2m}{E}} \frac{\mathcal{V}}{\hbar} \right) b_0 &= 0 \\ \left(1 - e^{i(\phi - \frac{\sqrt{2mE}}{\hbar}a)} \right) a_0 + \left(1 - e^{i(\phi + \frac{\sqrt{2mE}}{\hbar}a)} \right) b_0 &= 0. \end{aligned} \quad (2.143)$$

The system admits non-trivial solutions ($a_0, b_0 \neq 0$) if and only if the determinant of the coefficient matrix does vanish; that is equivalent to a second order equation for $e^{i\phi}$:

$$\begin{aligned} &\left(1 - e^{i(\phi - \frac{\sqrt{2mE}}{\hbar}a)} - i\sqrt{\frac{2m}{E}} \frac{\mathcal{V}}{\hbar} \right) \left(1 - e^{i(\phi + \frac{\sqrt{2mE}}{\hbar}a)} \right) \\ &+ \left(1 - e^{i(\phi + \frac{\sqrt{2mE}}{\hbar}a)} + i\sqrt{\frac{2m}{E}} \frac{\mathcal{V}}{\hbar} \right) \left(1 - e^{i(\phi - \frac{\sqrt{2mE}}{\hbar}a)} \right) \\ &= 2e^{2i\phi} - \left(\left(2 - i\sqrt{\frac{2m}{E}} \frac{\mathcal{V}}{\hbar} \right) e^{i\frac{\sqrt{2mE}}{\hbar}a} + \left(2 + i\sqrt{\frac{2m}{E}} \frac{\mathcal{V}}{\hbar} \right) e^{-i\frac{\sqrt{2mE}}{\hbar}a} \right) e^{i\phi} \\ &+ 2 = 0, \end{aligned} \quad (2.144)$$

which can be rewritten in the form:

$$\begin{aligned} e^{2i\phi} - \left(2 \cos\left(\frac{\sqrt{2mE}}{\hbar}a\right) + \sqrt{\frac{2m}{E}} \frac{\mathcal{V}}{\hbar} \sin\left(\frac{\sqrt{2mE}}{\hbar}a\right) \right) e^{i\phi} + 1 \\ \equiv e^{2i\phi} - 2Ae^{i\phi} + 1 = 0. \end{aligned} \quad (2.145)$$

Equation (2.145) can be solved by a real ϕ if and only if $A^2 < 1$, as can be immediately verified by using the resolutive formula for second degree equations.

We have therefore an inequality, involving the energy E together with the amplitude \mathcal{V} and the period a of the potential, which is a necessary and sufficient condition for the existence of physically acceptable solutions of the Schrödinger equation:

$$\left(\cos\left(\frac{\sqrt{2mE}}{\hbar}a\right) + \sqrt{\frac{m}{2E}} \frac{\mathcal{V}}{\hbar} \sin\left(\frac{\sqrt{2mE}}{\hbar}a\right) \right)^2 < 1, \quad (2.146)$$

hence

$$\begin{aligned} \cos^2\left(\frac{\sqrt{2mE}}{\hbar}a\right) + \frac{m}{2E} \frac{\mathcal{V}^2}{\hbar^2} \sin^2\left(\frac{\sqrt{2mE}}{\hbar}a\right) \\ + 2\sqrt{\frac{m}{2E}} \frac{\mathcal{V}}{\hbar} \sin\left(\frac{\sqrt{2mE}}{\hbar}a\right) \cos\left(\frac{\sqrt{2mE}}{\hbar}a\right) < 1 \end{aligned} \quad (2.147)$$

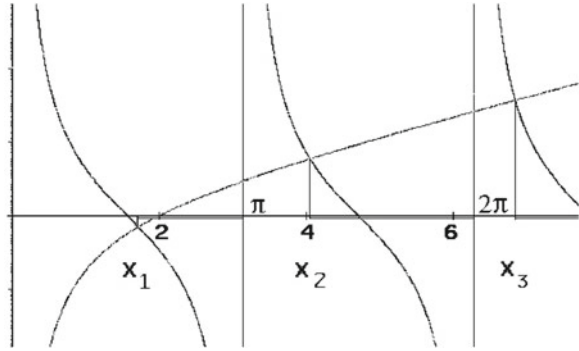
and therefore

$$\begin{aligned} 1 - \cos^2\left(\frac{\sqrt{2mE}}{\hbar}a\right) - \frac{m}{2E} \frac{\mathcal{V}^2}{\hbar^2} \sin^2\left(\frac{\sqrt{2mE}}{\hbar}a\right) \\ - 2\sqrt{\frac{m}{2E}} \frac{\mathcal{V}}{\hbar} \sin\left(\frac{\sqrt{2mE}}{\hbar}a\right) \cos\left(\frac{\sqrt{2mE}}{\hbar}a\right) \\ = \left(1 - \frac{m}{2E} \frac{\mathcal{V}^2}{\hbar^2}\right) \sin^2\left(\frac{\sqrt{2mE}}{\hbar}a\right) \\ - 2\sqrt{\frac{m}{2E}} \frac{\mathcal{V}}{\hbar} \sin\left(\frac{\sqrt{2mE}}{\hbar}a\right) \cos\left(\frac{\sqrt{2mE}}{\hbar}a\right) < 0, \end{aligned} \quad (2.148)$$

leading finally to:

$$\cot\left(\frac{\sqrt{2mE}}{\hbar}a\right) < \frac{1}{2} \left(\sqrt{\frac{2E}{m}} \frac{\hbar}{\mathcal{V}} - \sqrt{\frac{m}{2E}} \frac{\mathcal{V}}{\hbar} \right). \quad (2.149)$$

Fig. 2.5 The plot of inequality (2.149) identifying the first three bands of allowed values of $\sqrt{2mE}a/\hbar$ for the choice of the Kronig–Penney parameter $\gamma = \hbar^2/(maV) = 1/2$



Both sides of last inequality are plotted in Fig. 2.5 for a particular choice of the parameter $\gamma = \hbar^2/(maV) = 1/2$. The variable used in the figure is $x = \sqrt{2mE}a/\hbar$, so that the two plotted functions are $f_1 = \cot x$ and $f_2 = (\gamma x - 1/(\gamma x))/2$. The intervals where the inequality (2.149) is satisfied are those enclosed between x_1 and π , x_2 and 2π , x_3 and 3π and so on. Indeed in these regions the uniformly increasing function f_2 is greater than the oscillating function f_1 . The result shows therefore that the permitted energies correspond to a series of intervals $(x_n, n\pi)$, which are called *bands*, separated by a series of forbidden *gaps*.

As we shall discuss in the next chapter, electrons in a solid, which are compelled by the *Pauli exclusion principle* to occupy each a different energy level, may fill completely a certain number of bands, so that they can only absorb energies greater than a given minimum quantity, corresponding to the gap with the next free band: in such situation electrons behave as bound particles. Alternatively, if the electrons fill partially a given band, they can absorb arbitrarily small energies, thus behaving as free particles. In the first case the solid is an *insulator*, in the second it is a *conductor*.

Having determined the phase $\phi(E)$ from (2.145) and taking into account (2.140), it can be seen that, by a simple transformation of the wave function:

$$\psi_E(x) \equiv e^{i\phi(E)x/a} \hat{\psi}_E(x) \equiv e^{\pm i p(E)x/\hbar} \hat{\psi}_E(x), \quad (2.150)$$

equation (2.140) can be translated into a periodicity constraint:

$$\hat{\psi}_E(x + a) = \hat{\psi}_E(x).$$

Therefore wave functions in a periodic potential can be written as in (2.150), i.e. like plane waves, which are called *Bloch waves*, modulated by periodic functions $\hat{\psi}_E(x)$.

It must be noticed that the momentum associated with Bloch waves, $p(E) = (\hbar/a)\phi(E)$, cannot take all possible real values, as in the case of free particles, but is limited to the interval $(-\hbar\pi/a, \hbar\pi/a)$, which is known as the *first Brillouin zone*. This limitation can be seen as the mathematical reason underlying the presence of bands.

On the other hand, the relation which in a given band gives the electron energy as a function of the Bloch momentum (dispersion relation) is very intricate from the analytical point of view. It is indeed the inverse function of $p(E) = (\hbar/a) \arccos(A(E))$ with $A(E)$ defined by (2.145). For that reason we limit ourselves to some qualitative remarks.

By noticing that in the lower ends of the bands, x_n , $n = 1, 2, \dots$, the parameter A in (2.145) is equal to

$$\cos x_n + \frac{\sin x_n}{\gamma x_n} = \frac{\sin x_n}{2} \left(\gamma x_n + \frac{1}{\gamma x_n} \right) = (-1)^{n+1}, \quad (2.151)$$

we have: $e^{i\phi}|_{x_n} = (-1)^{n+1}$. Hence $\phi(x_n) = 0$ for odd n and $\phi(x_n) = \pm\pi$ for even n . Instead in the upper ends, $x = n\pi$, we have $A = \cos n\pi = (-1)^n$ hence $\phi(n\pi) = 0$ for even n and $\phi(n\pi) = \pm\pi$ for odd n . Moreover, for a generic A between -1 and 1 , there are two solutions: $A \pm i\sqrt{1-A^2}$ corresponding to opposite phases ($\phi(E) = \pm \arctan(\sqrt{1-A^2}/A)$) interpolating between 0 and $\pm\pi$.

Therefore, based on Fig. 2.5, we come to the conclusion that in odd bands the minimum energy corresponds to states with $p = 0$, while states at the border of the Brillouin zone have the maximum possible energy. The opposite happens instead for even bands. Finally we observe that the derivative dE/dp vanishes at the border of the Brillouin zone, where $A^2 = 1$ and A has a non-vanishing derivative, indeed we have

$$\frac{dE}{dp} = \frac{a}{\hbar} \left(\frac{d(\arccos A(E))}{dE} \right)^{-1} = \pm \frac{a}{\hbar} \frac{\sqrt{1-A^2}}{dA(E)/dE}. \quad (2.152)$$

2.9 The Schrödinger Equation in a Central Potential

In the case of a particle moving in three dimensions under the influence of a central force field, the symmetry properties of the problem play a dominant role.

Indeed, already at the classical level, the invariance of the Hamiltonian, $H = p^2/(2M) + V(r)$, under rotations around the center, identified with the origin, implies conservation of the angular momentum $\mathbf{L} = \mathbf{r} \wedge \mathbf{p}$. Once \mathbf{L} is specified, the motion must be planar on a plane orthogonal to it. The absolute value of the angular momentum L identifies the areal velocity $L/(2M) = r^2\dot{\theta}/2$. It follows that the kinetic energy on the plane, which is given by $M/2[(\dot{r})^2 + r^2(\dot{\theta})^2]$, is equal to $m(\dot{r})^2/2 + L^2/(2Mr^2)$ and hence the energy in a central potential is given by:

$$E = \frac{M(\dot{r})^2}{2} + \frac{L^2}{2Mr^2} + V(r) = \frac{p_r^2}{2M} + \frac{L^2}{2Mr^2} + V(r). \quad (2.153)$$

Thus, if the angular momentum is specified, the energy appears as a function of the radius and of its time derivative and the equations of motions separate into an

equation for the radial motion and another equation for the angular motion. One has separation of variables.

In the framework of quantum mechanics this simple approach to the motion in a central potential does not work, because of the uncertainty principle, which forbids a complete determination of the angular momentum vector. This vector corresponds to the vector valued operator $-i\hbar \mathbf{r} \wedge \nabla$. Indeed, considering the relation shown in Sect. 2.4 between uncertainty in the distribution of pairs of observables and lack of commutativity of the corresponding operators, the angular momentum uncertainty follows from the fact that the operators corresponding to its components do not commute. For example, the x -component of the particle angular momentum around the center is given by $L_x = i\hbar(z\partial_y - y\partial_z)$ and the y -component is $L_y = i\hbar(x\partial_z - z\partial_x)$. These operators do not commute. Indeed

$$[L_x, L_y] \equiv L_x L_y - L_y L_x = \hbar^2(y\partial_x - x\partial_y) \equiv i\hbar L_z. \quad (2.154)$$

In much the same way we find

$$[L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y. \quad (2.155)$$

We can still exploit the consequences of the rotation invariance in the analysis of solutions of the stationary Schrödinger equation:

$$-\frac{\hbar^2}{2M} \nabla^2 \psi_E(\mathbf{r}) + V(r) \psi_E(\mathbf{r}) = E \psi_E(\mathbf{r}). \quad (2.156)$$

The standard method is based on Group Theory, but we do not assume our readers to be Group Theory experts, hence we adopt a different approach. The only Group Theory result that we exploit, as we have already done a few times in the preceding part of this text, is what we have called *symmetry principle*; if the Schrödinger equation is left invariant by a coordinate transformation, we can always find a complete set of solutions which do not change, but for a phase factor, under the transformation. This set is complete when all square integrable, or locally square integrable, solutions of physical interest can be written as linear combinations of elements of the set.

We start considering, among all possible rotations, those around one particular axis, for instance the z axis. These rotations transform $x \rightarrow x' = x \cos \phi - y \sin \phi$ and $y \rightarrow y' = y \cos \phi + x \sin \phi$, while z is left unchanged. An equivalent and simpler way of representing these rotations, making use of complex combinations of coordinates, is:

$$x'_\pm \equiv x' \pm iy' = e^{\pm i\phi} x_\pm, \quad \text{and} \quad z' = z. \quad (2.157)$$

We can represent the same rotations in spherical coordinates (r, θ, φ) , defined by

$$x_\pm = r \sin \theta \exp(\pm i\varphi), \quad \text{and} \quad z = r \cos \theta, \quad (2.158)$$

in which they are equivalent to the translations $\varphi \rightarrow \varphi' = \varphi + \phi$. According to the symmetry principle, we consider solutions of equation (2.156) transforming under the above rotations as $\psi_E \rightarrow e^{i\Phi} \psi_E$.

The phase Φ is necessarily a linear function of ϕ , as it appears by observing that for two subsequent rotations around the same axis, with angles ϕ and ϕ' , we have $\Phi(\phi) + \Phi(\phi') = \Phi(\phi + \phi')$. Then asking that for $\phi = 2\pi$ the wave function is left unchanged, i.e. that $\Phi(2\pi) = 2\pi m$ with m any relative integer, we obtain that, in spherical coordinates, we have a complete set of solutions of equation (2.156) of the form:

$$\psi_{E,m}(\mathbf{r}) \equiv \psi_{E,m}(r, \theta, \varphi) = \hat{\psi}_{E,m}(r, \theta) e^{im\varphi}. \quad (2.159)$$

It is an easy exercise to verify that:

$$L_z \psi_{E,m}(\mathbf{r}) = -i\hbar(x\partial_y - y\partial_x)\psi_{E,m}(\mathbf{r}) = -i\hbar \frac{\partial}{\partial \varphi} \psi_{E,m}(\mathbf{r}) = m\hbar \psi_{E,m}(\mathbf{r}), \quad (2.160)$$

which shows that the wave function satisfies Bohr's quantization rule for L_z .

The operator iL_z , being proportional to the φ -derivative, appears as the generator of rotations around the z -axis, in much the same way as the x -derivative generates translations of functions of the x variable. For isotropy reasons, this property of generating rotations extends to the other components of the angular momentum.

If operators, wave functions and numbers are related by equations analogous to (2.160), the wave function is called *eigenfunction* of the operator, and the coefficient in the right-hand side *eigenvalue*. Bohr's quantization rule is thus interpreted as an equation for the eigenvalues of L_z .

Now we must see how the other components of the angular momentum operator act on the solutions $\psi_{E,m}(\mathbf{r})$. We first note that any component of the angular momentum operator commutes with both the Laplacian operator and the distance from the center r . For example, the Leibniz rule gives:

$$\begin{aligned} \nabla^2 L_x &= i\hbar(\partial_x^2 + \partial_y^2 + \partial_z^2)(z\partial_y - y\partial_z) \\ &= i\hbar(z\partial_y - y\partial_z)(\partial_x^2 + \partial_y^2 + \partial_z^2) + 2i\hbar(\partial_z\partial_y - \partial_y\partial_z) = L_x \nabla^2. \end{aligned} \quad (2.161)$$

It is easy to verify that one gets analogous results replacing ∇^2 with r^2 and/or L_x with any other component of the angular momentum. Therefore we have, e.g., for the x component

$$L_x \left[-\frac{\hbar^2}{2M} \nabla^2 + V(r) \right] \psi_E(\mathbf{r}) = \left[-\frac{\hbar^2}{2M} \nabla^2 + V(r) \right] L_x \psi_E(\mathbf{r}) = E L_x \psi_E(\mathbf{r}). \quad (2.162)$$

It means that the action of any component of the angular momentum on a solution of equation (2.157) gives either a solution or zero.

This result extends to the square of the angular momentum corresponding to the operator

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2, \quad (2.163)$$

because L^2 commutes with both the Laplacian and $V(r)$. If A and B are operators commuting with C , then also A^m and B^n commute with C^k and, e.g., $A^2 + B^2$ commutes with C . Here A and B correspond to the components of \mathbf{L} , while C is either the Laplacian, or $V(r)$.

It also is an easy exercise to verify, taking into account Eqs. (2.154) and (2.155), that L^2 commutes with all the components of the angular momentum. Thus, using equations analogous to (2.162), we can show that L^2 transforms any solution $\psi_{E,m}$ of (2.157) into another solution, possibly proportional to the first one, with the same E and m . If there is a single solution, with given E and m , it is obvious that $L^2\psi_{E,m} \sim \psi_{E,m}$ and hence $\psi_{E,m}$ is an eigenfunction of L^2 . But in general there are many such solutions. Let us denote the mentioned solutions by $\psi_{E,m,i}$. We have:

$$L^2\psi_{E,m,i} = \sum_{j=1}^{N_m} l_{E,m,i,j} \psi_{E,m,j}. \quad (2.164)$$

This means that the operator L^2 acts as the multiplication by the matrix $l_{E,m,i,j}$ on the wave function space spanned by the $\psi_{E,m,i}$'s, which is the set of linear combinations of the $\psi_{E,m,i}$'s with fixed m .

Identifying eigenfunctions and eigenvalues of L^2 is a crucial step in the analysis of the solutions to equation (2.156). For this it is convenient to choose the complex coordinates (2.157), introducing the operators:

$$L_{\pm} \equiv L_x \pm iL_y = \pm\hbar(2z\partial_{x_{\mp}} - x_{\pm}\partial_z), \quad (2.165)$$

for which the commutation relations (2.155) are translated into⁵:

$$[L_z, L_{\pm}] = \pm\hbar L_{\pm}, \quad [L_+, L_-] = 2\hbar L_z. \quad (2.166)$$

Thus we have:

$$L_z L_{\pm} \psi_{E,m,i} = \hbar(m \pm 1) L_{\pm} \psi_{E,m,i}, \quad (2.167)$$

which means that either $L_{\pm} \psi_{E,m,i}$ vanishes, or it satisfies (2.160) with the quantum number m increased/decreased by one.

Now, for a given value of E , m cannot increase indefinitely. Indeed, from Eq. (2.153), we see that the energy of the particle is the sum of a purely radial part, $p_r^2/(2M) + V(r)$, and of two positive terms: $(L_x^2 + L_y^2)/(2Mr^2)$ and $L_z^2/(2Mr^2) = \hbar^2 m^2/(2Mr^2)$. Given a square integrable wave function which is a single particle

⁵In spherical coordinates one has $L_{\pm} = \hbar i \exp(\pm i\varphi)[\cot\theta\partial_{\varphi} \mp i\partial_{\theta}]$.

bound state solution of equation (2.156) with a given energy, the single above mentioned terms are affected by uncertainties. But we can compute their average values.

Since L_+ does not act on the radial variable, it is clear that the average value of the first radial term remains fixed when m increases.⁶ In contrast the average values of $(L_x^2 + L_y^2)/(2Mr^2)$ and $L_z^2/(2Mr^2)$ change, the second one increasing by $(\hbar^2 m/2M)\langle 1/r^2 \rangle$. Here, given an operator X , $\langle X \rangle$ denotes its average value. The average value of positive quantities are necessarily positive and $\langle 1/r^2 \rangle$ does not change under the action of L_+ because it is a radial property. Therefore the variations of $\langle (L_x^2 + L_y^2)/(2Mr^2) \rangle$ cannot compensate the indefinite increase of $\hbar^2 m^2/(2M)\langle 1/r^2 \rangle$. Thus this must stop at a certain value of m . We denote by l_E the maximum, integer value of m which depends on E . The corresponding wave functions $\psi_{E,l_E,\alpha}$ satisfy $L_+ \psi_{E,l_E,\alpha} = 0$. We have:

$$L^2 \psi_{E,l_E,\alpha} = \hbar^2 l_E(l_E + 1) \psi_{E,l_E,\alpha} . \quad (2.168)$$

because, from the commutation rule in (2.154), we get:

$$L^2 = L_- L_+ + L_z^2 + \hbar L_z = L_+ L_- + L_z^2 - \hbar L_z . \quad (2.169)$$

Also, writing $\psi_{E,l_E,\alpha}$ as a function of the variables x_+ , x_-x_+ and z , and using

$$L_z = \hbar(x_+ \partial_{x_+} - x_- \partial_{x_-}) , \quad (2.170)$$

we have, from $L_z \psi_{E,l_E,\alpha} = l_E \psi_{E,l_E,\alpha}$:

$$\psi_{E,l_E,\alpha} = x_+^{l_E} g_{E,l_E,\alpha}(x_-x_+, z) \quad (2.171)$$

and, from $L_+ \psi_{E,l_E,\alpha} = 0$, we have:

$$\psi_{E,l_E,\alpha} = x_+^{l_E} f_{E,l_E,\alpha}(r) . \quad (2.172)$$

Therefore we have separation of variables because this wave function is equal to the product of a purely angular factor, $(\sin \theta \exp(i\varphi))^{l_E}$ and a purely radial one, $r^{l_E} f_{E,l_E,\alpha}(r)$.

Starting from $\psi_{E,l_E,\alpha}$, we can build a sequence of solutions of equation (2.156), that we denote by $\psi_{E,l_E,m,\alpha}$, being understood the identification $\psi_{E,l_E,l_E,\alpha} \equiv \psi_{E,l_E,\alpha}$. These new wave functions are identified, up to a multiplicative constant, by:

$$\psi_{E,l_E,m,\alpha} \sim L_-^{l_E-m} \psi_{E,l_E,\alpha} , \quad (2.173)$$

⁶This argument assumes wave function factorization into radial and angular factors. An alternative and simpler argument is based on the assumption that $\sum_m N_m$ is finite. This is easily justified in the case of a finite range potential, since we know that the number of independent states with limited energy in a finite volume is finite.

This sequence must stop when m reaches $-l_E$ because, using the second identity in (2.169) and $L^2\psi_{E,l_E,m,\alpha} = \hbar^2 l_E(l_E + 1)\psi_{E,l_E,m,\alpha}$, we have:

$$L_+ L_- \psi_{E,l_E,m,\alpha} = \hbar^2 (l_E(l_E + 1) - m^2 + m) \psi_{E,l_E,m,\alpha} , \quad (2.174)$$

which implies that $L_- \psi_{E,l_E,-l_E,\alpha} = 0$. Then from (2.165) we find that

$$\psi_{E,l_E,-l_E,\alpha} \sim x_-^{l_E} f_{E,l_E,\alpha}(r) . \quad (2.175)$$

So, for each α , we have found a multiplet of $2l_E + 1$ eigenfunctions of L^2 which are built starting from (2.172) and repeatedly acting on it by L_- . All the eigenfunctions of the multiplet have the same radial dependence. One might wonder if the alternate action of L_+ and L_- might produce more solutions with the same m belonging to the same multiplet but not proportional to each other. The negative answer follows directly from Eq. (2.174) which shows that this alternate action changes the wave function by a multiplicative constant. Hence the $2l_E + 1$ wave functions $\psi_{E,l_E,m,\alpha}$ span, for each value of α , an independent linear space invariant under the action of the angular momentum components.

The above analysis, which has begun from the solutions of equation (2.156) with maximum m ($m = l_E$), can be repeated considering the remaining solutions of equation (2.156) which are linearly independent of those belonging to the identified multiplets. We start considering the independent solutions of the set $\psi_{E,l_E-1,i}$. If their number exceeds, by p , that of the already identified multiplets, we can select p linear combinations of the $\psi_{E,l_E-1,i}$'s that, using the same notation introduced above, we denote by $\psi_{E,l_E-1,l_E-1,\beta}$, which are annihilated by L_+ , that is, such that $L_+ \psi_{E,l_E-1,l_E-1,\beta} = 0$. Indeed, if $L_+ \psi_{E,l_E-1,l_E-1,\beta}$ does not vanish, it must be linearly dependent on the $L_+ \psi_{E,l_E,l_E-1,\alpha}$'s, since these span the linear space of the solutions with maximum m . That is, we must have:

$$L_+ \left[\psi_{E,l_E-1,l_E-1,\beta} - \sum_{\alpha} c_{\alpha\beta} \psi_{E,l_E,l_E-1,\alpha} \right] = 0 . \quad (2.176)$$

But the wave function in brackets does not vanish because $\psi_{E,l_E-1,l_E-1,\beta}$ is chosen linearly independent of the members of the already built multiplets, therefore

$$\hat{\psi}_{E,l_E-1,l_E-1,\beta} \equiv \psi_{E,l_E-1,l_E-1,\beta} - \sum_{\alpha} c_{\alpha\beta} \psi_{E,l_E,l_E-1,\alpha} , \quad (2.177)$$

is a solution with $m = l_E - 1$ which is annihilated by L_+ . In this way we can finally build the chosen set of p independent solutions annihilated by L_+ .

From these solutions, repeatedly acting with L_- , we can build p new multiplets of eigenfunctions of L^2 . Continuing this procedure we show that, among the $N = \sum_i N_i$ independent solutions of equation (2.156), we can select N independent linear

combinations belonging to multiplets of eigenfunctions of L^2 and, of course L_z , with eigenvalues $\hbar^2 l(l+1)$ ($l_E \geq l \geq 0$) and $\hbar l \geq \hbar m \geq -\hbar l$, respectively.

We have seen that the angular dependence of the wave functions is identified once the quantum number l and m are given, while the radial dependence is identified by the multiplet. In much the same way as in (2.172) and (2.175), the wave functions are given as the product of radial functions, left invariant by the action of L_{\pm} , by homogeneous polynomials, called *harmonic polynomials*, that we denote by $\mathcal{Y}_{l,m}(\mathbf{r})$.

$$\psi_{E,l,m,\alpha}(\mathbf{r}) = \mathcal{Y}_{l,m}(\mathbf{r}) f_{E,l,\alpha}(r) . \quad (2.178)$$

We can also deduce the transformation properties of the wave functions given in (2.178) under spatial reflection $\mathbf{r} \rightarrow -\mathbf{r}$, usually called *parity transformation*, using the fact that the $\mathcal{Y}_{l,m}(\mathbf{r})$'s are homogeneous polynomials of degree l . The result is $\psi_{E,l,m,\alpha}(-\mathbf{r}) = (-1)^l \psi_{E,l,m,\alpha}(\mathbf{r})$. The harmonic polynomials, which are built by repeatedly acting on x_{\pm}^l by L_{\mp} , are called harmonic since they satisfy⁷

$$\nabla^2 \mathcal{Y}_{l,m}(\mathbf{r}) = 0, \quad \mathbf{r} \cdot \nabla \mathcal{Y}_{l,m}(\mathbf{r}) = l \mathcal{Y}_{l,m}(\mathbf{r}) = 0, \quad (2.179)$$

the second equation being equivalent to homogeneity. Indeed both Eq. (2.179) hold true for x_{\pm}^l and the homogeneous operators L_{\pm} commute with the Laplacian. For the time being we do not specify any normalization prescription for these harmonic polynomials except that implied by the equation

$$\mathcal{Y}_{l,-m} = (-1)^m \mathcal{Y}_{l,m}^* . \quad (2.180)$$

In order to make the construction clear it is convenient to give a few simple examples of harmonic polynomials:

$$\begin{aligned} \mathcal{Y}_{0,0}(\mathbf{r}) &\sim 1, \quad \mathcal{Y}_{1,\pm}(\mathbf{r}) \sim \mp x_{\pm}, \quad \mathcal{Y}_{1,0}(\mathbf{r}) \sim z \\ \mathcal{Y}_{2,\pm 2}(\mathbf{r}) &\sim x_{\pm}^2, \quad \mathcal{Y}_{2,\pm 1}(\mathbf{r}) \sim \mp z x_{\pm}, \quad \mathcal{Y}_{2,0}(\mathbf{r}) \sim 2z^2 - x_+ x_- , \end{aligned} \quad (2.181)$$

where the normalization is left free, but the sign is fixed assuming positive sign of $\mathcal{Y}_{l,0}$ on the positive z -axis and considering the sign induced by the action of L_{\pm} defined in (2.165).

It is now possible to consider that the basic purpose of the presented construction was to insert into the Schrödinger equation in a central potential (2.156) the maximum possible information about the angular momentum of the particle. This is equivalent to choosing the solutions of the form in (2.178) and reducing (2.156) to an equation for the radial wave function $f_{E,l,\alpha}(r)$, which is deduced computing the action of the Laplacian on a generic product $\mathcal{Y}_{l,m}(\mathbf{r})f(r)$. We have:

⁷In complex coordinates the Laplacian operator is given by: $4\partial_{x_+}\partial_{x_-} + \partial_z^2$.

$$\begin{aligned}
\nabla^2(\mathcal{Y}_{l,m}(\mathbf{r})f(r)) &= f(r)\nabla^2\mathcal{Y}_{l,m}(\mathbf{r}) + \mathcal{Y}_{l,m}(\mathbf{r})\nabla^2f(r) \\
&+ 2(\nabla\mathcal{Y}_{l,m}(\mathbf{r})) \cdot \nabla f(r) = \mathcal{Y}_{l,m}(\mathbf{r})\nabla \cdot \left(\mathbf{r} \frac{f'(r)}{r}\right) + 2(\mathbf{r} \cdot \nabla\mathcal{Y}_{l,m}(\mathbf{r})) \frac{f'(r)}{r} \\
&= \mathcal{Y}_{l,m}(\mathbf{r}) \left[2(l+1) \frac{f'(r)}{r} + f''(r) \right], \tag{2.182}
\end{aligned}$$

therefore the Schrödinger equation for $f_{E,l,\alpha}(r)$ becomes:

$$-\frac{\hbar^2}{2M} \left(f''_{E,l,\alpha}(r) + 2(l+1) \frac{f'_{E,l,\alpha}(r)}{r} \right) + V(r)f_{E,l,\alpha}(r) = E f_{E,l,\alpha}(r). \tag{2.183}$$

In spherical coordinates the harmonic polynomials appear as polynomials in $\cos\theta$ multiplied by $r^l \sin^m\theta \exp(\pm im\varphi)$. In order to complete the separations of the r dependence in the solutions of (2.156) we introduce the *spherical harmonics*:

$$Y_{l,m}(\theta, \varphi) = \frac{\mathcal{Y}_{l,m}(\mathbf{r})}{r^l}, \tag{2.184}$$

now specifying the normalization conditions:

$$\int_0^{2\pi} d\varphi \int_{-1}^1 d\cos\theta Y_{l,m}^*(\theta, \varphi) Y_{l',m'}(\theta, \varphi) = \delta_{l,l'} \delta_{m,m'}. \tag{2.185}$$

This is an orthonormalization condition for the spherical harmonics, which is particularly convenient for normalizing the wave functions. For reader's convenience, we give the explicit form of spherical harmonics up to $l = 2$:

$$\begin{aligned}
Y_{0,0} &= \sqrt{\frac{1}{4\pi}}; & Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \cos\theta; & Y_{1,\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\varphi}; \\
Y_{2,0} &= \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1); & Y_{2,\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\varphi}; \\
Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\varphi}. \tag{2.186}
\end{aligned}$$

The solutions of the Schrödinger equation are written in terms of the spherical harmonics in the form:

$$\psi_{E,l,m,\alpha}(\mathbf{r}) = Y_{l,m}(\theta, \varphi) \frac{\chi_{E,l,\alpha}(r)}{r}, \tag{2.187}$$

where, if the wave function is normalized, $|\chi_{E,l,\alpha}(r)|^2$ is the probability density of finding the particle at a distance r from the center. The equation for $\chi_{E,l,\alpha}(r)$ is obtained replacing in (2.183) $f_{E,l,\alpha}(r)$ by $r^{-(l+1)}\chi_{E,l,\alpha}(r)$. The radial Schrödinger equation becomes:

$$-\frac{\hbar^2}{2M}\chi''_{E,l,\alpha}(r) + \frac{\hbar^2 l(l+1)}{2Mr^2}\chi_{E,l,\alpha}(r) + V(r)g\chi_{E,l,\alpha}(r) = E\chi_{E,l,\alpha}(r), \quad (2.188)$$

as expected from Eq.(2.153). Indeed this is the one-dimensional stationary Schrödinger equation corresponding to the energy associated with the radial motion given in (2.153).

Let us discuss this point in few more details. Consider the energy appearing in (2.153) as an operator, whose action on the wave function specifies the right-hand side of the stationary Schrödinger equation (2.156). The term proportional to the Laplacian in (2.156), written in spherical coordinates, apparently corresponds to the sum of the first two terms in (2.153). The first term, which is proportional to the square of the radial momentum p_r , corresponds to the first term in (2.188), because the radial momentum, which is the variable conjugate to r , corresponds to the operator $-i\hbar\partial_r$. The second term is proportional to L^2 . Having written the solutions to equation (2.156) as products of radial functions and of eigenfunctions of the operator L^2 , whose eigenvalues are $\hbar^2 l(l+1)$ for non-negative integer l , it is clear that the second term in (2.188) corresponds to the term proportional to L^2 in (2.153).

This proves that we have obtained the quantum mechanical equivalent of the classical separation of variables described at the beginning of this section. In the following subsections we shall study the simplest solutions to the radial equation in a few cases with simple potentials.

2.9.1 A Piecewise Constant Potential and the Free Particle Case

The strategy for the solution to the Schrödinger equation in the case of a piecewise constant potential $V(r)$ is essentially the same as in the one dimensional case, we have only to pay special attention to the additional constraint that the wave function must vanish in $r = 0$, otherwise the related three dimensional probability density would be divergent in a position where the potential is flat. In particular, in the S wave case (that being the usual way of indicating the case $l = 0$) Eq. (2.188) coincides with the one dimensional Schrödinger equation, therefore we can obtain its solutions as a linear combination of the functions $\sin(\sqrt{2M(E-V)}r/\hbar)$ and $\cos(\sqrt{2M(E-V)}r/\hbar)$ for $E > V$ and $\exp(\pm\sqrt{2M(E-V)}r/\hbar)$ in the opposite case. In the case of a spherical potential well:

$$V(r) = -V_0\Theta(R-r), \quad (2.189)$$

where $V_0 > 0$ and $\Theta(x)$ is the step function ($\Theta(x) = 1$ for $x > 0$ and $\Theta(x) = 0$ for $x < 0$), the (S wave) radial equation coincides with the one-dimensional Schrödinger equation discussed in Sect. 2.6 for the parity odd wave functions in a square well with width $L = 2R$. Thus one can find the equation for the binding energy in (2.106).

For $l > 0$ Eq. (2.188) can be written in the form:

$$\chi''_{E,l}(r) + \left[\sigma q^2 - \frac{l(l+1)}{r^2} \right] \chi_{E,l}(r) = 0. \quad (2.190)$$

with

$$q = \sqrt{\frac{2M}{\hbar^2} |E - V|} \quad \text{and} \quad \sigma = \frac{E - V}{|E - V|}, \quad (2.191)$$

this implies that sine, cosine and exponentials must be replaced by new special functions (which are called *spherical Bessel functions*), which can be explicitly constructed using the recursive equation:

$$q \chi_{E,l+1}(r) = \frac{l+1}{r} \chi_{E,l}(r) - \chi'_{E,l}(r). \quad (2.192)$$

This recursive equation is proved as follows. Assuming Eq. (2.192) and using (2.190) we obtain

$$q \chi'_{E,l+1} = \sigma q^2 \chi_{E,l} - q(l+1) \frac{\chi_{E,l+1}}{r}. \quad (2.193)$$

Using again Eqs. (2.192) and (2.193),

$$\begin{aligned} \chi''_{E,l+1} &= \sigma q \chi'_{E,l} - \frac{(l+1)}{r} [\chi'_{E,l+1} - \frac{\chi_{E,l+1}}{r}] \\ &= -\sigma q^2 \chi_{E,l+1} + \frac{l+1}{r} [\sigma q \chi_{E,l} - \chi'_{E,l+1}] + (l+1) \frac{\chi_{E,l+1}}{r^2} \\ &= -\sigma q^2 \chi_{E,l+1} + \frac{(l+2)(l+1)}{r^2} \chi_{E,l+1}. \end{aligned} \quad (2.194)$$

This shows that, by (2.192), we can obtain, from a solution of equation (2.190), another solution of the same equation with l increased by one.⁸ For the internal case, $\sigma = 1$, we have in particular:

$$\chi_{E,0}(r) = \sin(qr), \quad \chi_{E,1}(r) = \frac{\sin(qr)}{qr} - \cos(qr). \quad (2.195)$$

while analogous solutions (with real exponentials replacing trigonometric functions, as usual) are found in the external region for $E < 0$, i.e. for bound states. The asymptotic property:

$$\chi_{E,l}(r) \xrightarrow{qr \rightarrow \infty} \sin\left(qr - \frac{l\pi}{2}\right), \quad (2.196)$$

is a direct consequence of Eq. (2.192).

⁸The spherical Bessel functions, $j_l(qr)$ are identified with $\chi_{E,l+1}(r)/(qr)$ normalized according to (2.192) and $\chi_{E,0}(qr) = \sin(qr)$.

If, for instance, we want to study the possible bound states in P wave (i.e. $l = 1$) in the above potential well, setting the energy to $-B$ and defining $q_i = \sqrt{2MB/\hbar^2}$ and $q_e = \sqrt{2M(V_0 - B)/\hbar^2}$ we must continuously connect the internal solution $\sin(q_i r)/q_i r - \cos(q_i r)$, which vanishes in $r = 0$, with the external solution which vanishes as $r \rightarrow \infty$, i.e. $a e^{-q_e(r-R)}(1/q_e r + 1)$. This leads to the system:

$$\frac{\sin(q_i R) - q_i R \cos(q_i R)}{q_i} = a \frac{1 + q_e R}{q_e}$$

$$\frac{\sin(q_i R)(1 - q_i^2 R^2) - q_i R \cos(q_i R)}{q_i} = a \frac{1 + q_e R + q_e^2 R^2}{q_e}.$$

Therefore, setting $y = \sqrt{2MV_0}R/\hbar$, $x = q_i R$ and hence $q_e R = \sqrt{y^2 - x^2}$, we have the transcendental equation:

$$\tan x = x \frac{y^2 - x^2}{y^2 + x^2 \sqrt{y^2 - x^2}}.$$

Considering the bound state condition: $0 \leq x \leq y$, the above equation requires $0 \leq \tan x/x \leq 1$ and $\tan y/y = 0$. This implies the absence of $l = 1$ bound states for $y < \pi$ while we have seen, comparing with the one dimensional case, that the first $l = 0$ bound state appears for $y = \pi/2$.

We explicitly notice that, for $V = 0$, solutions to equation (2.190) provide the wave functions for the free particle problem. Let us discuss in particular the case $l = 0$: from (2.186), (2.187) and (2.195) we deduce that solutions with zero angular momentum and $E > 0$ are

$$\psi_{E,l=0}(\mathbf{r}) \propto \frac{\sin kr}{r}, \quad (2.197)$$

where $\hbar k = \sqrt{2ME}$. If we insert time dependence explicitly, such a solution can be rewritten in the form

$$\psi_{E,l=0}(\mathbf{r}, t) \propto e^{-iEt/\hbar} \frac{\sin kr}{r} \propto \frac{e^{i(pr-Et)/\hbar}}{r} - \frac{e^{-i(pr+Et)/\hbar}}{r} \quad (2.198)$$

where $p = k\hbar$. From that it is clear that the solution is the sum of two spherical waves, the first propagating outwards, the second inwards. This can be confirmed also by an explicit computation of the probability current density, which will show that the two waves lead to the same probability flux across every spherical surface centered around the origin, with a different sign for the inward and outward solution.

Analogous considerations hold for solutions with $l > 0$. In this way one finds wave functions associated with particles with fixed energy and angular momentum, which are alternative to the standard plane wave solutions, corresponding to fixed energy and momentum. We will go back to free particle solutions when we discuss the scattering problem.

2.9.2 The Coulomb Potential

It is obviously of great interest to study bound states in a Coulomb potential, which permits an analysis of the energy levels of the hydrogen atom. To this purpose, let us consider the motion of a particle of mass m in a central potential $V(r) = -e^2/(4\pi\epsilon_0 r)$, where ϵ_0 is the vacuum dielectric constant and e is (minus) the charge of the (electron) proton in MKS units; M is actually the reduced mass of the proton-electron system, $M = m_e m_p / (m_e + m_p)$, which is equal to the electron mass within a good approximation. In this case it is convenient to start from Eq. (2.183), which we rewrite as

$$f''_{B,l}(r) + 2(l+1) \frac{f'_{B,l}(r)}{r} + \frac{2Me^2}{4\pi\epsilon_0 \hbar^2 r} f_{B,l}(r) = \frac{2MB}{\hbar^2} f_{B,l}(r), \quad (2.199)$$

where $B \equiv -E$ is the binding energy. Before proceeding further, let us perform a change of variables specifying the relevant parameters: we introduce Bohr's radius $a_0 = 4\pi\epsilon_0 \hbar^2 / (Me^2) \simeq 0.52 \times 10^{-10}$ m and Rydberg's energy constant $E_R \equiv \hbar R \equiv Me^4 / (2\hbar^2 (4\pi\epsilon_0)^2) \simeq 13.6$ eV, which are the typical length and energy scales which can be constructed in terms of the physical constants involved in the problem. Equation (2.199) can be rewritten in terms of the dimensionless radial variable $\rho \equiv r/a_0$ and of the dimensionless binding energy $B/E_R \equiv \lambda^2$ (with $\lambda \geq 0$), as follows:

$$f''_{\lambda,l}(\rho) + 2(l+1) \frac{f'_{\lambda,l}(\rho)}{\rho} + \frac{2}{\rho} f_{\lambda,l}(\rho) = \lambda^2 f_{\lambda,l}(\rho). \quad (2.200)$$

Let us first consider the asymptotic behavior of the solution as $\rho \rightarrow \infty$: in this limit the second and the third term on the left hand side can be neglected, so that the solution of equation (2.200) is asymptotically also solution of $f''_{\lambda,l}(\rho) = \lambda^2 f_{\lambda,l}(\rho)$, i.e. $f_{\lambda,l}(\rho) \sim e^{\pm\lambda\rho}$ for $\rho \gg 1$. The asymptotically divergent behavior must obviously be rejected since we are looking for a solution corresponding to a normalizable, single particle, bound state. We shall therefore write our solution in the form $f_{\lambda,l}(\rho) = h_{\lambda,l}(\rho)e^{-\lambda\rho}$, where $h_{\lambda,l}(\rho)$ should not diverge too strongly for $\rho \rightarrow \infty$, thus overcoming the damping exponential factor. The differential equation satisfied by $h_{\lambda,l}(\rho)$ easily follows from (2.200):

$$h''_{\lambda,l} + \left(\frac{2(l+1)}{\rho} - 2\lambda \right) h'_{\lambda,l} + \frac{2}{\rho} (1 - \lambda(l+1)) h_{\lambda,l} = 0. \quad (2.201)$$

Because the coefficients of this linear differential equation are analytic for ρ finite and strictly positive, $h_{\lambda,l}(\rho)$ should also be an analytic function in this domain. Therefore we can expand $h_{\lambda,l}(\rho)$ in power series of ρ , finding a recursion relation for its coefficients. We shall then impose that the series stops at some finite order so as to keep the asymptotic behavior of $f_{\lambda,l}(\rho)$ as $\rho \rightarrow \infty$ unchanged.

In order to understand what is the first term ρ^s of the series that we must take into account, let us consider the behavior of Eq. (2.201) as $\rho \rightarrow 0$. In this limit, setting $h_{\lambda,l} \sim \rho^s$, it can be easily checked that (2.201) is satisfied at the leading order in ρ only if $s(s-1) = -2s(l+1)$, whose solutions are $s = 0$ and $s = -2l - 1$. Last possibility must be rejected, otherwise the probability density related to our solution would not be integrable around the origin. Hence we write:

$$h_{\lambda,l}(\rho) = c_0 + c_1\rho + c_2\rho^2 + \cdots + c_h\rho^h + \cdots = \sum_{h=0}^{\infty} c_h\rho^h, \quad (2.202)$$

with $c_0 \neq 0$. Inserting the last expression into (2.201), we obtain the following recurrence relation for the coefficients c_h :

$$c_{h+1} = 2 \frac{\lambda(h+l+1) - 1}{(h+1)(h+2(l+1))} c_h \quad (2.203)$$

which, apart from an overall normalization constant fixing the starting coefficient c_0 , completely determines our solution in terms of l and λ . However, if the recurrence relation never stops, it becomes asymptotically (i.e. for large h):

$$c_{h+1} \simeq \frac{2\lambda}{h} c_h$$

which can be easily checked to be the same relation relating the coefficients in the Taylor expansion of $\exp(2\lambda\rho)$. Therefore, if the series does not stop, the asymptotic behavior of $f_{\lambda,l}(\rho)$ is corrupted, bringing in fact back the unwanted divergent behavior $f_{\lambda,l}(\rho) \sim e^{\lambda\rho}$. The series stops if and only if the coefficient on the right hand side of (2.203) vanishes for some given value $h = k \geq 0$, hence

$$\lambda(k+l+1) - 1 = 0 \quad \Rightarrow \quad \lambda = \frac{1}{k+l+1}. \quad (2.204)$$

In this case $h_{\lambda,l}(\rho)$ is simply a polynomial of degree k in ρ , which is completely determined (neglecting an overall normalization) as a function of l and k : these polynomials belong to a well know class of special functions and are usually called Laguerre's associated polynomials. We have so found that, for a given value of l , the admissible solutions with negative energy, i.e. the hydrogen bound states, can be enumerated according to a non-negative integer k and the energy levels are quantized according to (2.204).

If we replace k by a new, integer and strictly positive, quantum number n given by:

$$n = k + l + 1 = \lambda^{-1}, \quad (2.205)$$

which is usually called the *principal quantum number*, then, according to (2.204) and to the definition of λ , the energy levels of the hydrogen atom are given by

$$E_n = -\frac{E_R}{n^2} = -\frac{Me^4}{8\epsilon_0^2 h^2 n^2},$$

in perfect agreement with the Balmer–Rydberg series for line spectra and with the qualitative result obtained in Sect. 2.2 using Bohr’s quantization rule.

It is important to note that, in the general case of a motion in a central field, energy levels related to different values of the angular momentum l are expected to be different, since they are related to the solutions of different equations of the form given in (2.183). Stated otherwise, the only expected degeneracy is that related to the rotational symmetry of the problem, leading to degenerate wave function multiplets of dimension $2l + 1$, as discussed above. However, in the hydrogen atom case, we have found a quite different result: according to Eq. (2.205), for a fixed value of the integer $n > 0$, there are n different multiplets, corresponding to $l = 0, 1, \dots, (n-1)$, having the same energy. The degeneracy is therefore

$$\sum_{l=0}^{n-1} (2l + 1) = n^2$$

instead of $2l + 1$. Unexpected additional degeneracies like this one are usually called “accidental”, even if in this case the degeneracy is not so accidental. Indeed the motion in a Coulomb (or gravitational) field has a larger symmetry than simply the rotational one. We will not go into details, but just remind the reader of a particular integral of motion which is only present, among all possible central potentials, in the case of the Coulomb (gravitational) field: that is Lenz’s vector, which completely fixes the orientation of classical orbits. Another central potential leading to a similar “accidental” degeneracy is that corresponding to the three-dimensional isotropic harmonic oscillator. Actually, the Coulomb potential and the harmonic oscillator are joined in Classical Mechanics by Bertrand’s theorem, which states that they are the only central potentials whose classical orbits are always closed.

Let us finish by giving the explicit form of the hydrogen wave functions in a few cases. Writing them in a form similar to that given in (2.187), and in particular as

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r)Y_{l,m}(\theta, \varphi),$$

we have

$$\begin{aligned} R_{1,0}(r) &= 2(a_0)^{-3/2} \exp(-r/a_0), \\ R_{2,0}(r) &= 2(2a_0)^{-3/2} \left(1 - \frac{r}{2a_0}\right) \exp(-r/2a_0), \\ R_{2,1}(r) &= (2a_0)^{-3/2} \frac{r}{\sqrt{3}a_0} \exp(-r/2a_0). \end{aligned}$$

2.9.3 The Isotropic Harmonic Oscillator

We go on with our introduction to the Schrödinger equation with central potentials reconsidering the case of the isotropic harmonic oscillator, that we shall discuss in a moment. We briefly recall the main results. The Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \frac{k}{2} r^2 \right] \psi_E = E \psi_E , \quad (2.206)$$

written in the form (2.134), appears separable in Cartesian coordinates and it is possible to find solutions written as the product of one-dimensional solutions $\psi_{n_x, n_y, n_z}(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z)$, and the corresponding energy is the sum of one-dimensional energies,

$$E_{n_x, n_y, n_z} = \hbar\omega(n_x + n_y + n_z + 3/2) = \hbar\omega(n + 3/2) ,$$

where $n = n_x + n_y + n_z$ and $\omega = \sqrt{k/m}$. In particular the ground state wave function is $\psi_0(\mathbf{r}) = (\alpha^2/\pi)^{3/4} \exp(-\alpha^2 r^2/2)$, where $\alpha = \sqrt{m\omega/\hbar}$ is the inverse of the typical length scale of the system introduced in (2.116). Using the operator formalism we introduce three raising operators

$$\begin{aligned} A_x^\dagger &= \frac{1}{\sqrt{\hbar\omega}} X_- = \frac{1}{\sqrt{2}} \left(\alpha x - \frac{1}{\alpha} \partial_x \right) \\ A_y^\dagger &= \frac{1}{\sqrt{\hbar\omega}} Y_- = \frac{1}{\sqrt{2}} \left(\alpha y - \frac{1}{\alpha} \partial_y \right) \\ A_z^\dagger &= \frac{1}{\sqrt{\hbar\omega}} Z_- = \frac{1}{\sqrt{2}} \left(\alpha z - \frac{1}{\alpha} \partial_z \right) , \end{aligned} \quad (2.207)$$

and we write the generic solution shown above in the form:

$$\psi_{n_x, n_y, n_z}(x, y, z) = \frac{(A_x^\dagger)^{n_x} (A_y^\dagger)^{n_y} (A_z^\dagger)^{n_z}}{\sqrt{n_x! n_y! n_z!}} \psi_0(\mathbf{r}) , \quad (2.208)$$

where the square root in the denominator is the normalization factor (see Eq. (2.133)). As we have shown in Sect. 2.7, these solutions are degenerate, in the sense that there are $(n+1)(n+2)/2$ solutions corresponding to the same energy $E_n = \hbar\omega(n+3/2)$ if $n = n_x + n_y + n_z$, and form a complete set. They also have the same transformation properties under reflection of all coordinate axes (parity transformation): indeed, since the ground state is parity even and each raising operator is parity odd, it is apparent that the solution corresponding to n_x, n_y, n_z has parity $(-1)^{n_x+n_y+n_z} = (-1)^n$. However they have no well defined angular momentum property, their form does not correspond to that shown in (2.187). Our purpose is to identify the solutions with well defined angular momentum quantum numbers, that is l and m : they will

form an alternative complete set, i.e. a different orthonormal basis for the linear space of solutions corresponding to each energy level.

With this purpose it is useful to study the commutation rules of the angular momentum components with the raising operators and to take into account that the ground state is rotation invariant, that is $L_i \psi_0(r) = 0$, for $i = \pm, z$. In order to simplify the commutation rules we adapt our raising operators to the choice of complex coordinates x_{\pm}, z introducing:

$$A_{\pm}^{\dagger} = \frac{1}{\sqrt{2}} \left(\alpha x_{\pm} - \frac{2}{\alpha} \partial_{x_{\mp}} \right) = A_x^{\dagger} \pm i A_y^{\dagger}. \quad (2.209)$$

They satisfy the commutation rules:

$$\begin{aligned} [L_z, A_z^{\dagger}] &= 0, \quad [L_z, A_{\pm}^{\dagger}] = \pm \hbar A_{\pm}^{\dagger}, \quad [L_{\pm}, A_z^{\dagger}] = \mp \hbar A_{\pm}^{\dagger} \\ [L_{\pm}, A_{\mp}^{\dagger}] &= \pm 2\hbar A_z^{\dagger}, \quad [L_{\pm}, A_{\pm}^{\dagger}] = 0, \end{aligned} \quad (2.210)$$

which can be easily verified to coincide with those between angular momentum components and coordinates, after the substitution $A_z^{\dagger} \leftrightarrow z$ and $A_{\pm}^{\dagger} \leftrightarrow x_{\pm}$.

Due to the same correspondence and to the rotation invariance of ψ_0 , given a polynomial $P(x_+, x_-, z)$ in the coordinates and the wave function $P(x_+, x_-, z)\psi_0(r)$, together with another wave function written in the operator formalism as $P(A_+^{\dagger}, A_-^{\dagger}, A_z^{\dagger})\psi_0(r)$, we can state that if

$$L_i P(x_+, x_-, z)\psi_0(r) = Q_i(x_+, x_-, z)\psi_0(r), \quad (2.211)$$

then

$$L_i P(A_+^{\dagger}, A_-^{\dagger}, A_z^{\dagger})\psi_0(r) = Q_i(A_+^{\dagger}, A_-^{\dagger}, A_z^{\dagger})\psi_0(r). \quad (2.212)$$

Notice that the A^{\dagger} operators commute among themselves, thus $P(A_+^{\dagger}, A_-^{\dagger}, A_z^{\dagger})$ is a well defined differential operator and $P(A_+^{\dagger}, A_-^{\dagger}, A_z^{\dagger})\psi_0(r)$ is a well defined wave function. The left-hand sides of the above equations are computed by repeatedly commuting L_i with the coordinates x_+, x_-, z , in the first equation, and with the raising operators $A_+^{\dagger}, A_-^{\dagger}, A_z^{\dagger}$ in the second one, until L_i reaches and annihilates ψ_0 . The strict correspondence of the commutation rules guarantees the validity of the above equations.⁹

⁹This one-to-one correspondence between the action of the generators of rotations on the coordinates and on the raising operators can be generalized to other linear, in fact unitary, transformations of the coordinates, transforming homogeneous polynomials into homogeneous polynomials of the same degree. These transformations act within degenerate multiplets of solutions of the Schrödinger equation and clarify the origin of the additional degeneracy which is found for the central harmonic potential.

Hence in particular, considering the harmonic homogeneous polynomials, introduced in (2.178), and recalling that:

$$L^2 \mathcal{Y}_{l,m}(x_+, x_-, z) \psi_0(r) = \hbar^2 l(l+1) \mathcal{Y}_{l,m}(x_+, x_-, z) \psi_0(r) \quad (2.213)$$

and that

$$L_z \mathcal{Y}_{l,m}(x_+, x_-, z) \psi_0(r) = \hbar m \mathcal{Y}_{l,m}(x_+, x_-, z) \psi_0(r), \quad (2.214)$$

we have:

$$L^2 \mathcal{Y}_{l,m}(A_+^\dagger, A_-^\dagger, A_z^\dagger) \psi_0(r) = \hbar^2 l(l+1) \mathcal{Y}_{l,m}(A_+^\dagger, A_-^\dagger, A_z^\dagger) \psi_0(r), \quad (2.215)$$

and

$$L_z \mathcal{Y}_{l,m}(A_+^\dagger, A_-^\dagger, A_z^\dagger) \psi_0(r) = \hbar m \mathcal{Y}_{l,m}(A_+^\dagger, A_-^\dagger, A_z^\dagger) \psi_0(r). \quad (2.216)$$

In this way we have identified a degenerate set of solutions of the Schrödinger equation corresponding to the energy $E_l = \hbar\omega(l + 3/2)E$ and with the angular momentum given above. However this does not exhaust the solutions with the same energy. Indeed for any positive integer $k \leq [l/2]$, considering that

$$\begin{aligned} L^2 \mathcal{Y}_{l-2k,m}(x_+, x_-, z) (r^2)^k \psi_0(r) \\ = \hbar^2 (l-2k)(l-2k+1) \mathcal{Y}_{l-2k,m}(x_+, x_-, z) (r^2)^k \psi_0(r) \end{aligned} \quad (2.217)$$

and that

$$L_z \mathcal{Y}_{l-2k,m}(x_+, x_-, z) (r^2)^k \psi_0(r) = \hbar m \mathcal{Y}_{l-2k,m}(x_+, x_-, z) (r^2)^k \psi_0(r) \quad (2.218)$$

we have

$$\begin{aligned} L^2 \mathcal{Y}_{l-2k,m}(A_+^\dagger, A_-^\dagger, A_z^\dagger) (A_+^\dagger A_-^\dagger + (A_z^\dagger)^2)^k \psi_0(r) \\ = \hbar^2 (l-2k)(l-2k+1) \mathcal{Y}_{l-2k,m}(A_+^\dagger, A_-^\dagger, A_z^\dagger) (A_+^\dagger A_-^\dagger + (A_z^\dagger)^2)^k \psi_0(r) \end{aligned} \quad (2.219)$$

and

$$\begin{aligned} L_z \mathcal{Y}_{l-2k,m}(A_+^\dagger, A_-^\dagger, A_z^\dagger) (A_+^\dagger A_-^\dagger + (A_z^\dagger)^2)^k \psi_0(r) \\ = \hbar m \mathcal{Y}_{l-2k,m}(A_+^\dagger, A_-^\dagger, A_z^\dagger) (A_+^\dagger A_-^\dagger + (A_z^\dagger)^2)^k \psi_0(r). \end{aligned} \quad (2.220)$$

Therefore we have $2l - 4k + 1$ further solutions with the same energy E_l and angular momentum $l - 2k$. Notice that we have not considered the problem of normalizing the above wave functions. In this way, for any l , we have identified

$$(2l+1) + (2l-4+1) + \dots = (l+1)(l+2)/2$$

independent solutions with energy E_l . These solutions form a complete degenerate set, i.e. a new basis, alternative to that described by Eq. (2.136), for the linear space of solutions of energy E_l . Their angular momenta correspond to all possible non-negative integers ranging from l down to zero (or one), but keeping the same parity of l . This last property can be easily understood, recalling that all solutions belonging to the same energy level of the isotropic harmonic oscillator have the same transformation properties under parity (they are even or odd depending on the parity of l , i.e. they have parity $(-1)^l$), and that, on the other hand, the solutions with fixed angular momentum \bar{l} have parity $(-1)^{\bar{l}}$.

2.9.4 The Scattering Solutions

In the previous examples we have considered the determination of bound state solutions for some simple cases of central potentials. Now, to conclude, we consider a scattering experiment: a beam of particles of given energy is launched towards a fixed target. One is interested in determining the distribution of products after the collision, with the assumption that far away from the target, both before and after the collisions, a free particle approximation holds true. We limit ourselves to the case of elastic scattering in which the final scattered particles have the same nature as the beam ones and their energy loss is only due to the recoil of the scatterer. The experiment is based on the measure of the angular distribution of particles scattered at a certain angle with respect to the initial beam, which is assumed to be as monochromatic and parallel as possible. In principle, there should be a single scatterer which should initially be at rest and should interact with a single beam particle. However in practice the effect of a single scatterer, at the atomic level, would be too tiny to be observable. Therefore, in most cases, one uses many scatterers which are contained, e.g., in a piece of matter, a target, or else in a second beam crossing the first one.

A typical and renown example is Rutherford's experiment in which an almost parallel beam of alpha particles emitted by some radioactive material (Radium) and selected by a suitable diaphragm, crosses a thin golden target.¹⁰ Since the alpha particles are heavy, their interaction with the atomic electrons is negligible and, if the target is thin enough, the scattered alpha particles have interacted with a single atomic nucleus of gold.

The scattered particles are detected by observing the sparks they produce impinging on a phosphorescent screen. The physical goal is to compare the intensity of particles scattered at small angles with that at large angles. Nuclei with radii of the same order of magnitude as the atomic radii should not scatter alpha particles at large angles, while this should happen for much smaller nuclei, because the electric forces generated by large nuclei are much smaller than those due to almost point-like ones. Rutherford was able to show that the nuclear radii are smaller than 10^{-14} m, and

¹⁰As a matter of fact the experiment was suggested by Rutherford, but performed by Geiger and Madsen.

therefore he suggested his atomic model which has been discussed in the first pages of this chapter.

In order to translate these qualitative considerations into quantitative ones, one usually counts the number of scattered particles (sparks) detected per unit time in a small solid angle around a given direction. This number should be proportional to the number of particles carried by the initial beam per unit time, that is, that of the particles crossing the beam section per unit time, and to the number of gold atoms which are present in the beam-target intersection, this is proportional to the area of the beam section. The coefficient of proportionality should thus have the dimensions of an area divided by a solid angle; it is usually written in differential form as $d\sigma/d\Omega(E, \theta)$ and is called the differential cross section. $d\Omega$ is the infinitesimal solid angle, θ is the polar angle taken with respect to the beam direction. The quantity σ , which is obtained after integration of the previous quantity over $d\Omega$, is an area called *cross section*, because classically it coincides with the cross section of the scatterer as seen by the beam. It is evident that θ is the only relevant angular variable here: we have assumed isotropy of the scatterer and invariance of the beam under rotations around the z axis.

Even if in many cases the mass of the scatterer M_s is much larger than that of the beam particles, m_p , and therefore practically the scatterer does not recoil, the process can always be described in relative coordinates. Then the recoil effects are taken into account replacing m_p by the reduced mass $m = M_s m_p / (M_s + m_p)$. Once this is done the above described elastic scattering process is represented assuming a wave function $\psi_k(r, \theta)$ which, at large distances, tends to

$$\psi_k(r, \theta) \xrightarrow{r \rightarrow \infty} e^{ikr \cos \theta} + \frac{f(\cos \theta)}{r} e^{ikr} . \quad (2.221)$$

We note that the collective interpretation of this wave function corresponds to a flux, parallel to the z axis, of ingoing particles with flux density (the number of particles per unit time crossing a unitary area orthogonal to the beam axis) $J_z = \hbar k / m$, and a radially scattered outgoing angular flux. The number of particles scattered per unit time and unit solid angle is equal to $J_r = |f(\cos \theta)|^2 \hbar k / m$. The ratio of these two quantities which can be computed from Eq. (2.221) is just the *differential cross section*:

$$\frac{d\sigma}{d\Omega}(\cos \theta) = |f(\cos \theta)|^2 , \quad (2.222)$$

and can be directly measured as described above. Therefore the physically interesting question is how one can compute $f(\cos \theta)$.

To start with, let us consider how a plane wave proceeding along the z axis, $\exp(ikz) = \exp(ikr \cos \theta)$, i.e. like the ingoing wave in (2.221), can be expanded in a series of spherical harmonics multiplied by functions of r , i.e. in a series of free particle solutions with fixed angular momentum. As we have seen, if the particle is free, the radial functions are solutions of equation (2.190), i.e. they coincide with spherical Bessel functions $j_l(kr) = \chi_{E,l}(r)/(kr)$. We note that the above plane wave

is left invariant by the rotations around the z axis, thus only the $Y_{l,0}$'s should appear among the spherical harmonics appearing in the expansion. Indeed we have:

$$\exp(ikz) = \sum_{l=0}^{\infty} i^l \sqrt{4\pi(2l+1)} j_l(kr) Y_{l,0}(\cos \theta) . \quad (2.223)$$

The values of the coefficients in this expansion follow from the orthonormality of the spherical harmonics, Eq. (2.185), and from the equation

$$2\pi \int_{-1}^1 dx e^{iyx} Y_{l,0}(x) \xrightarrow{y \rightarrow \infty} i^l \sqrt{4\pi(2l+1)} \frac{\sin(y - \frac{l\pi}{2})}{y} , \quad (2.224)$$

which can be proved taking into account that the $Y_{l,0}(z)$'s are polynomials in z with parity $(-1)^l$, that the following two equations hold:

$$Y_{l,0}(1) = \sqrt{\frac{2l+1}{4\pi}} , \quad (2.225)$$

$$\int_{-1}^1 dy e^{ixy} x^n \xrightarrow{y \rightarrow \infty} \frac{e^{iy} - (-1)^n e^{-iy}}{iy} = i^n \frac{2}{y} \sin(y - \frac{n\pi}{2}) , \quad (2.226)$$

and, finally, comparing (2.226) with the asymptotic behavior of the spherical Bessel functions given in (2.196).

The physical interesting question is how the plane wave is deformed in the presence of a central potential $V(r)$ which we assume vanishing at large r faster than r^{-1} . It is clear that, because of the presence of a non-trivial potential $V(r)$, the asymptotic behavior of the component with angular momentum l of the radial wave functions does not coincide with the free one, that is, with the spherical Bessel function $\sim \sin(kr - l\pi/2)/r$. In contrast we have an asymptotic radial wave function $\sim \sin(kr - l\pi/2 + \delta_l)/r$, where δ_l is called *phase shift*. Here we show how, given the whole sequence δ_l , for $l = 0, \dots, \infty$, we can compute $f(\cos \theta)$.

We note, first of all, that the asymptotic form of the plane wave in (2.223) is:

$$\begin{aligned} e^{ikz} &\xrightarrow{kr \rightarrow \infty} \sum_{l=0}^{\infty} i^l \sqrt{4\pi(2l+1)} Y_{l,0}(\cos \theta) \frac{\sin(kr - \frac{l\pi}{2})}{kr} \\ &= \sum_{l=0}^{\infty} \frac{\sqrt{4\pi(2l+1)}}{2ikr} Y_{l,0}(\cos \theta) \left[e^{ikr} - (-1)^l e^{-ikr} \right] . \end{aligned} \quad (2.227)$$

Assuming for $f(\cos \theta)$ the decomposition

$$f(\cos \theta) = \sum_{l=0}^{\infty} \sqrt{4\pi(2l+1)} f_l Y_{l,0}(\cos \theta) , \quad (2.228)$$

we translate equation (2.221) into:

$$\psi_k(r, \theta) \xrightarrow{r \rightarrow \infty} \sum_{l=0}^{\infty} \frac{\sqrt{4\pi(2l+1)}}{2ikr} Y_{l,0}(\cos \theta) \left[(1 + 2ikf_l) e^{ikr} - (-1)^l e^{-ikr} \right]. \quad (2.229)$$

Here we must insert the above given information about the asymptotic behavior of the radial wave functions related to the phase shifts. This is possible if, and only if, the *unitarity constraint*

$$2ikf_l = e^{2i\delta_l} - 1, \quad (2.230)$$

is fulfilled, and one has

$$\psi_k(r, \theta) \xrightarrow{r \rightarrow \infty} \sum_{l=0}^{\infty} \frac{i^l \sqrt{4\pi(2l+1)}}{kr} e^{i\delta_l} Y_{l,0}(\cos \theta) \sin(kr - \frac{l\pi}{2} + \delta_l), \quad (2.231)$$

and

$$f(\cos \theta) = \sum_{l=0}^{\infty} \frac{\sqrt{4\pi(2l+1)}}{k} e^{i\delta_l} \sin \delta_l Y_{l,0}(\cos \theta), \quad (2.232)$$

from which one can compute the differential and the total cross section defined as

$$\begin{aligned} \sigma &= 2\pi \int_{-1}^1 d \cos \theta |f(\cos \theta)|^2 = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \\ &= 4\pi \sum_{l=0}^{\infty} \frac{2l+1}{k^2 + k^2 \cot^2 \delta_l}. \end{aligned} \quad (2.233)$$

Taking into account (2.225) it is easy to verify that:

$$\sigma = 4\pi \frac{\text{Im} f(1)}{k}. \quad (2.234)$$

This is a very general property of scattering, which relates the total cross section to the differential cross section in the forward direction ($\cos \theta = 1$), which is usually called *the optical theorem*.

Few examples of phase shift calculations are given in the problems (see in particular 2.41, 2.52 and 2.53), here we consider the example of the scattering by a rigid ball of radius R , in which the radial wave function satisfies the free particle equation with the vanishing condition at $r = R$. For $l = 0$ we have $\sin(kR - \delta_0) = 0$ and hence $\delta_0 = kR$. For $l = 1$ the free wave function is $\frac{\sin(kR - \delta_1)}{kR} - \cos(kR - \delta_1)$ and hence we have $\delta_1 = kR - \tan^{-1}(kR)$, which for small energies vanishes as $(kR)^3$. Going further, it is possible to verify that for small energies the phase shifts $\delta_l \sim (kR)^{2l+1}$. This property holds true in general, if one identifies R with the (finite) range of the

potential. The coefficient of k in the first term of the low energy expansion of δ_0 is called *scattering length*.

In the case at hand, for small energies, we have $\sigma \simeq 4\pi R^2(1 + O((kR)^2))$, that is, four times the geometric section of the ball, which is equal to the classical cross section. This proves the existence of diffractive contributions to the cross section. In the general expression of the low energy cross section the scattering length replaces R in the above formula.

For finite range potentials, at high energy, $\sin \delta_l$ must vanish for all l since an infinite number of l 's contribute to the cross section, which must approach the classical value, thus remaining finite. Therefore $\lim_{k \rightarrow \infty} \delta_l = n_l \pi$ with n_l integer.

Suggestions for Supplementary Readings

- E. H. Wichman: *Quantum Physics - Berkeley Physics Course*, volume 4 (Mcgraw-Hill Book Company, New York 1971)
- L. D. Landau, E. M. Lifchitz: *Quantum Mechanics - Non-relativistic Theory*, Course of Theoretical Physics, volume 3 (Pergamon Press, London 1958)
- L. I. Schiff: *Quantum Mechanics* 3d edn (Mcgraw-Hill Book Company, Singapore 1968)
- J. J. Sakurai: *Modern Quantum Mechanics* (The Benjamin-Cummings Publishing Company Inc., Menlo Park 1985)
- E. Persico: *Fundamentals of Quantum Mechanics* (Prentice - Hall Inc., Englewood Cliffs 1950).

Problems

2.1 A diatomic molecule can be simply described as two point-like objects of mass $m = 10^{-26}$ kg placed at a fixed distance $d = 10^{-9}$ m. Describe what are the possible values of the molecule energy according to Bohr's quantization rule. Compute the energy of the photons which are emitted when the system decays from the $(n + 1)$ -th to the n -th energy level.

Answer: $E_{n+1} - E_n = (\hbar^2/2I)(n + 1)^2 - (\hbar^2/2I)n^2 = (2n + 1)\hbar^2/(md^2) \simeq 1.1 \times 10^{-24}(2n + 1)$ J. Notice that in Sommerfeld's perfected theory, mentioned in Sect. 2.2, the energy of a rotator is given by $E_n = \hbar^2 n(n + 1)/2I$, so that the factor $2n + 1$ in the solution must be replaced by $2n + 2$.

2.2 An artificial satellite of mass $m = 1$ kg rotates around the Earth on a circular orbit of radius practically equal to that of the Earth itself, i.e. roughly 6370 km. If the satellite orbits are quantized according to Bohr's rule, what is the radius variation when going from one quantized level to the next (i.e. from n to $n + 1$)?

Answer: If g indicates the gravitational acceleration at the Earth surface, the radius of the n -th orbit is given by $r_n = n^2 \hbar^2 / (m^2 R^2 g)$. Therefore, if $r_n = R$, $\delta r_n \equiv r_{n+1} - r_n \simeq 2\hbar / (m\sqrt{Rg}) \simeq 2.6 \times 10^{-38}$ m.

2.3 An electron is accelerated through a potential difference $\Delta V = 10^8$ V, what is its wavelength according to de Broglie?

Answer: The energy gained by the electron is much greater than mc^2 , therefore it is ultra-relativistic and its momentum is $p \simeq E/c$. Hence $\lambda \simeq hc/e\Delta V \simeq 12.4 \times 10^{-15}$ m. The exact formula is instead $\lambda = hc/\sqrt{(e\Delta V + mc^2)^2 - m^2c^4}$.

2.4 An electron is constrained to bounce between two reflecting walls placed at a distance $d = 10^{-9}$ m from each other. Assuming that, as in the case of a stationary electromagnetic wave confined between two parallel mirrors, the distance d be equal to n half wavelengths, determine the possible values of the electron energy as a function of n .

Answer: $E_n = \hbar^2 \pi^2 n^2 / (2md^2) \simeq n^2 6.03 \times 10^{-20}$ J.

2.5 An electron of kinetic energy 1 eV is moving upwards under the action of its weight. Can it reach an altitude of 1 km? If yes, what is the variation of its de Broglie wavelength?

Answer: The maximum altitude reachable by the electron in a constant gravitational field would be $h = T/mg \simeq 1.6 \times 10^{10}$ m. After one kilometer the kinetic energy changes by $\delta T/T \simeq 5.6 \times 10^{-8}$, hence $\delta\lambda/\lambda \simeq 2.8 \times 10^{-8}$. Since the starting wavelength is $\lambda = h/\sqrt{2mT} \simeq 1.2 \times 10^{-9}$ m, the variation is $\delta\lambda \simeq 3.4 \times 10^{-17}$ m.

2.6 Ozone (O_3) is a triatomic molecule made up of three atoms of mass $m \simeq 2.67 \times 10^{-26}$ kg placed at the vertices of an equilateral triangle with sides of length l . The molecule can rotate around an axis P going through its center of mass and orthogonal to the triangle plane, or around another axis L which passes through the center of mass as well, but is orthogonal to the first axis. Making use of Bohr's quantization rule and setting $l = 10^{-10}$ m, compare the possible rotational energies in the two different cases of rotations around P or L .

Answer: The moments of inertia are $I_P = ml^2 = 2.67 \times 10^{-46}$ kg m² and $I_L = ml^2/2 = 1.34 \times 10^{-46}$ kg m². The rotational energies are then $E_{L,n} = 2E_{P,n} = \hbar^2 n^2 / 2I_L \simeq n^2 4.2 \times 10^{-23}$ J.

2.7 A table salt crystal is irradiated with an X-ray beam of wavelength $\lambda = 2.5 \times 10^{-10}$ m, the first diffraction peak ($d \sin \theta = \lambda$) is observed at an angle equal to 26.3° . What is the interatomic distance of salt?

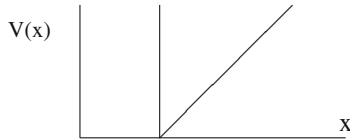
Answer: $d = \lambda / \sin \theta \simeq 5.6 \times 10^{-10}$ m.

2.8 In β decay a nucleus, with a radius of the order of $R = 10^{-14}$ m, emits an electron with a kinetic energy of the order of 1 MeV = 10^6 eV. Compare this value with that which according to the uncertainty principle is typical of an electron initially localized inside the nucleus (thus having a momentum $p \sim \hbar/R$).

Answer: The order of magnitude of the momentum of the particle is $p \sim \hbar/R \sim 10^{-20}$ N s, thus $pc \simeq 3 \times 10^{-12}$ J, which is much larger than the electron rest energy

$m_e c^2 \simeq 8 \times 10^{-14}$ J. Therefore the kinetic energy of the electron in the nucleus is about $pc = 3.15 \times 10^{-12}$ J $\simeq 20$ MeV.

2.9 An electron is placed in a constant electric field $\mathcal{E} = 1000$ V/m directed along the x axis and going out of a plane surface orthogonal to the same axis. The surface also acts on the electron as a reflecting plane where the electron potential energy $V(x)$ goes to infinity. The behavior of $V(x)$ is therefore as illustrated in the following figure.



Evaluate the order of magnitude of the minimal electron energy according to Heisenberg's Uncertainty Principle.

Answer: The total energy is given by $\epsilon = p^2/2m + V(x) = p^2/2m + e\mathcal{E}x$, with the constraint $x > 0$. From a classical point of view, the minimal energy would be realized for a particle at rest ($p = 0$) in the minimum of the potential. The uncertainty principle states instead that $\delta p \delta x \sim \hbar$, where δx is the size of a region around the potential minimum where the electron is localized. Therefore the minimal total energy compatible with the uncertainty principle can be written as a function of δx as $E(\delta x) \equiv \hbar^2/(2m\delta x^2) + e\mathcal{E}\delta x$ ($\delta x > 0$) and has a minimum

$$\epsilon_{\min} \sim \frac{3}{2} \left(\frac{\hbar^2 e^2 \mathcal{E}^2}{m} \right)^{1/3} \sim 0.6 \times 10^{-4} \text{ eV}.$$

2.10 An atom of mass $M = 10^{-26}$ kg is attracted towards a fixed point by an elastic force of constant $k = 1$ N/m; the atom is moving along a circular orbit in a plane orthogonal to the x axis. Determine the energy levels of the system by making use of Bohr's quantization rule for the angular momentum computed with respect to the fixed point.

Answer: Let ω be the angular velocity and r the orbital radius. The centripetal force is equal to the elastic one, hence $\omega = \sqrt{k/M}$. The total energy is given by $E = (1/2)M\omega^2 r^2 + (1/2)kr^2 = M\omega^2 r^2 = L\omega$, where $L = M\omega r^2$ is the angular momentum. Since $L = n\hbar$, we finally infer $E_n = n\hbar\omega \simeq n \cdot 1.05 \times 10^{-21}$ J $\simeq n \cdot 0.66 \times 10^{-2}$ eV.

2.11 Compute the number of photons emitted in one second by a lamp of power 10 W, if the photon wavelength is 0.5×10^{-6} m.

Answer: The energy of a single photon is $E = h\nu$ and $\nu = c/\lambda = 6 \times 10^{14}$ Hz, hence $E \simeq 4 \times 10^{-19}$ J. Therefore the number photons emitted in one second is 2.5×10^{19} .

2.12 A particle of mass $m = 10^{-28}$ kg is moving along the x axis under the influence of a potential energy given by $V(x) = v\sqrt{|x|}$, where $v = 10^{-15}$ J m^{-1/2}. Determine what is the order of magnitude of the minimal particle energy according to the uncertainty principle.

Answer: The total energy of the particle is given by

$$E = \frac{p^2}{2m} + v\sqrt{|x|}.$$

If the particle is localized in a region of size δx around the minimum of the potential ($x = 0$), according to the uncertainty principle it has a momentum at least of the order of $\delta p = \hbar/\delta x$. It is therefore necessary to minimize the quantity

$$E = \frac{\hbar^2}{2m\delta x^2} + v\sqrt{\delta x}$$

with respect to δx , finally finding that

$$E_{min} \simeq \left(\frac{\hbar^2 v^4}{m} \right)^{1/5} \left(2^{1/5} + 2^{-9/5} \right) \simeq 0.092 \text{ eV}.$$

It is important to notice that our result, apart from a numerical factor, could be also predicted on the basis of simple dimensional remarks. Indeed, it can be easily checked that $(\hbar^2 v^4/m)^{1/5}$ is the only possible quantity having the dimensions of an energy and constructed in terms of m , v and \hbar , which are the only physical constants involved in the problem. In the analogous classical problem \hbar is missing, and v and m are not enough to build a quantity with the dimensions of energy, hence the classical problem lacks the typical energy scale appearing at the quantum level.

2.13 An electron beam with kinetic energy equal to 10 eV is split into two parallel beams placed at different altitudes in the terrestrial gravitational field. If the altitude gap is $d = 10$ cm and if the beams recombine after a path of length L , say for which values of L the phases of the recombining beams are opposite (destructive interference). Assume that the upper beam maintains its kinetic energy, that the total energy is conserved for both beams and that the total phase difference accumulated during the splitting and the recombination of the beams is negligible.

Answer: De Broglie's wave describing the initial electron beam is proportional to $\exp(i px/\hbar - i Et/\hbar)$, where $p = \sqrt{2mE_k}$ is the momentum corresponding to a kinetic energy E_k and $E = E_k + mgh$ is the total energy. The beam is split into two beams, the first travels at the same altitude and is described by the same

wave function, the second travels 10 cm lower and is described by a wave function $\propto \exp(i p' x/\hbar - i E t/\hbar)$ where $p' = \sqrt{2mE'_k} = \sqrt{2m(E_k + mgd)}$ (obviously the total energy E stays unchanged). The values of L for which the two beams recombine with opposite phases are solutions of $(p' - p)L/\hbar = (2n + 1)\pi$ where n is an integer. The smallest value of L is $L = \pi\hbar/(p' - p)$. Notice that $mgd \simeq 10^{-30} \text{ J} \ll 10 \text{ eV} \simeq 1.6 \times 10^{-18} \text{ J}$ hence $p' - p \simeq \sqrt{2mE_k}(mgd/2E_k)$ and $L \simeq 2\pi\hbar E_k/(mgd\sqrt{2mE_k}) \simeq 696 \text{ m}$. This experiment, which clearly demonstrates the wavelike behavior of material particles, has been really performed using neutrons in place of electrons: that has various advantages, among which that of leading to smaller values of L because of the much heavier mass, as it is clear from the solution. That makes the setting of the experimental apparatus simpler.

2.14 An electron is moving in the $x - y$ plane under the influence of a magnetic induction field parallel to the z -axis. What are the possible energy levels according to Bohr's quantization rule?

Answer: The electron is subject to the force $e\mathbf{v} \wedge \mathbf{B}$ where \mathbf{v} is its velocity. Classically the particle, being constrained in the $x - y$ plane, would move on circular orbits with constant angular velocity $\omega = eB/m$, energy $E = 1/2 m\omega^2 r^2$ and any radius r . Bohr's quantization instead limits the possible values of r by $m\omega r^2 = n\hbar$. Finally one finds $E = 1/2 n\hbar\omega = n\hbar eB/(2m)$. This is an approximation of the exact solution for the quantum problem of an electron in a magnetic field (Landau's levels).

2.15 The positron is a particle identical to the electron but carrying an opposite electric charge. It forms a bound state with the electron, which is similar to the hydrogen atom but with the positron in place of the proton: that is called *positronium*. What are its energy levels according to Bohr's rule?

Answer: The computation goes exactly along the same lines as for the proton-electron system, but the reduced mass $\mu = m^2/(m + m) = m/2$ has to be used in place of the electron mass. Energy levels are thus

$$E_n = -\frac{me^4}{16\epsilon_0^2 \hbar^2 n^2}.$$

2.16 A particle of mass $M = 10^{-29} \text{ kg}$ is moving in two dimensions under the influence of a central potential

$$V = \sigma r,$$

where $\sigma = 10^5 \text{ N}$. Considering only circular orbits, what are the possible values of the energy according to Bohr's quantization rule?

Answer: Combining the equation for the centripetal force necessary to sustain the circular motion, $m\omega^2 r = \sigma$, with the quantization of angular momentum, $m\omega r^2 = n\hbar$, we obtain for the total energy, $E = 1/2 m\omega^2 r^2 + \sigma r$, the following quantized values

$$E_n = \frac{3}{2} \left(\frac{\hbar^2 \sigma^2}{m} \right)^{1/3} n^{2/3} \simeq 2 n^{2/3} \text{ GeV}.$$

Notice that the only possible combination of the physical parameters available in the problem with energy dimensions is $(\hbar^2 \sigma^2 / m)^{1/3}$. The potential proposed in this problem is similar to that believed to act among quarks, which are the elementary constituents of hadrons (a wide family of particles including protons, neutrons, mesons ...); σ is usually known as the *string tension*. Notice that the lowest energy coincides, identifying $\sigma = e\mathcal{E}$, with that obtained in Problem 2.9 using the uncertainty principle for the one-dimensional problem.

2.17 The momentum probability distribution for a particle with wave function $\psi(x)$ is given by

$$\left| \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{h}} e^{-i p x / \hbar} \psi(x) \right|^2 \equiv |\tilde{\psi}(p)|^2.$$

Compute the distribution for the following wave function $\psi(x) = e^{-a|x|/2} \sqrt{a/2}$ (a is real and positive) and verify the validity of the uncertainty principle in this case.

Answer: $\tilde{\psi}(p) = (\hbar a)^{3/2} / (\sqrt{4\pi}(p^2 + \hbar^2 a^2/4))$ hence

$$\Delta_x^2 = \frac{a}{2} \int_{-\infty}^{\infty} dx x^2 e^{-a|x|} = \frac{2}{a^2},$$

$$\Delta_p^2 = \frac{(\hbar a)^3}{4\pi} \int_{-\infty}^{\infty} dp \frac{p^2}{(p^2 + \frac{a^2 \hbar^2}{4})^2} = \frac{a^2 \hbar^2}{4},$$

so that $\Delta_x^2 \Delta_p^2 = \hbar^2/2 > \hbar^2/4$.

2.18 Show that a wave packet described by a real wave function has always zero average momentum. Compute the probability current for such packet.

Answer: From the relation

$$\tilde{\psi}(p) = \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{h}} e^{-i p x / \hbar} \psi(x)$$

and $\psi^*(x) = \psi(x)$ we infer

$$\tilde{\psi}^*(p) = \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{h}} e^{i p x / \hbar} \psi(x) = \tilde{\psi}(-p)$$

hence $|\tilde{\psi}(p)|^2 = |\tilde{\psi}(-p)|^2$. The probability distribution function is even in momentum space, so that the average momentum is zero. The probability current is zero as well, in agreement with the average zero momentum, i.e. with the fact that there is

not net matter transportation associated to this packet. Notice that the result does not change if $\psi(x)$ is multiplied by a constant complex factor $e^{i\phi}$.

2.19 The wave function of a free particle is

$$\psi(x) = \frac{1}{\sqrt{2Ph}} \int_{-P}^P dq e^{\frac{iqx}{\hbar}}$$

at time $t = 0$. What is the corresponding probability density $\rho(x)$ of locating the particle at a given point x ? What is the probability distribution function in momentum space? Give an integral representation of the wave function at a generic time t , assuming that the particle mass is m .

Answer: The probability density is $\rho(x) = |\psi(x)|^2 = \hbar/(\pi Px^2) \sin^2(Px/\hbar)$ while $\psi(x, t) = (1/\sqrt{2Ph}) \int_{-P}^P dq e^{i(qx - q^2 t/2m)/\hbar}$. The distribution in momentum is instead given by $|\tilde{\psi}(p)|^2 = \Theta(P^2 - p^2)/2P$, where Θ is the step function, $\Theta(y) = 0$ for $y < 0$ and $\Theta(y) = 1$ for $y \geq 0$. Notice that for the given distribution we have $\Delta_x^2 = \infty$. The divergent variance is strictly related to the sharp, step-like distribution in momentum space; indeed Δ_x^2 becomes finite as soon as the step is smoothed.

2.20 An electron beam hits the potential step sketched in the figure, coming from the right. In particular, the potential energy of the electrons is 0 for $x < 0$ and $-\mathcal{V} = -300$ eV for $x > 0$, while their kinetic energy in the original beam (thus for $x > 0$) is $E_k = 400$ eV. What is the reflection coefficient?



Answer: The wave function can be written, leaving aside an overall normalization coefficient which is not relevant for computing the reflection coefficient, as

$$\psi(x) = be^{-ik'x} \quad \text{for } x < 0, \quad \psi(x) = e^{-ikx} + ae^{ikx} \quad \text{for } x > 0$$

where $k = \sqrt{2mE_k}/\hbar = \sqrt{2m(E + \mathcal{V})}/\hbar$ and $k' = \sqrt{2m(E_k - \mathcal{V})}/\hbar = \sqrt{2mE}/\hbar$; m is the electron mass and $E = E_k - \mathcal{V}$ is the total energy of the electrons. The continuity conditions at the position of the step read

$$b = 1 + a, \quad bk' = (1 - a)k,$$

hence

$$b = \frac{2}{1 + k'/k}, \quad a = \frac{1 - k'/k}{1 + k'/k},$$

and

$$R = |a|^2 = \left(\frac{k - k'}{k + k'} \right)^2 = \frac{2E + \mathcal{V} - 2\sqrt{E(E + \mathcal{V})}}{2E + \mathcal{V} + 2\sqrt{E(E + \mathcal{V})}} = \frac{1}{9}.$$

2.21 An electron beam hits the same potential step considered in Problem 2.20, this time coming from the left with a kinetic energy $E = 100$ eV. What is the reflection coefficient in this case?

Answer: In this case we write:

$$\psi(x) = e^{ik'x} + be^{-ik'x} \quad \text{for } x < 0, \quad \psi(x) = ae^{ikx} \quad \text{for } x > 0,$$

where again $k = \sqrt{2m(E + \mathcal{V})}/\hbar$ and $k' = \sqrt{2mE}/\hbar$ with $E = E_k$ being the total energy. By solving the continuity conditions we find:

$$b = \frac{k'/k - 1}{1 + k'/k}; \quad R = |b|^2 = \left(\frac{k' - k}{k + k'} \right)^2 = \frac{2E + \mathcal{V} - 2\sqrt{E(E + \mathcal{V})}}{2E + \mathcal{V} + 2\sqrt{E(E + \mathcal{V})}} = \frac{1}{9}.$$

We would like to stress that the reflection coefficient coincides with that obtained in Problem 2.20: electron beams hitting the potential step from the right or from the left are reflected in exactly the same way, if their total energy E is the same, as it is in the present case. In fact this is a general result which is valid for every kind of potential barrier and derives directly from the invariance of the Schrödinger equation under time reversal: the complex conjugate of a solution is also a solution. It may seem a striking result, but it should not be so striking for those familiar with reflection of electromagnetic signals in the presence of unmatching impedances.

Notice also that there is actually a difference between the two cases, consisting in a different sign for the reflected wave. That is irrelevant for computing R but significant for considering interference effects involving the incident and the reflected waves. In the present case interference is destructive, hence the probability density is suppressed close to the step, while in Problem 2.20 the opposite happens. To better appreciate this fact consider the analogy with an oscillating rope made up of two different ropes having different densities (which is a system in some sense similar to ours), and try to imagine the different behaviors observed if you enforce oscillations shaking the rope from the heavier (right-hand in our case) or from the lighter (left-hand in our case) side. As an extreme and easier case, you could think of a single rope with a free end (one of the densities goes to zero) or with a fixed end (one of the densities goes to infinity): the shape of the rope at the considered endpoint is cosine-like in the first case and sine-like in the second case, exactly as for the cases of respectively the previous and the present problem in the limit $\mathcal{V} \rightarrow \infty$.

2.22 An electron beam hits, coming from the right, a potential step similar to that considered in Problem 2.20. However this time $-\mathcal{V} = -10$ eV and the kinetic energy of the incoming electrons is $E_k = 9$ eV. If the incident current is equal to $J = 10^{-3}$ A, compute how many electrons can be found, at a given time, along the negative x axis, i.e. how many electrons penetrate the step barrier reaching positions which would be classically forbidden.

Answer: The solution of the Schrödinger equation can be written as

$$\psi(x) = c e^{p'x/\hbar} \text{ for } x < 0, \quad \psi(x) = a e^{ipx/\hbar} + b e^{-ipx/\hbar} \text{ for } x > 0$$

where $p = \sqrt{2mE}$ and $p' = \sqrt{2m(\mathcal{V} - E)}$. Imposing continuity in $x = 0$ for both $\psi(x)$ and its derivative, we obtain $c = 2a/(1 + ip'/p)$ and $b = a(1 - ip'/p)/(1 + ip'/p)$. It is evident that $|b|^2 = |a|^2$, hence the reflection coefficient is one. Indeed the probability current $J(x) = -i\hbar/(2m)(\psi^*\partial_x\psi - \psi\partial_x\psi^*)$ vanishes on the left, where we have an evanescent wave function, hence no transmission. Nevertheless the probability distribution is non-vanishing for $x < 0$ and, on the basis of the collective interpretation, the total number of electrons on the left is given by

$$N = \int_{-\infty}^0 |\psi(x)|^2 dx = |c|^2 \hbar / (2p') = \frac{2|a|^2 \hbar p^2}{p'(p^2 + p'^2)}.$$

The coefficient a can be computed by asking that the incident current $J_{\text{el}} = eJ = e|a|^2 p/m \equiv 10^{-3}$ A. The final result is $N \simeq 1.2$.

2.23 An electron is confined inside a cubic box with reflecting walls and an edge of length $L = 2 \times 10^{-9}$ m. How many stationary states can be found with energy less than 1 eV? Take into account the spin degree of freedom, which in practice doubles the number of available levels.

Answer: Energy levels in a cubic box are $E_{n_x, n_y, n_z} = \pi^2 \hbar^2 (n_x^2 + n_y^2 + n_z^2) / (2mL^2)$, where $m = 0.911 \times 10^{-30}$ kg and n_x, n_y, n_z are positive integers. The constraint $E < 1$ eV implies $n_x^2 + n_y^2 + n_z^2 < 10.7$, which is satisfied by 7 different combinations ((1,1,1), (2,1,1), (2,2,1) plus all possible different permutations). Taking spin into account, the number of available levels is 14.

2.24 When a particle beam hits a potential barrier and is partially transmitted, a forward going wave is present on the other side of the barrier which, besides having a reduced amplitude with respect to the incident wave, has also acquired a phase factor which can be inferred by the ratio of the transmitted wave coefficient to that of the incident one. Assuming a thin barrier, describable as

$$V(x) = v \delta(x),$$

and that the particles are electrons of energy $E = 10$ eV, compute the value of v for which the phase difference is $-\pi/4$.

Suppose now that we have two beams of equal amplitude and phase and that one beam goes through the barrier while the other goes free. The two beams recombine after paths of equal length. What is the ratio of the recombined beam intensity to that one would have without the barrier?

Answer: On one side of the barrier the wave function is $e^{i\sqrt{2mEx}/\hbar} + a e^{-i\sqrt{2mEx}/\hbar}$, while it is $b e^{i\sqrt{2mEx}/\hbar}$ on the other side. Continuity and discontinuity constraints read $1+a = b$ and $b-1+a = \sqrt{2m/E}vb/\hbar$, from which $b = (1 + i\sqrt{m/2E}v/\hbar)^{-1}$ can be easily derived. Requiring that the phase of b be $-\pi/4$ is equivalent to $\sqrt{m/2E}v/\hbar = 1$, hence $v \simeq 2.0 \times 10^{-28}$ J m.

With this choice of v the recombined beam is $[1 + 1/(1 + i)]e^{i\sqrt{2mEx}/\hbar}$. The ratio of the intensity of the recombined beam to that one would have without the barrier is $|[1 + 1/(1 + i)]/2|^2 = 5/8$.

2.25 If a potential well in one dimension is so thin to be describable by a Dirac delta function:

$$V(x) = -VL\delta(x)$$

where V is the depth and L the width of the well, then it is possible to compute the bound state energies by recalling that for a potential energy of that kind the wave function is continuous while its first derivative has the following discontinuity:

$$\lim_{\epsilon \rightarrow 0} (\partial_x \psi(x + \epsilon) - \partial_x \psi(x - \epsilon)) = -\frac{2m}{\hbar^2} VL\psi(0) .$$

What are the possible energy levels?

Answer: The bound state wave function is

$$a e^{-\sqrt{2mB}x/\hbar} \quad \text{for } x > 0 \quad \text{and} \quad a e^{\sqrt{2mB}x/\hbar} \quad \text{for } x < 0$$

where the continuity condition for the wave function has been already imposed. $B = |E|$ is the absolute value of the energy (which is negative for a bound state). The discontinuity condition on the first derivative leads to an equation for B which has only one solution, $B = mV^2L^2/(2\hbar^2)$, thus indicating the existence of a single bound state.

2.26 A particle of mass m moves in the following one-dimensional potential:

$$V(x) = v(\alpha\delta(x-L) + \alpha\delta(x+L) - \frac{1}{L}\Theta(L^2 - x^2)) ,$$

where Θ is the step function, $\Theta(y) = 0$ for $y < 0$ and $\Theta(y) = 1$ for $y > 0$. Constants are such that

$$\frac{2mvL}{\hbar^2} = \left(\frac{\pi}{4}\right)^2 .$$

Find the conditions on $\alpha > 0$ for the existence of bound states.

Answer: The potential is such that $V(-x) = V(x)$: in this case the lowest energy level, if any, corresponds to an even wave function. We can thus limit the discussion to the region $x > 0$, where we have $\psi(x) = \cos kx$ for $x < L$ and $\psi(x) = ae^{-\beta x}$ for $x > L$, with the constraint $0 < k < \sqrt{2mv/(\hbar^2 L)} = \pi/(4L)$, since $\beta = \sqrt{2mv/(\hbar^2 L)} - k^2$ must be real in order to have a bound state, hence $kL < \pi/4$. Continuity and discontinuity constraints, respectively on $\psi(x)$ and $\psi'(x)$ in $x = L$, give: $\tan kL = (\beta + 2mv\alpha/\hbar^2)/k$. Setting $y \equiv kL$, we have

$$\tan y = \frac{\sqrt{\frac{\pi^2}{16} - y^2} + \frac{\pi^2}{16}\alpha}{y}.$$

The function on the left hand side grows from 0 to 1 in the interval $0 < y < \pi/4$, while the function on the right decreases from ∞ to $\alpha\pi/4$ in the same interval. Therefore an intersection (hence a bound state) exists only if $\alpha < 4/\pi$.

2.27 An electron moves in a one-dimensional potential corresponding to a square well of depth $V = 0.1$ eV and width $L = 3 \times 10^{-10}$ m. Show that in these conditions there is only one bound state and compute its energy in the thin well approximation, discussing also the validity of that limit.

Answer: There is one only bound state if the first odd state is absent. That is true if $y = \sqrt{2mVL}/(2\hbar) < \pi/2$, which is verified in our case since, using $m = 0.911 \times 10^{-30}$ kg, one obtains $y \simeq 0.243 < \pi/2$.

Setting $B \equiv -E$, where E is the negative energy of the bound state, B is obtained as a solution of

$$\tan\left(\frac{L\sqrt{2m(V-B)}}{2\hbar}\right) = \sqrt{\frac{B}{V-B}}.$$

The thin well limit corresponds to $V \rightarrow \infty$ and $L \rightarrow 0$ as the product VL is kept constant. Neglecting B with respect to V we can write

$$\tan\left(\frac{\sqrt{2mVL^2}}{2\hbar}\right) = \sqrt{\frac{B}{V}}.$$

In the thin well limit $VL^2 \rightarrow \text{constant} \cdot L \rightarrow 0$, hence we can replace the tangent by its argument, obtaining finally $B = mV^2L^2/(2\hbar^2) \simeq 0.59 \times 10^{-2}$ eV, which coincides with the result obtained in Problem 2.25. In this case the argument of the tangent is $y \sim 0.24$ and we have $\tan 0.24 \simeq 0.245$; therefore the exact result differs from that obtained in the thin well approximation by roughly 4%.

2.28 An electron moves in one dimension and is subject to forces corresponding to a potential energy:

$$V(x) = \mathcal{V}[-\delta(x) + \delta(x - L)].$$

What are the conditions for the existence of a bound state and what is its energy if $L = 10^{-9}$ m and $\mathcal{V} = 2 \times 10^{-29}$ J m?

Answer: A solution of the Schrödinger equation corresponding to a binding energy $B \equiv -E$ can be written as

$$\begin{aligned}\psi(x) &= e^{\sqrt{2mB}x/\hbar} \quad \text{for } x < 0, \\ \psi(x) &= ae^{\sqrt{2mB}x/\hbar} + be^{-\sqrt{2mB}x/\hbar} \quad \text{for } 0 < x < L, \\ \psi(x) &= ce^{-\sqrt{2mB}x/\hbar} \quad \text{for } L < x.\end{aligned}$$

Continuity and discontinuity constraints, respectively for the wave function and for its derivative in $x = 0$ and $x = L$, give: $a + b = 1$, $a - b - 1 = -\sqrt{2m/B}\mathcal{V}/\hbar$, $ae^{\sqrt{8mBL}/\hbar} + b = c$, $ae^{\sqrt{8mBL}/\hbar} - b + c = -c\sqrt{2m/B}\mathcal{V}/\hbar$.

The four equations are compatible if $e^{\sqrt{8mBL}/\hbar} = (1 - \frac{2B\hbar^2}{m\mathcal{V}^2})^{-1}$, which has a non-trivial solution $B \neq 0$ for any $L > 0$. Setting $y = \sqrt{2B/m}\hbar/\mathcal{V}$ the compatibility condition reads $e^{2m\mathcal{V}Ly/\hbar^2} = 1/(1 - y^2)$. Using the values of L and \mathcal{V} given in the text one obtains $e^{2m\mathcal{V}L/\hbar^2} \gg 1$, hence $2B\hbar^2/(m\mathcal{V}^2) \simeq 1$ within a good approximation, i.e. $B \simeq m\mathcal{V}^2/(2\hbar^2)$, which coincides with the result obtained in the presence of a single thin well. This approximation is indeed equivalent to the limit of a large distance L (hence $e^{2m\mathcal{V}L/\hbar^2} \gg 1$) between the two Dirac delta functions; it can be easily verified that in the same limit one has $b \simeq 1$ and $a \simeq 0$, so that, in practice, the state is localized around the attractive delta function in $x = 0$, which is the binding part of the potential, and does not feel the presence of the other term in the potential which is very far away.

As L is decreased, the binding energy lowers and the wave function amplitude, hence the probability density, gets asymmetrically shifted on the left, until the binding energy vanishes in the limit $L \rightarrow 0$. In practice, the positive delta function in $x = L$ acts as a repulsive term which asymptotically extracts, as $L \rightarrow 0$, the particle from its thin well.

2.29 A particle of mass $M = 10^{-26}$ kg moves along the x axis under the influence of an elastic force of constant $k = 10^{-6}$ N/m. The particle is in its ground state: compute its wave function and the mean value of x^2 , given by

$$\langle x^2 \rangle = \frac{\int_{-\infty}^{\infty} dx x^2 |\psi(x)|^2}{\int_{-\infty}^{\infty} dx |\psi(x)|^2}.$$

Answer:

$$\psi(x) = \left(\frac{kM}{\pi^2 \hbar^2}\right)^{1/8} e^{-\sqrt{kM}x^2/2\hbar}, \quad \langle x^2 \rangle = \frac{1}{2} \frac{\hbar}{\sqrt{kM}} \simeq 5 \cdot 10^{-19} \text{ m}^2.$$

2.30 A particle of mass $M = 10^{-25}$ kg moves in a 3-dimensional isotropic harmonic potential of elastic constant $k = 10$ N/m. How many states have energy less than 2×10^{-2} eV?

Answer: $E_{n_x, n_y, n_z} = \hbar\sqrt{k/M}(3/2 + n_x + n_y + n_z)$. Therefore $E_{n_x, n_y, n_z} < 2 \times 10^{-2}$ eV is equivalent to $n_x + n_y + n_z < 1.54$, corresponding to 4 possible states, $(n_x, n_y, n_z) = (0,0,0), (1,0,0), (0,1,0), (0,0,1)$.

2.31 A particle of mass $M = 10^{-26}$ kg moves in one dimension under the influence of an elastic force of constant $k = 10^{-6}$ N/m and of a constant force $F = 10^{-15}$ N acting in the positive x direction. Compute the wave function of the ground state and the corresponding mean value of the coordinate x , given by

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x |\psi(x)|^2}{\int_{-\infty}^{\infty} dx |\psi(x)|^2}.$$

Answer: As in the analogous classical case, the problem can be brought back to a simple harmonic oscillator with the same mass and elastic constant by a simple change of variable, $y = x - F/k$, which is equivalent to shifting the equilibrium position of the oscillator. Hence the energy levels are spaced as for the harmonic oscillator and the wave function of the ground state is

$$\psi(x) = \left(\frac{kM}{\pi^2 \hbar^2} \right)^{1/8} e^{-\frac{\sqrt{kM}}{2\hbar}(x-F/k)^2},$$

while $\langle x \rangle = F/k = 10^{-9}$ m.

2.32 A particle of mass $m = 10^{-30}$ kg and kinetic energy equal to 50 eV hits a square potential well of width $L = 2 \times 10^{-10}$ m and depth $V = 1$ eV. What is the reflection coefficient computed up to the first non-vanishing order in $\frac{V}{2E}$?

Answer: Let us choose the square well endpoints in $x = 0$ and $x = L$ and fix the potential to zero outside the well. Let ψ_s , ψ_c and ψ_d be respectively the wave functions for $x < 0$, $0 < x < L$ and $x > L$. If the particle comes from the left, then $\psi_s = e^{i\sqrt{2mEx}/\hbar} + a e^{-i\sqrt{2mEx}/\hbar}$, $\psi_c = b e^{i\sqrt{2m(E+V)x}/\hbar} + c e^{-i\sqrt{2m(E+V)x}/\hbar}$ and $\psi_d = d e^{i\sqrt{2mEx}/\hbar}$ where a and c are necessarily of order $V/2E$ while b and d are equal to 1 minus corrections of the same order. Indeed, as $V \rightarrow 0$ the solution must tend to a single plane wave. By applying the continuity constraints we obtain:

$$1 + a = b + c,$$

$$1 - a \simeq b - c + \frac{V}{2E},$$

$$be^{\frac{i\sqrt{2m(E+V)}L}{\hbar}} + ce^{-i\sqrt{2m(E+V)}L/\hbar} \simeq (b + \frac{V}{2E})e^{i\sqrt{2m(E+V)}L/\hbar} - ce^{-i\sqrt{2m(E+V)}L/\hbar},$$

which are solved by $a \simeq \frac{V}{4E}(e^{2i\sqrt{2m(E+V)}L/\hbar} - 1)$ and

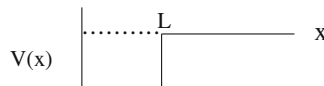
$$R = \frac{V^2}{4E^2} \sin^2 \left(\frac{\sqrt{2m(E+V)}L}{\hbar} \right) \simeq 0.96 \times 10^{-4}.$$

2.33 A particle of mass $m = 10^{-30}$ kg is confined inside a line segment of length $L = 10^{-9}$ m with reflecting endpoints, which is centered around the origin. In the middle of the line segment a thin repulsive potential barrier, describable as $V(x) = W\delta(x)$, acts on the particle, with $W = 2 \times 10^{-28}$ J m. Compare the ground state of the particle with what found in absence of the barrier.

Answer: Let us consider how the solutions of the Schrödinger equation in a line segment are influenced by the presence of the barrier. Odd solutions, contrary to even ones, do not change since they vanish right in the middle of the segment, so that the particle never feels the presence of the barrier. In order to discuss even solutions, let us notice that they can be written, shifting the origin in the left end of the segment, as $\psi_s \sim \sin(\sqrt{2mEx}/\hbar)$ for $x < L/2$ and $\psi_d \sim \sin(\sqrt{2mE}(L-x)/\hbar)$ for $x > L/2$. Setting $z \equiv \sqrt{2mEL}/(2\hbar)$ the discontinuity in the wave function derivative in the middle of the segment gives $\tan z = -z2\hbar^2/(mLW) \simeq -10^{-1}z$. Hence we obtain, for the ground state, $E \simeq \frac{2\hbar^2}{mL^2}\pi^2(1 - 2 \times 10^{-1}) \simeq 2.75 \times 10^{-19}$ J, slightly below the first excited level.

Notice that, increasing the intensity of the repulsive barrier W from 0 to ∞ , the ground level grows from $\pi^2\hbar^2/(2mL^2)$ to $2\pi^2\hbar^2/(mL^2)$, i.e. it is degenerate with the first excited level in the $W \rightarrow \infty$ limit. There is no contradiction with the expected non-degeneracy since, in that limit, the barrier acts as a perfectly reflecting partition wall which separates the original line segment into two non-communicating segments: the two degenerate lowest states (as well as all the other excited ones) can thus be seen as two different superpositions (symmetric and antisymmetric) of the ground states of each segment.

2.34 An electron beam corresponding to an electric current $I = 10^{-12}$ A hits, coming from the right, the potential step sketched in the figure. The potential energy diverges for $x < 0$ while it is $-V = -10$ eV for $0 < x < L$ and 0 for $x > L$, with $L = 10^{-11}$ m. The kinetic energy of the electrons is $E_k = 0.01$ eV for $x > L$. Compute the electric charge density as a function of x .



Answer: There is complete reflection in $x = 0$, hence the current density is zero along the whole axis and we can consider a real wave function. In particular we set $\psi(x) = a \sin(\sqrt{2mE}(x-L)/\hbar + \phi)$ for $x > L$ and $\psi(x) = b \sin(\sqrt{2m(E+V)}x/\hbar)$ for $0 < x < L$. Continuity conditions read $b \sin(\sqrt{2m(E+V)}L/\hbar) = a \sin \phi \simeq b \sin(\sqrt{2mV}L/\hbar)$, $b \cos(\sqrt{2m(E+V)}L/\hbar) = \sqrt{E/(E+V)}a \cos \phi \simeq \sqrt{E/V}a \cos \phi \simeq b \cos(\sqrt{2mV}L/\hbar)$ (notice that $\sqrt{2mV}L/\hbar \simeq 0.57$ rad hence $\cos(\sqrt{2mV}L/\hbar) \simeq 0.85$). That fixes $\sqrt{E/V} \tan(\sqrt{2mV}L/\hbar) \simeq \tan \phi \simeq \phi$ and $b = a\sqrt{E/V} / \cos(\sqrt{2mV}L/\hbar)$, while the incident current fixes the value of a , $I = ea^2\sqrt{2E/m}$. Finally we can write, for the charge density,

$$e\rho = I\sqrt{\frac{m}{2E}} \sin^2\left(\frac{\sqrt{2mE}}{\hbar}(x-L) + \phi\right)$$

for $x > L$ and

$$e\rho \sim I\sqrt{\frac{mE}{2V^2}} \sin^2\left(\frac{\sqrt{2mE}}{\hbar}x\right)$$

for $0 < x < L$.

2.35 Referring to the potential energy given in Problem 2.34, determine the values of V for which there is one single bound state.

Answer: It can be easily realized that any possible bound state of the potential well considered in the problem will coincide with one of the odd bound states of the square well having the same depth and extending from $-L$ to L . The condition for the existence of a single bound state is therefore $\pi/2 < \sqrt{2mV}L/\hbar < 3\pi/2$.

2.36 A ball of mass $m = 0.05$ kg moves at a speed of 3 m/s and without rolling towards a smooth barrier of thickness $D = 10$ cm and height $H = 1$ m. Using the formula for the tunnel effect, give a rough estimate about the probability of the ball getting through the barrier.

Answer: The transmission coefficient is roughly

$$T \sim \exp\left(-\frac{2D}{\hbar}\sqrt{2m(mgH - \frac{mv^2}{2})}\right) \simeq 10^{-1.3 \times 10^{32}}.$$

2.37 What is the quantum of energy for a simple pendulum of length $l = 1$ m making small oscillations?

Answer: In the limit of small oscillations the pendulum can be described as a harmonic oscillator of frequency $\nu = 2\pi\omega = 2\pi\sqrt{g/l}$, where $g \simeq 9.81$ m/s² is the gravitational acceleration on the Earth surface. The energy quantum is therefore $h\nu = 3.1 \times 10^{-34}$ J.

2.38 Compute the mean value of x^2 in the first excited state of a harmonic oscillator of elastic constant k and mass m .

Answer: The wave function of the first excited state is $\psi_1 \propto x e^{-x^2 \sqrt{km/(4\hbar^2)}}$, hence

$$\langle x^2 \rangle = \frac{\int_{-\infty}^{\infty} x^4 e^{-x^2 \sqrt{km/\hbar^2}} dx}{\int_{-\infty}^{\infty} x^2 e^{-x^2 \sqrt{km/\hbar^2}} dx} = \frac{3}{2} \sqrt{\frac{\hbar^2}{km}}.$$

2.39 A particle of mass M moves in a line segment with reflecting endpoints placed at distance L . If the particle is in the first excited state ($n = 2$), what is the mean quadratic deviation of the particle position from its average value, i.e. $\sqrt{\langle x^2 \rangle - \langle x \rangle^2}$?

Answer: Setting the origin in the middle of the segment, the wave function is $\psi(x) = \sqrt{2/L} \sin(2\pi x/L)$ inside the segment and vanishes outside. Obviously $\langle x \rangle = 0$ by symmetry, while

$$\langle x^2 \rangle = \frac{2}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} x^2 \sin^2\left(\frac{2\pi x}{L}\right) dx = L^2 \left(\frac{1}{12} - \frac{1}{8\pi^2} \right)$$

whose square root gives the requested mean quadratic deviation.

2.40 An electron beam of energy E hits, coming from the left, the following potential barrier: $V(x) = \mathcal{V}\delta(x)$ where \mathcal{V} is tuned to $\hbar\sqrt{2E/m}$. Compute the probability density on both sides of the barrier.

Answer: The wave function can be set to $e^{ikx} + a e^{-ikx}$ for $x < 0$ and to $b e^{ikx}$ for $x > 0$, where $k = \sqrt{2mE}/\hbar$. Continuity and discontinuity constraints for ψ and ψ' in $x = 0$ lead to

$$a = \frac{1}{\frac{ik\hbar^2}{m\mathcal{V}} - 1} = \frac{1}{i - 1}, \quad b = \frac{\frac{ik\hbar^2}{m\mathcal{V}}}{\frac{ik\hbar^2}{m\mathcal{V}} - 1} = \frac{1}{i + 1}.$$

The probability density is therefore $\rho = 1/2$ for $x < 0$, while for $x > 0$ it is $\rho = 3/2 - \sqrt{2} \sin(2kx + \pi/4)$.

2.41 A particle moves in one dimension under the influence of the potential given in Problem 2.34. Assuming that

$$\sqrt{2mV} \frac{L}{\hbar} = \frac{\pi}{2} + \delta, \quad \text{with } \delta \ll 1,$$

show that, at the first non-vanishing order in δ , one has $B \simeq V\delta^2$, where $B = -E$ and E is the energy of the bound state. Compute the ratio of the probability of the particle being inside the well to that of being outside.

Answer: The depth of the potential is slightly above the minimum for having at least one bound state (see the solution of Problem 2.36), therefore we expect a small binding energy. In particular the equation for the bound state energy, which can be derived by imposing the continuity constraints, is $\cot(\sqrt{2m(V-B)}L/\hbar) = -\sqrt{B/(V-B)}$. The particular choice of parameters implies $B \ll V$, so that $\cot(\sqrt{2m(V-B)}L/\hbar) \simeq \cot(\pi/2(1 - B/(2V)) + \delta) \simeq -\delta + \pi B/(4V) \simeq -\sqrt{B/V}$, hence $B \simeq V\delta^2$. Therefore the wave function is well approximated by $k \sin(\pi x/2L)$ inside the well and by $ke^{-\sqrt{2mB}(x-L)/\hbar} \simeq ke^{-\pi\delta(x-L)/2L}$ outside, where k is a normalization constant. The ratio of probabilities is $\pi\delta/2$: the very small binding energy is reflected in the large probability of finding the particle outside the well.

2.42 A particle of mass $m = 10^{-30}$ kg and kinetic energy $E = 13.9$ eV hits a square potential barrier of width $L = 10^{-10}$ m and height $V = E$. Compute the reflection coefficient R .

Answer: Let us fix in $x = 0$ and in $x = L$ the edges of the square potential barrier, and suppose the particle comes from the left. The wave function is $\psi(x) = e^{ikx} + ae^{-ikx}$ for $x < 0$ and $\psi(x) = d e^{ikx}$ for $x > L$, where $k = \sqrt{2mE}/\hbar \simeq 2 \times 10^{10} \text{ m}^{-1}$. Instead for $0 \leq x \leq L$ the wave function satisfies the differential equation $\psi'' = 0$, which has the general integral $\psi(x) = bx + c$. The continuity conditions for ψ and ψ' in $x = 0$ and $x = L$ read

$$1 + a = c; \quad ik(1 - a) = b; \quad bL + c = d e^{ikL}; \quad b = ik d e^{ikL}.$$

Dividing last two equations and substituting the first two we get

$$a = \frac{ikL}{ikL - 2}; \quad R = |a|^2 = \frac{k^2 L^2}{4 + k^2 L^2} \simeq \frac{1}{2}.$$

It is interesting to verify that the same result can be obtained by taking carefully the limit $E \rightarrow V$ in (2.80).

2.43 A particle whose wave function is, for asymptotically large negative times (that is $-t \gg m/(\hbar k_0 \Delta)$), a Gaussian wave packet

$$\psi(x, t) = \frac{1}{\sqrt{(2\pi)^{3/2} \Delta}} \int dk e^{i(kx - \hbar k^2 t/(2m))} e^{-(k - k_0)^2/(2\Delta)^2}$$

with $k_0/\Delta \gg 1$, interacts in the origin through the potential $V(x) = \mathcal{V}\delta(x)$ and its wave function splits into reflected and transmitted components. Considering values of the time for which the spreading of the packets can be neglected, that is $|t| \ll m/(\hbar\Delta^2)$ (see Sect. 2.4), compute the transmitted and reflected components of the wave packet.

Answer: The Gaussian wave packet has been studied in detail in Sect. 2.4, it is therefore straightforward to check that, for large negative times, the solution that we are seeking is a wave packet centered in $x = vt$, with $v = \hbar k_0/m$, i.e. a packet approaching the barrier from the left and hitting it at $t \simeq 0$.

It has been shown in Sect. 2.5.2 (see also Problem 2.24) that the generic solution of the time independent Schrödinger equation, obtained in the case of a single plane wave e^{ikx} hitting the barrier from the left, is

$$\psi_k(x) = \Theta(-x)[\exp(ikx) - i\kappa/(k + i\kappa) \exp(-ikx)] + \Theta(x)k/(k + i\kappa) \exp(ikx)$$

where Θ is the step function ($\Theta(x) = 0$ for $x < 0$ and $\Theta(x) = 1$ for $x \geq 0$) and $\kappa = mV/\hbar^2$.

The present problem consists in finding a solution of the time dependent Schrödinger equation which, for asymptotically large negative times and $x < 0$, must be a given superposition of progressive plane waves corresponding to the incoming wave packet. Given the linearity of the Schrödinger equation, the solution must be a linear superposition of the generic solutions given above, with the same coefficients of the incoming packet, i.e.

$$\psi(x, t) = \frac{1}{\sqrt{(2\pi)^{3/2}\Delta}} \int dk \psi_k(x) e^{-i\hbar k^2 t/(2m)} e^{-(k-k_0)^2/(2\Delta)^2}.$$

This decomposes into two components for $x < 0$ and a single transmitted component for $x > 0$.

The first, ingoing component on the negative semi-axis, which corresponds to $\psi_k(x) = \exp(ikx)$, is a standard Gaussian packet which, as discussed above, crosses the origin for $t \sim 0$ and hence disappears for larger times. On the contrary, as we shall show in a while, the second, reflected component describes a packet moving backward, which crosses the origin for $t \sim 0$, hence appears as a part of the solution for $x < 0$ for positive times (i.e. after reflection of the original packet), when it must be taken into account. In much the same way we shall compute the transmitted component, which is a packet moving forward and which appears on the positive semi-axis for positive times. Now we work out the details.

We represent the transmitted and reflected wave packets by

$$\frac{1}{\sqrt{(2\pi)^{3/2}\Delta}} \int_{-\infty}^{\infty} dt \exp(-F_{T/R}(k, x, t))$$

$$F_T(k, x, t) = (k - k_0)^2/(2\Delta)^2 - i(kx - \hbar k^2 t/(2m)) - \ln(k/(k + i\kappa))$$

$$F_R(k, x, t) = (k - k_0)^2/(2\Delta)^2 + i(kx + \hbar k^2 t/(2m)) - \ln(-i\kappa/(k + i\kappa)).$$

Then we have the equations:

$$\partial_k F_T(k, x, t) = (k - k_0)/\Delta^2 - i(x - \hbar k/m + \kappa/(k + i\kappa)) = 0$$

$$\partial_k F_R(k, x, t) = (k - k_0)/\Delta^2 + i(x + \hbar k/m - i/(k + i\kappa)) = 0.$$

The equation for F_T has three solutions: $k_1 \sim k_0$, $k_2 \sim 0$ and $k_3 \sim -i\kappa$ up to corrections of order Δ^2 . The first solution has a second derivative of order $1/\Delta^2$, to be compared with the second derivatives of the other two solutions, which are of order $1/\Delta^4$, hence it is the dominant solution, in the same sense discussed in Sect. 2.4, thus we concentrate on it. Setting again $v = \hbar k_0/m$ we have $k_1 = k_0 + i\Delta^2(x - vt + \kappa/(k_0(k_0 + i\kappa))) + O(\Delta^4)$ and

$$F_T(k_1, x, t) = F_T(k_0, x, t) - \partial_k^2 F_T(k_0, x, t)(k_1 - k_0)^2/2$$

$$= -i(k_0 x - \hbar k_0^2 t/(2m)) - \ln(k_0/(k_0 + i\kappa)) + [x - vt + \kappa/(k_0(k_0 + i\kappa))]^2 \Delta^2/2 + O(\Delta^4).$$

Therefore we have a wave packet centered in $x = vt - \kappa/(k_0^2 + \kappa^2)$. An analogous analysis on the reflected packet gives:

$$F_R(k_1, x, t) = F_R(k_0, x, t) - \partial_k^2 F_R(k_0, x, t)(k_1 - k_0)^2/2$$

$$= i(k_0 x + \hbar k_0^2 t/(2m)) - \ln(-i\kappa/(k_0 + i\kappa)) + (x + vt - i/(k_0 + i\kappa))^2 \Delta^2/2 + O(\Delta^4).$$

Now the packet is centered in $x = -vt + \kappa/(k_0^2 + \kappa^2)$.

The result is almost as anticipated, apart from the fact that the appearance of the transmitted and reflected wave packets is delayed (advanced) with respect to the time the incoming packet hits the potential barrier (well). For large, positive times the particle is in a superposition of reflected and transmitted state, the probability of finding it in one of the two states after a measurement of its position (i.e. the integral of the probability density over the corresponding packets) is given approximately by the reflection or transmission coefficients computed for $k \sim k_0$.

2.44 A particle of mass m moves in one dimension under the influence of the potential

$$V(x) = V_0 \Theta(x) - \mathcal{V} \delta(x).$$

If $\mathcal{V} = 3 \times 10^{-29}$ J m and $m = 10^{-30}$ kg, identify the values of V_0 for which the particle has bound states. Assuming the existence of a bound state whose binding energy is $B \ll V_0$, compute the ratio of the probabilities for the particle to be found on the right and on the left-hand side of the origin.

Answer: The wave function of a bound state with energy $-B$ would be

$$\psi_B(x) = N[\Theta(-x) \exp(\sqrt{2mB}x/\hbar) + \Theta(x) \exp(-\sqrt{2m(B+V_0)}x/\hbar)]$$

where Θ is the step function, N is the normalization factor and the condition $\sqrt{B} + \sqrt{B+V_0} = \sqrt{2mV}/\hbar$ must be satisfied. Since $\sqrt{V_0} \leq \sqrt{B} + \sqrt{B+V_0} < \infty$ the above condition has a solution provided $\sqrt{2mV}/\hbar \geq \sqrt{V_0}$, hence for $V_0 \leq 2mV^2/\hbar^2 \simeq 1.62 \times 10^{-19} \text{ J} \simeq 1 \text{ eV}$. The probabilities for the particle to be found on the right and on the left of the origin are respectively $N^2\hbar/(2\sqrt{2m(B+V_0)})$ and $N^2\hbar/(2\sqrt{2mB})$, their ratio for small B is $\sqrt{B/V_0} \simeq \sqrt{2m/V_0}V/\hbar - 1$.

2.45 A particle of mass m is bound between two spherical perfectly reflecting walls of radii R and $R + \Delta$. The potential energy between the walls is $V_0 = -\hbar^2\pi^2/(2m\Delta^2)$. If the total energy of the particle cannot exceed $E_M = 6\hbar^2/(2mR^2)$ compute, in the $\Delta \rightarrow 0$ limit in which the particle is bound on the sphere of radius R , the maximum possible value of its superficial probability density on the intersection point of the sphere with the positive z axis.

Answer: In the $\Delta \rightarrow 0$ limit, the radial Schrödinger equation tends to the one-dimensional Schrödinger equation of a particle between two reflecting walls with potential energy between the walls equal to $\tilde{V} = -\hbar^2\pi^2/(2m\Delta^2) + l(l+1)\hbar^2/(2mR^2)$. Therefore the possible energy values are $E_{n,l} = (n^2-1)\hbar^2\pi^2/(2m\Delta^2) + l(l+1)\hbar^2/(2mR^2)$. Only the energies $E_{1,l} = l(l+1)\hbar^2/(2mR^2)$ remain finite as $\Delta \rightarrow 0$. In spherical coordinates, the corresponding wave functions are, in the $\Delta \rightarrow 0$ limit, $\Psi_{l,m} = \sqrt{2/(\Delta R^2)} \sin(\pi(r-R)/\Delta) Y_{l,m}(\theta, \phi)$.

The harmonic functions $Y_{l,m}$ with $m \neq 0$ are proportional to powers of x_{\pm} , hence they vanish on the z axis, therefore and on account of the energy bound, among the possible solutions, we only consider $\Psi_{l,0}$ for $0 \leq l \leq 2$. Forgetting the radial dependence which, in the $\Delta \rightarrow 0$ limit corresponds to a probability density equal to $\delta(r-R)$, these are $\Psi_{0,0} = 1/(R\sqrt{4\pi})$, $\Psi_{1,0} = \sqrt{3/4\pi} \cos\theta/R$ and $\Psi_{2,0} = \sqrt{5/16\pi} (3\cos^2\theta - 1)/R$. The wave function of the particle with the above constraints is written as the linear combination $a_0\Psi_{0,0} + a_1\Psi_{1,0} + a_2\Psi_{2,0}$, with the normalization condition $|a_0|^2 + |a_1|^2 + |a_2|^2 = 1$. On the positive z axis the wave function is $1/\sqrt{4\pi}[a_0 + \sqrt{3}a_1 + \sqrt{5}a_2]/R^2$. It is fairly obvious that the maximum absolute value is reached when $a_0 = a_1 = 0$, hence the maximum superficial probability density of the particle is $5/(4\pi R^2)$. The result can be generalized to the case in which different values of the angular momentum can be reached, indeed it can be proved that $|\Psi_{l,0}(\theta=0)|^2 = (2l+1)/(4\pi R^2)$.

2.46 A particle of mass m moves along the x axis under the influence of the double well potential:

$$V(x) = -V[\delta(x+L) + \delta(x-L)],$$

with $V > 0$. Study the solutions of the stationary Schrödinger equation. Since the potential is even under x reflection, the solutions are either even or odd. Show that in the even case there is a single solution for any value of L , discuss the range of values of the binding energy B and, in particular, how B depends on L for small L , i.e. when $\alpha(L) \equiv 2mVL/\hbar^2 \ll 1$. Compute the “force” between the two wells in

this limit. In the odd solution case, compute the range of $\alpha(L)$ for which there are bound solutions and compare the even with the odd binding energies.

Answer: Starting from the even case, we write the solution between the wells as $\psi_I(x) = \cosh kx$, with $B = \hbar^2 k^2 / (2m)$, and the external solution as $\psi_E(x) = a \exp(-k(|x| - L))$. The continuity conditions on the wells give: $a = \cosh(kL)$ and $k(\sinh(kL) + a) = \alpha(L) \cosh(kL)/L$. Setting $kL = y$ we get the transcendental equation $\tanh y = \alpha(L)/y - 1$. This equation has a single solution $y(\alpha(L))$, corresponding to a single bound state, for any positive value of $\alpha(L)$. In particular for small $\alpha(L)$ also $y(\alpha(L))$ is small and the equation is approximated by $y - y^3/3 = \alpha(L)/y - 1$ which, up to the second order in $\alpha(L)$, has the positive y solution $y(\alpha(L)) = \alpha(L) - \alpha^2(L)$. The corresponding binding energy is computed noticing that $B = \hbar^2 y^2 / (2mL^2)$, from which we have $B = 2m\mathcal{V}^2/\hbar^2 - 8m^2\mathcal{V}^3L/\hbar^4 + O(\alpha^4(L))$. This implies that there is an attractive force between the two wells which, in the small $\alpha(L)$ limit, is equal to $F = 8m^2\mathcal{V}^3/\hbar^4$, furthermore $B \leq B_{max} = 2m\mathcal{V}^2/\hbar^2$; notice that B_{max} is the binding energy for a single well $-2\mathcal{V}\delta(x)$, which is indeed the limit of $V(x)$ as $L \rightarrow 0$. For large $\alpha(L)$ also $y(\alpha(L))$ is large and the transcendental equation is well approximated by $1 = \alpha(L)/y - 1$, which gives $y(\alpha(L)) = \alpha(L)/2$, so that the binding energy reaches its minimum value $B_{min} = m\mathcal{V}^2/(2\hbar^2)$, which coincides with the binding energy of a single well.

In the odd case the solution between the wells becomes $\psi_I(x) = \sinh kx$ while the external one does not change, therefore the transcendental equation becomes $\tanh y = y/(\alpha(L) - y)$. Here the right-hand side is concave downward and positive, while the left-hand side is concave upward and positive for $0 < y < \alpha(L)$, it has a singularity in $\alpha(L)$ and it is negative beyond the singularity. Therefore the equation has a solution for $0 < y < \alpha$ if, and only if, the left-hand side is steeper in the origin than the right-hand side, that is if $\alpha(L) > 1$. For large values of $\alpha(L)$, $y(\alpha(L))$ tends to $\alpha(L)/2$ from below; notice that in the even case the same limit is reached from above.

In conclusion, for any value of the distance between the two wells, there is an even solution, whose binding energy is larger than that of a single well; on the contrary an odd solution exists only if $L > \hbar^2/(2m\mathcal{V})$, with a binding energy lower than that of a single well. In the limit of large separation between the two wells, both the odd and the even level approach the energy of a single well, one from above and the other from below, i.e. we get asymptotically two degenerate levels. The presence of two slightly splitted levels (the even ground state and the odd first excited state) is a phenomenon common to other symmetric double well potentials; an example is given by the Ammonia molecule (NH_3), in which the Nitrogen atom has two symmetric equilibrium positions on both sides of the plane formed by the three Hydrogen atoms.

2.47 A particle of mass m is constrained to move on a plane surface where it is subject to an isotropic harmonic potential of angular frequency ω . Which are the stationary states which are found, for the first excited level, by separation of variables in Cartesian coordinates? Show that the probability current density for such states

vanishes. Are there any stationary states belonging to the same level having a non-zero current density? Find those having the maximum possible current density and give a physical interpretation for them.

Answer: For the first excited level, $E_1 = 2\hbar\omega$, the two following stationary states are found in Cartesian coordinates (see Eqs. (2.136) and (2.133)):

$$\psi_{1,0} = \frac{\sqrt{2}\alpha^2 x}{\sqrt{\pi}} e^{-\alpha^2(x^2+y^2)/2}; \quad \psi_{0,1} = \frac{\sqrt{2}\alpha^2 y}{\sqrt{\pi}} e^{-\alpha^2(x^2+y^2)/2}$$

where $\alpha = \sqrt{m\omega/\hbar}$. In both cases the current density

$$\mathbf{J} = -\frac{i\hbar}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*) = \frac{\hbar}{m} \text{Im} (\psi^* \nabla \psi)$$

vanishes, since the wave functions are real. However it is possible to find different stationary states, corresponding to linear combinations of the two states above, having a non-zero current. Indeed for the most general state, which up to an overall irrelevant phase factor can be written as

$$\psi = a \psi_{1,0} + \sqrt{1-a^2} e^{i\phi} \psi_{0,1}$$

where $a \in [0, 1]$ is a real parameter, the probability current density is

$$\mathbf{J} = \frac{2\hbar\alpha^4}{m\pi} e^{-\alpha^2(x^2+y^2)} a \sqrt{1-a^2} \sin \phi \mathbf{j}$$

where $(j_x, j_y) = (-y, x)$. The current field is independent, up to an overall factor, of the particular state chosen and describes a circular flow around the origin, hence in general a state with a non-zero average angular momentum; moreover $\nabla \cdot \mathbf{J} = 0$, as expected for a stationary state. The current vanishes for $a = 0, 1$ or $\phi = 0, \pi$ and is maximum for $a = 1/\sqrt{2}$ and $\phi = \pm\pi/2$, corresponding to the states:

$$\psi_{\pm} = \frac{1}{\sqrt{2}} (\psi_{1,0} \pm i \psi_{0,1}) = \frac{\alpha^2}{\sqrt{\pi}} e^{-\alpha^2(x^2+y^2)/2} (x \pm i y) = \frac{\alpha^2}{\sqrt{\pi}} e^{-\alpha^2 r^2/2} x_{\pm}$$

where $r^2 = x^2 + y^2$, which are easily recognized as the states having a well defined angular momentum $L = \pm\hbar$.

2.48 Starting from the definition of the corresponding harmonic polynomials given in (2.182) and computing the normalization constants, verify Eq. (2.186) for the first spherical harmonics.

Answer: For $l = 0$: $\mathcal{Y}_{0,0}$ is a constant, after normalization over the solid angle one finds $Y_{0,0} = \sqrt{\frac{1}{4\pi}}$. For $l = 1$: $\mathcal{Y}_{1,1} \sim -x_+$. The corresponding normalization con-

stant for $Y_{1,1} = -c_{1,1} \sin \theta e^{i\varphi}$ is given by the equation: $1/|c_{1,1}|^2 = 2\pi \int_{-1}^1 dx(1 - x^2) = 8\pi/3$. This, together with (2.180), fixes $Y_{1,\pm 1}$. The normalization constant for $Y_{1,0} = c_{1,0} \cos \theta$ is given by the equation: $1/|c_{1,0}|^2 = 2\pi \int_{-1}^1 dx x^2 = 4\pi/3$. The sign is fixed by the condition that $Y_{l,0}(1) > 0$. For $l = 2$: $\mathcal{Y}_{2,2} \sim x_+^2$. The corresponding normalization constant for $Y_{2,2} = c_{2,2} \sin^2 \theta e^{2i\varphi}$ is given by the equation: $1/|c_{2,2}|^2 = 2\pi \int_{-1}^1 dx(1 - x^2)^2 = 32\pi/15$. This, together with (2.180), fixes $Y_{2,\pm 2}$. $\mathcal{Y}_{2,1} \sim zx_+$. The corresponding normalization constant for $Y_{2,1} = c_{2,1} \cos \theta \sin \theta e^{i\varphi}$ is given by the equation: $1/|c_{2,1}|^2 = 2\pi \int_{-1}^1 dx x^2(1 - x^2) = 8\pi/15$. This, together with (2.180), fixes $Y_{2,\pm 1}$. The normalization constant for $Y_{2,0} = c_{2,0}(3 \cos^2 \theta - 1)$ is given by the equation: $1/|c_{2,0}|^2 = 2\pi \int_{-1}^1 dx(3x^2 - 1)^2 = 16\pi/5$. The sign is fixed by the condition that $Y_{l,0}(1) > 0$.

2.49 A particle of mass m moves in three dimensions under the influence of the central potential $V(r) = -\hbar^2 \alpha / (2mR) \delta(r - R)$, with α positive. Compute the values of α for which the particle has a bound state with non-zero angular momentum.

Answer: For zero angular momentum (S-wave), the solution to the differential equation for the radial wave function $\chi(r)$ defined in (2.187), satisfying the regularity conditions in the origin and at infinity, is equivalent to the odd solution for the one-dimensional double well potential given in Problem 2.46 (setting $L = R$), hence $\chi_{<} \propto \sinh(kr)$ for $r < R$ and $\chi_{>} \propto \exp(k(R - r))$ for $r > R$, the bound state energy being $E = -\hbar^2 k^2 / (2m)$ with $k > 0$. We know, from Problem 2.46, that such solution exists only if $\alpha > 1$.

We consider now the P-wave case ($l = 1$). The solution satisfying the correct regularity conditions can be obtained from that written in the S-wave case by applying the recursive equation (2.192). It is, up to an overall normalization factor, $\chi_{<} = \sinh(kr)/(kr) - \cosh(kr)$ for $r < R$ and $\chi_{>} = a \exp(k(R - r))[1/(kr) + 1]$ for $r > R$. The continuity conditions at $r = R$, written in terms of $kR = x$, are given by $\sinh x/x - \cosh x = a(1 + x)/x$ and $\cosh x/x - \sinh x(1 + x^2)/x^2 + a(1 + 1/x + 1/x^2) = \alpha(\sinh x/x^2 - \cosh x/x)$, from which we have $\tanh x = x(1 + x - x^2/\alpha)/(1 + x + x^3/\alpha)$. We know that the graphs of both sides of this equation cross at most once for $x > 0$ since we have seen in the one-dimensional case, e.g. in Sect. 2.6, that a thin potential well has at most a single bound state. It remains to be verified if they cross. The graphs are tangent to each other in the origin and, for $x \rightarrow \infty$, the left-hand side tends to $+1$ and the right-hand side to -1 , therefore if the left-hand side is steeper in the origin the graphs do not cross, otherwise they cross once and there is a bound state. Considering the Taylor expansions of both sides we have $\tanh x \simeq x - x^3/3$ and $x(1 + x - x^2/\alpha)/(1 + x + x^3/\alpha) \simeq x - x^3/\alpha$. The conclusion is that there is a bound state if $\alpha > 3$. It should be clear that if no bound state can be found for $l = 1$ (i.e. $\alpha < 3$), none will be found for $l > 1$ as well, because of the increased centrifugal potential.

2.50 Compute the S -wave scattering length for a particle with mass M in the potential well given in Eq. (2.189).

Answer: Introducing the dimensionless parameters $x = \sqrt{2MER}/\hbar$ and $y = \sqrt{2MV_0R}/\hbar$, one has, up to an over all normalization factor, the internal solution, for $r < R$, $\chi_{<} = \sin(\sqrt{x^2 + y^2}r/R)$ and, the external solution, for $r > R$, $\chi_{>} = a \sin(xr/R + \delta_0)$. The continuity conditions at $r = R$ give $x \tan \sqrt{x^2 + y^2} = \sqrt{x^2 + y^2} \tan(x + \delta_0)$, from which we get

$$x \cot \delta_0 = \frac{1 + x \tan x \tan \sqrt{x^2 + y^2}/\sqrt{x^2 + y^2}}{\tan \sqrt{x^2 + y^2}/\sqrt{x^2 + y^2} - \tan x/x}.$$

The scattering length is apparently equal to $y/(\tan y - y)$. It is positive if $y < \pi/2$, that is in the absence of bound states.

2.51 A particle with mass m moves in three dimensions under the influence of the central potential $V(r) = -\hbar^2\alpha/(2mR)\delta(r - R)$ with α positive. Compute which are the values of α for which the particle has a bound state in S and P waves.

Answer: We note that the S -wave equation gives a bound state if $\alpha > 1$ as we can see comparing with the one dimensional case with a reflecting wall in the origin. Then we consider the solution of the P -wave radial Schrödinger equation. Due to the regularity conditions in the origin and at infinity, the radial wave function defined in Eq. (2.195) is, up to an over all normalization factor, $\chi_{<} = \sinh(kr)/(kr) - \cosh(kr)$ for $r < R$ and $\chi_{>} = a \exp(k(R - r))[1/(kr) + 1]$ for $r > R$, the bound state energy being $-\hbar^2k^2/(2m)$ and $k > 0$. The continuity conditions at $r = R$, written in terms of $kr = x$, are given by $\sinh x/x - \cosh x = a(1 + x)/x$ and $\cosh x/x - \sinh x(1 + x^2)/x^2 + a(1 + 1/x + 1/x^2) = \alpha(\sinh x/x^2 - \cosh x/x)$, from which we have $\tanh x = x(1 + x - x^2/\alpha)/(1 + x + x^3/\alpha)$. The graphs of both sides of this equation are tangent to each other in the origin and, for $x \rightarrow \infty$, the left-hand side tends to $+1$ and the right-hand side to -1 , therefore if the left-hand side is steeper in the origin the graphs do not cross, otherwise they cross once and there is a bound state. Considering the Taylor expansions of both sides we have $\tanh x \simeq x - x^3/3$ and $x(1 + x - x^2/\alpha)/(1 + x + x^3/\alpha) \simeq x - x^3/\alpha$. The conclusion is that there is a bound state if $\alpha > 3$.

2.52 A particle with mass m moves in three dimensions under the influence of the central potential $V(r) = -\hbar^2\alpha/(2mR)\delta(r - R)$. Compute the S -wave phase shift comparing the case of α positive with that of α negative.

Answer: Denoting the solutions as in Problem 2.51 one has, up to an over all normalization factor, $\chi_{<}(r) \sim \sin kr$, $\chi_{>}(r) \sim a \sin(kr + \delta_0)$. The (dis-)continuity relations give, for $x = kR$, $x \cot \delta_0 = (2x^2/\alpha - x \sin(2x))/2 \sin^2 x$. The solution of physical interest corresponds to δ_0 vanishing with x , thus $\delta_0 = \alpha x/(1 - \alpha) + O(x^2)$. Therefore in the present case the scattering length is equal to $\alpha R/(1 - \alpha)$, which is negative either with $\alpha > 1$, or with α negative, otherwise the scattering length is

positive. If the scattering length is positive the low energy phase shift increases with the energy, otherwise it decreases. It is worth recalling here that the potential has a bound state with $l = 0$ for $\alpha > 1$. Thus we see that, when there is a bound state, the scattering length is negative.

If the equation $2x/\alpha = \sin 2x$ has solutions, these correspond to energies for which $\delta_0 = \pi/2 \pm n\pi$ and hence $\sin^2 \delta_0$ reaches its maximum value. If $1/\alpha = 1 - \epsilon$ with ϵ and x small, from Eq. (2.233) we have that the S -wave contribution to the total cross section is

$$\sigma_S \simeq \frac{4\pi R^2}{x^2 + \epsilon^2}.$$

For $1 > \alpha > 0$ the phase shift starts increasing without reaching π and vanishes at high energy. If α is negative the phase shift starts decreasing but for large enough energy goes back to zero.

2.53 A particle with mass m moves in three dimensions under the influence of the central potential $V(r) = -\hbar^2 y^2/(2mR^2)\Theta(R - r) + \hbar^2 \alpha/(2mR)\delta(r - R)$ with $y = \pi - \epsilon$, $\alpha = \pi/\epsilon - 1/2$ and $\epsilon \ll 1$. Compute the S -wave phase shift in the energy range $kR = O(\epsilon)$.

Answer: Denoting the internal and external solutions as in Problems 2.51 and 2.52, and introducing the variable $x = kR$ we have, up to an over all normalization factor, $\chi_{<}(r) \sim \sin(\sqrt{y^2 + x^2}r/R)$, $\chi_{>}(r) \sim a \sin(xr/R + \delta_0)$. The (dis-)continuity relations give $\sqrt{y^2 + x^2} \cot \sqrt{y^2 + x^2} = x \cot(x + \delta_0) - \alpha$. After short calculations we get:

$$x \cot \delta_0 = \frac{\sqrt{y^2 + x^2} \cot \sqrt{y^2 + x^2} + \alpha + x \tan x}{1 - \tan x (\sqrt{y^2 + x^2} \cot \sqrt{y^2 + x^2} + \alpha)/x},$$

and, with the given choice of the parameters, $\sqrt{y^2 + x^2} \cot \sqrt{y^2 + x^2} + \alpha = (1 - x^2/\epsilon^2)/2 + O(\epsilon^2)$. Thus $x \cot \delta_0 \simeq (1 - x^2/\epsilon^2)/(1 + x^2/\epsilon^2)$. The corresponding S -wave cross section is

$$\sigma_0(x) = 4\pi R^2 \frac{(1 + x^2/\epsilon^2)^2}{x^2(1 + x^2/\epsilon^2)^2 + (1 - x^2/\epsilon^2)^2}.$$

For $x = 0$ we have $\sigma_0(0) \simeq 4\pi R^2$ and the cross section has a sharp maximum for $x = \epsilon$, indeed $\sigma(\epsilon) = 4\pi R^2/\epsilon^2$. This is usually called a resonance. The phase shift grows and crosses $\pi/2$, while the cross section reaches its maximum possible value, λ^2/π .

2.54 A particle with mass m moves in three dimensions under the influence of the central potential $V(r) = -\hbar^2 y^2/(2mR^2)\Theta(R - r) + \hbar^2 \alpha/(2mR)\delta(r - R)$ with $y = \pi - \epsilon$, $\alpha = \pi/\epsilon - 1/2$ and $\epsilon \ll 1$. Discuss the existence of bound states in S wave.

Answer: Denoting the internal and external solutions as in Problems 2.51 and 2.52, and introducing the parameter $x = \sqrt{2mBR}/\hbar$ we have, up to an over all normalization factor, $\chi_{<}(r) \sim \sin(\sqrt{y^2 - x^2}r/R)$, $\chi_{>}(r) \sim a \exp(-xr/R)$. Then, the (dis-)continuity relations give: $\sqrt{y^2 - x^2} \cot \sqrt{y^2 - x^2} = -x - \alpha$. It is not difficult to verify that for large α and $y < \pi$ the above equation has no solution. Once again we find positive scattering length in the absence of bound states.

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