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ELEMENTARY QUANTUM MECHANICS

HARET C. ROSU

e-mail: rosu@ifug3.ugto.mx

fax: 0052-47187611

phone: 0052-47183089


$$\hbar / 2\pi$$

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Abstract

This is the first graduate course on elementary quantum mechanics in Internet written for the benefit of undergraduate and graduate students. It is a translation (with corrections) of the Romanian version of the course, which I did at the suggestion of several students from different countries. The topics included refer to the postulates of quantum mechanics, one-dimensional barriers and wells, angular momentum and spin, WKB method, harmonic oscillator, hydrogen atom, quantum scattering, and partial waves.

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There are about 25 illustrative problems.

Spacetime nonrelativistic atomic units

$$a_H = \hbar^2/m_e e^2 = 0.529 \cdot 10^{-8} \text{cm}$$

$$t_H = \hbar^3/m_e e^4 = 0.242 \cdot 10^{-16} \text{sec}$$

Planck relativistic units of space and time

$$l_P = \hbar/m_P c = 1.616 \cdot 10^{-33} \text{cm}$$

$$t_P = \hbar/m_P c^2 = 5.390 \cdot 10^{-44} \text{sec}$$

0. FORWARD

The energy quanta occurred in 1900 in the work of Max Planck (Nobel prize, 1918) on the black body electromagnetic radiation. Planck's "quanta of light" have been used by Einstein (Nobel prize, 1921) to explain the photoelectric effect, but the first "quantization" of a quantity having units of action (the angular momentum) belongs to Niels Bohr (Nobel Prize, 1922). This opened the road to the universalization of quanta, since the action is the basic functional to describe any type of motion. However, only in the 1920's the formalism of quantum mechanics has been developed in a systematic manner. The remarkable works of that decade contributed in a decisive way to the rising of quantum mechanics at the level of fundamental theory of the universe, with successful technological applications. Moreover, it is quite probable that many of the cosmological mysteries may be disentangled by means of various quantization procedures of the gravitational field, advancing our understanding of the origins of the universe. On the other hand, in recent years, there is a strong surge of activity in the information aspect of quantum mechanics. This aspect, which was generally ignored in the past, aims at a very attractive "quantum computer" technology.

At the philosophical level, the famous paradoxes of quantum mechanics, which are perfect examples of the difficulties of 'quantum' thinking, are actively pursued ever since they have been first posed. Perhaps the most famous of them is the EPR paradox (Einstein, Podolsky, Rosen, 1935) on the existence of elements of physical reality, or in EPR words: "If, without in any way disturbing a system, we can predict with certainty (i.e., with probability equal to unity) the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity." Another famous paradox is that of Schrödinger's cat which is related to the fundamental quantum property of entanglement and the way we understand and detect it. What one should emphasize is that all these delicate points are the source of many interesting and innovative experiments (such as the so-called "teleportation" of quantum states) pushing up the technology.

Here, I present eight elementary topics in nonrelativistic quantum mechanics from a course in Spanish ("castellano") on quantum mechanics that I taught in the Instituto de Física, Universidad de Guanajuato (IFUG), León, Mexico, during the semesters of 1998.

Haret C. Rosu

1. THE QUANTUM POSTULATES

The following six postulates can be considered as the basis for theory and experiment in quantum mechanics in its most used form, which is known as the Copenhagen interpretation.

- P1.-** To any physical quantity L , which is well defined at the classical level, one can associate a hermitic operator \hat{L} .
- P2.-** To any stationary physical state in which a quantum system can be found one can associate a (normalized) wavefunction. ψ ($\|\psi\|_{\mathcal{L}^2}^2 = 1$).
- P3.-** In (appropriate) experiments, the physical quantity L can take only the eigenvalues of \hat{L} . Therefore the eigenvalues should be real, a condition which is fulfilled only by hermitic operators.
- P4.-** What one measures is always the mean value \bar{L} of the physical quantity (i.e., operator) \hat{L} in a state ψ_n , which, theoretically speaking, is the corresponding diagonal matrix element
- $$\langle \psi_n | \hat{L} | \psi_n \rangle = \bar{L}.$$
- P5.-** The matrix elements of the operators corresponding to the cartesian coordinate and momentum, \hat{x}_i and \hat{p}_k , when calculated with the wavefunctions f and g satisfy the Hamilton equations of motion of classical mechanics in the form:

$$\begin{aligned} \frac{d}{dt} \langle f | \hat{p}_i | g \rangle &= - \langle f | \frac{\partial \hat{H}}{\partial \hat{x}_i} | g \rangle \\ \frac{d}{dt} \langle f | \hat{x}_i | g \rangle &= \langle f | \frac{\partial \hat{H}}{\partial \hat{p}_i} | g \rangle, \end{aligned}$$

where \hat{H} is the hamiltonian operator, whereas the derivatives with respect to operators are defined as at point 3 of this chapter.

- P6.-** The operators \hat{p}_i and \hat{x}_k have the following commutators:

$$\begin{aligned} [\hat{p}_i, \hat{x}_k] &= -i\hbar\delta_{ik}, \\ [\hat{p}_i, \hat{p}_k] &= 0, \\ [\hat{x}_i, \hat{x}_k] &= 0 \end{aligned}$$

$$\hbar = h/2\pi = 1.0546 \times 10^{-27} \text{ erg.sec.}$$

1.- The correspondence between classical and quantum quantities

This can be done by substituting x_i, p_k with \hat{x}_i, \hat{p}_k . The function L is supposed to be analytic (i.e., it can be developed in Taylor series). If the L function does not contain mixed products $x_k p_k$, the operator \hat{L} is directly hermitic.

Exemple:

$$T = (\sum_i^3 p_i^2)/2m \longrightarrow \hat{T} = (\sum_i^3 \hat{p}_i^2)/2m.$$

If L contains mixed products $x_i p_i$ and higher powers of them, \hat{L} is not hermitic, and in this case L is substituted by $\hat{\Lambda}$, the hermitic part of \hat{L} ($\hat{\Lambda}$ is an autoadjunct operator).

Exemple:

$$w(x_i, p_i) = \sum_i p_i x_i \longrightarrow \hat{w} = 1/2 \sum_i^3 (\hat{p}_i \hat{x}_i + \hat{x}_i \hat{p}_i).$$

In addition, one can see that we have no time operator. In quantum mechanics, time is only a parameter that can be introduced in many ways. This is so because time does not depend on the canonical variables, merely the latter depend on time.

2.- Probability in the discrete part of the spectrum

If ψ_n is an eigenfunction of the operator \hat{L} , then:

$$\bar{L} = \langle n | \hat{L} | n \rangle = \langle n | \lambda_n | n \rangle = \lambda_n \langle n | n \rangle = \delta_{nn} \lambda_n = \lambda_n.$$

Moreover, one can prove that $\bar{L}^k = (\lambda_n)^k$.

If the function ϕ is not an eigenfunction of \hat{L} , one can make use of the expansion in the complete system of eigenfunctions of \hat{L} to get:

$$\hat{L}\psi_n = \lambda_n \psi_n, \quad \phi = \sum_n a_n \psi_n$$

and combining these two relationships one gets:

$$\hat{L}\phi = \sum_n \lambda_n a_n \psi_n.$$

In this way, one is able to calculate the matrix elements of the operator \hat{L} :

$$\langle \phi | \hat{L} | \phi \rangle = \sum_{n,m} a_m^* a_n \lambda_n \langle m | n \rangle = \sum_m |a_m|^2 \lambda_m,$$

telling us that the result of the experiment is λ_m with a probability $|a_m|^2$.

If the spectrum is discrete, according to **P4** this means that $|a_m|^2$, that is the coefficients of the expansion in a complete set of eigenfunctions, determine the probabilities to observe the eigenvalue λ_n .

If the spectrum is continuous, using the following definition

$$\phi(\tau) = \int a(\lambda) \psi(\tau, \lambda) d\lambda,$$

one can calculate the matrix elements in the continuous part of the spectrum

$$\begin{aligned} \langle \phi | \hat{L} | \phi \rangle &= \int d\tau \int a^*(\lambda) \psi^*(\tau, \lambda) d\lambda \int \mu a(\mu) \psi(\tau, \mu) d\mu \\ &= \int \int a^*(\lambda) a(\mu) \mu \int \psi^*(\tau, \lambda) \psi(\tau, \mu) d\tau d\lambda d\mu \\ &= \int \int a^*(\lambda) a(\mu) \mu \delta(\lambda - \mu) d\lambda d\mu \\ &= \int a^*(\lambda) a(\lambda) \lambda d\lambda \\ &= \int |a(\lambda)|^2 \lambda d\lambda. \end{aligned}$$

In the continuous case, $|a(\lambda)|^2$ should be understood as the probability density for observing the eigenvalue λ belonging to the continuous spectrum. Moreover, the following holds

$$\bar{L} = \langle \phi | \hat{L} | \phi \rangle.$$

One usually says that $\langle \mu | \Phi \rangle$ is the representation of $|\Phi\rangle$ in the representation μ , where $|\mu\rangle$ is an eigenvector of \hat{M} .

3.- Definition of the derivate with respect to an operator

$$\frac{\partial F(\hat{L})}{\partial \hat{L}} = \lim_{\epsilon \rightarrow 0} \frac{F(\hat{L} + \epsilon \hat{I}) - F(\hat{L})}{\epsilon}.$$

4.- The operators of cartesian momenta

Which is the explicit form of \hat{p}_1 , \hat{p}_2 and \hat{p}_3 , if the arguments of the wavefunctions are the cartesian coordinates x_i ?

Let us consider the following commutator:

$$\begin{aligned} [\hat{p}_i, \hat{x}_i^2] &= \hat{p}_i \hat{x}_i^2 - \hat{x}_i^2 \hat{p}_i \\ &= \hat{p}_i \hat{x}_i \hat{x}_i - \hat{x}_i \hat{p}_i \hat{x}_i + \hat{x}_i \hat{p}_i \hat{x}_i - \hat{x}_i \hat{x}_i \hat{p}_i \\ &= (\hat{p}_i \hat{x}_i - \hat{x}_i \hat{p}_i) \hat{x}_i + \hat{x}_i (\hat{p}_i \hat{x}_i - \hat{x}_i \hat{p}_i) \\ &= [\hat{p}_i, \hat{x}_i] \hat{x}_i + \hat{x}_i [\hat{p}_i, \hat{x}_i] \\ &= -i\hbar \hat{x}_i - i\hbar \hat{x}_i = -2i\hbar \hat{x}_i. \end{aligned}$$

In general, the following holds:

$$\hat{p}_i \hat{x}_i^n - \hat{x}_i^n \hat{p}_i = -ni\hbar \hat{x}_i^{n-1}.$$

Then, for all analytic functions we have:

$$\hat{p}_i \psi(x) - \psi(x) \hat{p}_i = -i\hbar \frac{\partial \psi}{\partial x_i}.$$

Now, let $\hat{p}_i \phi = f(x_1, x_2, x_3)$ be the manner in which \hat{p}_i acts on $\phi(x_1, x_2, x_3) = 1$. Then:

$$\hat{p}_i \psi = -i\hbar \frac{\partial \psi}{\partial x_i} + f_1 \psi \text{ and similar relationships hold for } x_2 \text{ and } x_3.$$

From the commutator $[\hat{p}_i, \hat{p}_k] = 0$ it is easy to get $\nabla \times \vec{f} = 0$ and therefore $f_i = \nabla_i F$.

The most general form of \hat{p}_i is $\hat{p}_i = -i\hbar \frac{\partial}{\partial x_i} + \frac{\partial F}{\partial x_i}$, where F is an arbitrary function. The function F can be eliminated by the unitary transformaton $\hat{U}^\dagger = \exp(\frac{i}{\hbar} F)$.

$$\begin{aligned}
\hat{p}_i &= \hat{U}^\dagger \left(-i\hbar \frac{\partial}{\partial x_i} + \frac{\partial F}{\partial x_i} \right) \hat{U} \\
&= \exp^{\frac{i}{\hbar} F} \left(-i\hbar \frac{\partial}{\partial x_i} + \frac{\partial F}{\partial x_i} \right) \exp^{-\frac{i}{\hbar} F} \\
&= -i\hbar \frac{\partial}{\partial x_i}
\end{aligned}$$

leading to $\hat{p}_i = -i\hbar \frac{\partial}{\partial x_i} \longrightarrow \hat{p} = -i\hbar \nabla$.

5.- Calculation of the normalization constant

Any wavefunction $\psi(x) \in \mathcal{L}^2$ of variable x can be written in the form:

$$\psi(x) = \int \delta(x - \xi) \psi(\xi) d\xi$$

that can be considered as the expansion of ψ in eigenfunction of the operator position (cartesian coordinate) $\hat{x}\delta(x - \xi) = \xi\delta(x - \xi)$. Thus, $|\psi(x)|^2$ is the probability density of the coordinate in the state $\psi(x)$. From here one gets the interpretation of the norm

$$\|\psi(x)\|^2 = \int |\psi(x)|^2 dx = 1.$$

Intuitively, this relationship tells us that the system described by $\psi(x)$ should be encountered at a certain point on the real axis, although we can know only approximately the location.

The eigenfunctions of the momentum operator are:

$-i\hbar \frac{\partial \psi}{\partial x_i} = p_i \psi$, and by integrating one gets $\psi(x_i) = A \exp^{\frac{i}{\hbar} p_i x_i}$. x and p have continuous spectra and therefore the normalization is performed by means of the Dirac delta function.

Which is the explicit way of getting the normalization constant ?

This is a matter of the following Fourier transforms:

$$f(k) = \int g(x) \exp^{-ikx} dx, \quad g(x) = \frac{1}{2\pi} \int f(k) \exp^{ikx} dk.$$

It can also be obtained with the following procedure. Consider the unnormalized wavefunction of the free particle

$\phi_p(x) = A \exp^{\frac{ipx}{\hbar}}$ and the formula

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp^{ik(x-x')} dx .$$

One can see that

$$\begin{aligned}
 & \int_{-\infty}^{\infty} \phi_{p'}^*(x) \phi_p(x) dx \\
 &= \int_{-\infty}^{\infty} A^* \exp\left(\frac{-ip'x}{\hbar}\right) A \exp\left(\frac{ipx}{\hbar}\right) dx \\
 &= \int_{-\infty}^{\infty} |A|^2 \exp\left(\frac{ix(p-p')}{\hbar}\right) dx \\
 &= |A|^2 \hbar \int_{-\infty}^{\infty} \exp\left(\frac{ix(p-p')}{\hbar}\right) d\frac{x}{\hbar} \\
 &= 2\pi\hbar |A|^2 \delta(p-p')
 \end{aligned}$$

and therefore the normalization constant is:

$$A = \frac{1}{\sqrt{2\pi\hbar}}.$$

Moreover, the eigenfunctions of the momentum form a complete system (in the sense of the continuous case) for all functions of the \mathcal{L}^2 class.

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int a(p) \exp\left(\frac{ipx}{\hbar}\right) dp$$

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int \psi(x) \exp\left(\frac{-ipx}{\hbar}\right) dx.$$

These formulae provide the connection between the x and p representations.

6.- The momentum (p) representation

The explicit form of the operators \hat{p}_i and \hat{x}_k can be obtained either from the commutation relationships or through the usage of the kernels

$$\begin{aligned}
x(p, \beta) &= U^\dagger x U = \frac{1}{2\pi\hbar} \int \exp\frac{-ipx}{\hbar} x \exp\frac{i\beta x}{\hbar} dx \\
&= \frac{1}{2\pi\hbar} \int \exp\frac{-ipx}{\hbar} (-i\hbar \frac{\partial}{\partial \beta} \exp\frac{i\beta x}{\hbar}).
\end{aligned}$$

The integral is of the form: $M(\lambda, \lambda') = \int U^\dagger(\lambda, x) \widehat{M} U(\lambda', x) dx$, and using $\hat{x}f = \int x(x, \xi) f(\xi) d\xi$, the action of \hat{x} on $a(p) \in \mathcal{L}^2$ is:

$$\begin{aligned}
\hat{x}a(p) &= \int x(p, \beta) a(\beta) d\beta \\
&= \int (\frac{1}{2\pi\hbar} \int \exp\frac{-ipx}{\hbar} (-i\hbar \frac{\partial}{\partial \beta} \exp\frac{i\beta x}{\hbar}) dx) a(\beta) d\beta \\
&= \frac{-i}{2\pi} \int \int \exp\frac{-ipx}{\hbar} \frac{\partial}{\partial \beta} \exp\frac{i\beta x}{\hbar} a(\beta) dx d\beta \\
&= \frac{-i\hbar}{2\pi} \int \int \exp\frac{-ipx}{\hbar} \frac{\partial}{\partial \beta} \exp\frac{i\beta x}{\hbar} a(\beta) d\frac{x}{\hbar} d\beta \\
&= \frac{-i\hbar}{2\pi} \int \int \exp\frac{ix(\beta-p)}{\hbar} \frac{\partial}{\partial \beta} a(\beta) d\frac{x}{\hbar} d\beta \\
&= -i\hbar \int \frac{\partial a(p)}{\partial \beta} \delta(\beta - p) d\beta = -i\hbar \frac{\partial a(p)}{\partial p},
\end{aligned}$$

where $\delta(\beta - p) = \frac{1}{2\pi} \int \exp\frac{ix(\beta-p)}{\hbar} d\frac{x}{\hbar}$.

The momentum operator in the p representation is defined by the kernel:

$$\begin{aligned}
p(p, \beta) &= \widehat{U}^\dagger p \widehat{U} \\
&= \frac{1}{2\pi\hbar} \int \exp\frac{-ipx}{\hbar} (-i\hbar \frac{\partial}{\partial x}) \exp\frac{i\beta x}{\hbar} dx \\
&= \frac{1}{2\pi\hbar} \int \exp\frac{-ipx}{\hbar} \beta \exp\frac{i\beta x}{\hbar} dx = \beta \lambda(p - \beta)
\end{aligned}$$

leading to $\hat{p}a(p) = pa(p)$.

It is worth noting that \hat{x} and \hat{p} , although hermitic operators for all $f(x) \in \mathcal{L}^2$, are not hermitic for their own eigenfunctions.

If $\hat{p}a(p) = p_o a(p)$ and $\hat{x} = \hat{x}^\dagger$ $\hat{p} = \hat{p}^\dagger$, then

$$\langle a | \hat{p}\hat{x} | a \rangle - \langle a | \hat{x}\hat{p} | a \rangle = -i\hbar \langle a | a \rangle$$

$$p_o[\langle a | \hat{x} | a \rangle - \langle a | \hat{x} | a \rangle] = -i\hbar \langle a | a \rangle$$

$$p_o[\langle a | \hat{x} | a \rangle - \langle a | \hat{x} | a \rangle] = 0$$

The left hand side is zero, whereas the right hand side is indefinite, which is a contradiction.

7.- Schrödinger and Heisenberg representations

The equations of motion given by **P5** have different interpretations because in the expression $\frac{d}{dt}\langle f | \hat{L} | f \rangle$ one can consider the temporal dependence as belonging either to the wavefunctions or operators, or both to wavefunctions and operators. We shall consider herein only the first two cases.

- For an operator depending on time $\hat{O} = \hat{O}(t)$ we have:

$$\hat{p}_i = -\frac{\partial \hat{H}}{\partial \hat{x}_i}, \quad \hat{x}_i = \frac{\partial \hat{H}}{\partial \hat{p}_i}$$

$$[\hat{p}, f] = \hat{p}f - f\hat{p} = -i\hbar \frac{\partial f}{\partial \hat{x}_i}$$

$$[\hat{x}, f] = \hat{x}f - f\hat{x} = -i\hbar \frac{\partial f}{\partial \hat{p}_i}$$

and the Heisenberg equations of motion are easily obtained:

$$\dot{\hat{p}}_i = \frac{-i}{\hbar} [\hat{p}, \hat{H}], \quad \dot{\hat{x}}_i = \frac{-i}{\hbar} [\hat{x}, \hat{H}].$$

- If the wavefunctions are time dependent one can still use $\hat{p}_i = \frac{-i}{\hbar} [\hat{p}_i, \hat{H}]$, because being a consequence of the commutation relations it does not depend on representation

$$\frac{d}{dt} \langle f | \hat{p}_i | g \rangle = \frac{-i}{\hbar} \langle f | [\hat{p}_i, \hat{H}] | g \rangle.$$

If now \hat{p}_i and \hat{H} do not depend on time, taking into account the hermiticity, one gets:

$$\begin{aligned} & \left(\frac{\partial f}{\partial t}, \hat{p}_i g \right) + \left(\hat{p}_i f, \frac{\partial g}{\partial t} \right) \\ &= \frac{-i}{\hbar} (f, \hat{p}_i \hat{H} g) + \frac{i}{\hbar} (f, \hat{H} \hat{p}_i g) \\ &= \frac{-i}{\hbar} (\hat{p}_i f, \hat{H} g) + \frac{i}{\hbar} (\hat{H} f, \hat{p}_i g) \\ & \left(\frac{\partial f}{\partial t} + \frac{i}{\hbar} \hat{H} f, \hat{p}_i g \right) + \left(\hat{p}_i f, \frac{\partial g}{\partial t} - \frac{i}{\hbar} \hat{H} g \right) = 0 \end{aligned}$$

The latter relationship holds for any pair of functions $f(x)$ and $g(x)$ at the initial moment if each of them satisfies the equation

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi.$$

This is the Schrödinger equation. It describes the system by means of time-independent operators and makes up the so-called Schrödinger representation.

In both representations the temporal evolution of the system is characterized by the operator \hat{H} , which can be obtained from Hamilton's function of classical mechanics.

Example: \hat{H} for a particle in a potential $U(x_1, x_2, x_3)$ we have:

$\hat{H} = \frac{\hat{p}^2}{2m} + U(x_1, x_2, x_3)$, which in the x representation is:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_x^2 + U(x_1, x_2, x_3).$$

8.- The connection between the S and H representations

P5 is correct in both Schrödinger's representation and Heisenberg's. This is why, the mean value of any observable coincides in the two

representations. Thus, there is a unitary transformation that can be used for passing from one to the other. Such a transformation is of the form $\hat{s}^\dagger = \exp\frac{-i\hat{H}t}{\hbar}$. In order to pass to the Schrödinger representation one should use the Heisenberg transform $\psi = \hat{s}^\dagger f$ with f and \hat{L} , whereas to pass to Heisenberg's representation the Schrödinger transform $\hat{\Lambda} = \hat{s}^\dagger \hat{L} \hat{s}$ with ψ and $\hat{\Lambda}$ is of usage. One can obtain the Schrödinger equation as follows: since in the transformation $\psi = \hat{s}^\dagger f$ the function f does not depend on time, we shall derivate the transformation with respect to time to get:

$$\frac{\partial \psi}{\partial t} = \frac{\partial \hat{s}^\dagger}{\partial t} f = \frac{\partial}{\partial t} (\exp\frac{-i\hat{H}t}{\hbar}) f = \frac{-i}{\hbar} \hat{H} \exp\frac{-i\hat{H}t}{\hbar} f = \frac{-i}{\hbar} \hat{H} \hat{s}^\dagger f = \frac{-i}{\hbar} \hat{H} \psi.$$

Therefore:

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi.$$

Next we get the Heisenberg equations: putting the Schrödinger transform in the form $\hat{s} \hat{\Lambda} \hat{s}^\dagger = \hat{L}$ and performing the derivatives with respect to time one gets Heisenberg's equation

$$\begin{aligned} \frac{\partial \hat{L}}{\partial t} &= \frac{\partial \hat{s}}{\partial t} \hat{\Lambda} \hat{s}^\dagger + \hat{s} \hat{\Lambda} \frac{\partial \hat{s}^\dagger}{\partial t} = \frac{i}{\hbar} \hat{H} \exp\frac{i\hat{H}t}{\hbar} \hat{\Lambda} \hat{s}^\dagger - \frac{i}{\hbar} \hat{s} \hat{\Lambda} \exp\frac{-i\hat{H}t}{\hbar} \hat{H} \\ &= \frac{i}{\hbar} (\hat{H} \hat{s} \hat{\Lambda} \hat{s}^\dagger - \hat{s} \hat{\Lambda} \hat{s}^\dagger \hat{H}) = \frac{i}{\hbar} (\hat{H} \hat{L} - \hat{L} \hat{H}) = \frac{i}{\hbar} [\hat{H}, \hat{L}]. \end{aligned}$$

Thus, we have:

$$\frac{\partial \hat{L}}{\partial t} = \frac{i}{\hbar} [\hat{H}, \hat{L}].$$

Moreover, Heisenberg's equation can be written in the form:

$$\frac{\partial \hat{L}}{\partial t} = \frac{i}{\hbar} \hat{s} [\hat{H}, \hat{\Lambda}] \hat{s}^\dagger.$$

\hat{L} is known as an integral of motion, which, if $\frac{d}{dt} \langle \psi | \hat{L} | \psi \rangle = 0$, is characterized by the following commutators:

$$[\hat{H}, \hat{L}] = 0, \quad [\hat{H}, \hat{\Lambda}] = 0.$$

9.- Stationary states

The states of a quantum system described by the eigenfunctions of \hat{H} are called stationary states and the corresponding set of eigenvalues is known as the energy spectrum of the system. In such cases, the Schroedinger equation is:

$$i\hbar \frac{\partial \psi_n}{\partial t} = E_n \psi_n = \hat{H} \psi_n.$$

The solutions are of the form: $\psi_n(x, t) = \exp \frac{-iE_n t}{\hbar} \phi_n(x)$.

- The probability is the following:

$$\begin{aligned} \delta(x) &= | \psi_n(x, t) |^2 = | \exp \frac{-iE_n t}{\hbar} \phi_n(x) |^2 \\ &= \exp \frac{iE_n t}{\hbar} \exp \frac{-iE_n t}{\hbar} | \phi_n(x) |^2 = | \phi_n(x) |^2. \end{aligned}$$

Thus, the probability is constant in time.

- In the stationary states, the mean value of any commutator of the form $[\hat{H}, \hat{A}]$ is zero, where \hat{A} is an arbitrary operator:

$$\begin{aligned} \langle n | \hat{H} \hat{A} - \hat{A} \hat{H} | n \rangle &= \langle n | \hat{H} \hat{A} | n \rangle - \langle n | \hat{A} \hat{H} | n \rangle \\ &= \langle n | E_n \hat{A} | n \rangle - \langle n | \hat{A} E_n | n \rangle \\ &= E_n \langle n | \hat{A} | n \rangle - E_n \langle n | \hat{A} | n \rangle = 0. \end{aligned}$$

- The virial theorem in quantum mechanics - if \hat{H} is a hamiltonian operator of a particle in the field $U(r)$, using $\hat{A} = 1/2 \sum_{i=1}^3 (\hat{p}_i \hat{x}_i - \hat{x}_i \hat{p}_i)$ one gets:

$$\begin{aligned}
\langle \psi | [\hat{A}, \hat{H}] | \psi \rangle &= 0 = \langle \psi | \hat{A}\hat{H} - \hat{H}\hat{A} | \psi \rangle \\
&= \sum_{i=1}^3 \langle \psi | \hat{p}_i \hat{x}_i \hat{H} - \hat{H} \hat{p}_i \hat{x}_i | \psi \rangle \\
&= \sum_{i=1}^3 \langle \psi | [\hat{H}, \hat{x}_i] \hat{p}_i + \hat{x}_i [\hat{H}, \hat{p}_i] | \psi \rangle.
\end{aligned}$$

Using several times the commutators and $\hat{p}_i = -i\hbar\nabla_i$, $\hat{H} = \hat{T} + U(r)$, one can get:

$$\begin{aligned}
\langle \psi | [\hat{A}, \hat{H}] | \psi \rangle &= 0 \\
&= -i\hbar(2 \langle \psi | \hat{T} | \psi \rangle - \langle \psi | \vec{r} \cdot \nabla U(r) | \psi \rangle).
\end{aligned}$$

This is the virial theorem. If the potential is $U(r) = U_0 r^n$, then a form of the virial theorem similar to that in classical mechanics can be obtained with the only difference that it refers to mean values

$$\overline{T} = \frac{n}{2} \overline{U}.$$

- For a Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(r)$ and $[\vec{r}, H] = \frac{-i\hbar}{m}\vec{p}$, calculating the matrix elements one finds:

$$(E_k - E_n) \langle n | \vec{r} | k \rangle = \frac{i\hbar}{m} \langle n | \hat{p} | k \rangle.$$

10.- The nonrelativistic probability current density

The following integral:

$$\int |\psi_n(x)|^2 dx = 1,$$

is the normalization of an eigenfunction of the discrete spectrum in the coordinate representation. It appears as a condition on the microscopic motion in a finite region of space.

For the wavefunctions of the continuous spectrum $\psi_\lambda(x)$ one cannot give a direct probabilistic interpretation.

Let us consider a given wavefunction $\phi \in \mathcal{L}^2$, that we write as a linear combination of eigenfunctions of the continuum:

$$\phi = \int a(\lambda)\psi_\lambda(x)dx.$$

One says that ϕ corresponds to an infinite motion.

In many cases, the function $a(\lambda)$ is not zero only in a small neighborhood of a point $\lambda = \lambda_0$. In such a case, ϕ is known as a wavepacket.

We shall calculate now the rate of change of the probability of finding the system in the volume Ω .

$$P = \int_{\Omega} |\psi(x, t)|^2 dx = \int_{\Omega} \psi^*(x, t)\psi(x, t)dx.$$

Derivating the integral with respect to time leads to

$$\frac{dP}{dt} = \int_{\Omega} (\psi \frac{\partial \psi^*}{\partial t} + \psi^* \frac{\partial \psi}{\partial t})dx.$$

Using now the Schrödinger equation in the integral of the right hand side, one gets:

$$\frac{dP}{dt} = \frac{i}{\hbar} \int_{\Omega} (\psi \hat{H} \psi^* - \psi^* \hat{H} \psi)dx.$$

Using the identity $f \nabla^2 g - g \nabla^2 f = \text{div}[(f) \text{grad}(g) - (g) \text{grad}(f)]$ and also the Schrödinger equation in the form:

$$\hat{H} \psi = \frac{\hbar^2}{2m} \nabla^2 \psi$$

and substituting in the integral, one gets:

$$\begin{aligned} \frac{dP}{dt} &= \frac{i}{\hbar} \int_{\Omega} [\psi (-\frac{\hbar^2}{2m} \nabla^2 \psi^*) - \psi^* (-\frac{\hbar^2}{2m} \nabla^2 \psi)] dx \\ &= - \int_{\Omega} \frac{i\hbar}{2m} (\psi \nabla^2 \psi^* - \psi^* \nabla^2 \psi) dx \\ &= - \int_{\Omega} \text{div} \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi) dx. \end{aligned}$$

By means of the divergence theorem, the volume integral can be transformed in a surface one leading to:

$$\frac{dP}{dt} = - \oint \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi) dx.$$

The quantity $\vec{J}(\psi) = \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi)$ is known as the probability density current, for which one can easily get the following continuity equation

$$\frac{d\rho}{dt} + \text{div}(\vec{J}) = 0.$$

- If $\psi(x) = AR(x)$, where $R(x)$ is a real function, then: $\vec{J}(\psi) = 0$.
- For momentum eigenfunctions $\psi(x) = \frac{1}{(2\pi\hbar)^{3/2}} \exp \frac{i\vec{p}\vec{x}}{\hbar}$, one gets:

$$\begin{aligned} J(\psi) &= \frac{i\hbar}{2m} \left(\frac{1}{(2\pi\hbar)^{3/2}} \exp \frac{i\vec{p}\vec{x}}{\hbar} \left(\frac{i\vec{p}}{\hbar(2\pi\hbar)^{3/2}} \exp \frac{-i\vec{p}\vec{x}}{\hbar} \right) \right. \\ &\quad \left. - \left(\frac{1}{(2\pi\hbar)^{3/2}} \exp \frac{-i\vec{p}\vec{x}}{\hbar} \frac{i\vec{p}}{\hbar(2\pi\hbar)^{3/2}} \exp \frac{i\hbar\vec{p}\vec{x}}{\hbar} \right) \right) \\ &= \frac{i\hbar}{2m} \left(-\frac{2i\vec{p}}{\hbar(2\pi\hbar)^3} \right) = \frac{\vec{p}}{m(2\pi\hbar)^3}, \end{aligned}$$

which shows that the probability density current does not depend on the coordinate.

11.- Operator of spatial transport

If \hat{H} is invariant at translations of arbitrary vector \vec{a} ,

$$\hat{H}(\vec{r} + \vec{a}) = \hat{H}(\vec{r}),$$

then there is an operator $\hat{T}(\vec{a})$ which is unitary $\hat{T}^\dagger(\vec{a})\hat{H}(\vec{r})\hat{T}(\vec{a}) = \hat{H}(\vec{r} + \vec{a})$.

Commutativity of translations

$$\hat{T}(\vec{a})\hat{T}(\vec{b}) = \hat{T}(\vec{b})\hat{T}(\vec{a}) = \hat{T}(\vec{a} + \vec{b}),$$

implies that \hat{T} is of the form $\hat{T} = \exp^{i\hat{k}a}$, where $\hat{k} = \frac{\hat{p}}{\hbar}$.

In the infinitesimal case:

$$\hat{T}(\delta\vec{a})\hat{H}\hat{T}(\delta\vec{a}) \approx (\hat{I} + i\hat{k}\delta\vec{a})\hat{H}(\hat{I} - i\hat{k}\delta\vec{a}),$$

$$\hat{H}(\vec{r}) + i[\hat{K}, \hat{H}]\delta\vec{a} = \hat{H}(\vec{r}) + (\nabla\hat{H})\delta\vec{a}.$$

Moreover, $[\hat{p}, \hat{H}] = 0$, where \hat{p} is an integral of the motion. The sistem of wavefunctions of the form $\psi(\vec{p}, \vec{r}) = \frac{1}{(2\pi\hbar)^{3/2}} \exp\frac{i\vec{p}\vec{r}}{\hbar}$ and the unitary transformation leads to $\exp\frac{i\vec{p}\vec{a}}{\hbar} \psi(\vec{r}) = \psi(\vec{r} + \vec{a})$. The operator of spatial transport $\hat{T}^\dagger = \exp\frac{-i\vec{p}\vec{a}}{\hbar}$ is the analog of $\hat{s}^\dagger = \exp\frac{-i\hat{H}t}{\hbar}$, which is the operator of time ‘transport’ (shift).

12.- Exemple: The ‘crystal’ (lattice) Hamiltonian

If \hat{H} is invariant for a discrete translation (for exemple, in a crystal lattice) $\hat{H}(\vec{r} + \vec{a}) = \hat{H}(\vec{r})$, where $\vec{a} = \sum_i \vec{a}_i n_i$, $n_i \in N$ and a_i are baricentric vectors, then:

$$\hat{H}(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}),$$

$$\hat{H}(\vec{r} + \vec{a})\psi(\vec{r} + \vec{a}) = E\psi(\vec{r} + \vec{a}) = \hat{H}(\vec{r})\psi(\vec{r} + \vec{a}).$$

Consequently, $\psi(\vec{r})$ and $\psi(\vec{r} + \vec{a})$ are wavefunctions for the same eigenvalue of \hat{H} . The relationship between $\psi(\vec{r})$ and $\psi(\vec{r} + \vec{a})$ can be sought for in the form $\psi(\vec{r} + \vec{a}) = \hat{c}(\vec{a})\psi(\vec{r})$, where $\hat{c}(\vec{a})$ is a g x g matrix (g is the order of degeneration of level E). Two column matrices, $\hat{c}(\vec{a})$ and $\hat{c}(\vec{b})$ commute and therefore they are diagonalizable simultaneously.

Moreover, for the diagonal elements, $c_{ii}(\vec{a})c_{ii}(\vec{b}) = c_{ii}(\vec{a} + \vec{b})$ holds for $i=1,2,\dots,g$, having solutions of the type $c_{ii}(a) = \exp^{ik_i a}$. Thus, $\psi_k(\vec{r}) = U_k(\vec{r}) \exp^{i\vec{k}\vec{a}}$, where \vec{k} is a real arbitrary vector and the function $U_k(\vec{r})$ is periodic of period \vec{a} , $U_k(\vec{r} + \vec{a}) = U_k(\vec{r})$.

The assertion that the eigenfunctions of a periodic \hat{H} of the lattice type $\hat{H}(\vec{r} + \vec{a}) = \hat{H}(\vec{r})$ can be written $\psi_k(\vec{r}) = U_k(\vec{r}) \exp^{i\vec{k}\vec{a}}$, where $U_k(\vec{r} + \vec{a}) = U_k(\vec{r})$ is known as Bloch’s theorem. In the continuous case, U_k should be constant, because the constant is the only function periodic for any \vec{a} . The vector $\vec{p} = \hbar\vec{k}$ is called quasimomentum (by analogy with the continuous case). The vector \vec{k} is not determined univoquely, because one can add any vector \vec{g} for which $g a = 2\pi n$, where $n \in N$.

The vector \vec{g} can be written $\vec{g} = \sum_{i=1}^3 \vec{b}_i m_i$, where m_i are integers and b_i are given by

$$\vec{b}_i = 2\pi \frac{\hat{a}_j \times \vec{a}_k}{\vec{a}_i \cdot (\vec{a}_j \times \vec{a}_k)},$$

for $i \neq j \neq k$. \vec{b}_i are the baricentric vectors of the lattice.

Recommended references

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1N. Notes

1. For “the creation of quantum mechanics...”, Werner Heisenberg has been awarded the Nobel prize in 1932 (delivered in 1933). The paper “Zür Quantenmechanik. II”, [“On quantum mechanics.II”, *Zf. f. Physik* **35**, 557-615 (1926) (received by the Editor on 16 November 1925) by M. Born, W. Heisenberg and P. Jordan, is known as the “work of the three people”, being considered as the work that really opened the vast horizons of quantum mechanics.
2. For “the statistical interpretation of the wavefunction” Max Born was awarded the Nobel prize in 1954.

1P. Problems

Problem 1.1: Let us consider two operators, A and B, which commutes by hypothesis. In this case, one can derive the following relationship:

$$e^A e^B = e^{(A+B)} e^{(1/2)[A,B]}.$$

Solution

Defining an operator $F(t)$, as a function of real variable t , of the form:

$$F(t) = e^{(At)}e^{(Bt)},$$

$$\text{then: } \frac{dF}{dt} = Ae^{At}e^{Bt} + e^{At}Be^{Bt} = (A + e^{At}Be^{-At})F(t).$$

Applying now the formula $[A, F(B)] = [A, B]F'(B)$, we have

$$[e^{At}, B] = t[A, B]e^{At}, \text{ and therefore: } e^{At}B = Be^{At} + t[A, B]e^{At}.$$

Multiplying both sides of the latter equation by \exp^{-At} and substituting in the first equation, we get:

$$\frac{dF}{dt} = (A + B + t[A, B])F(t).$$

The operators A , B and $[A, B]$ commutes by hypothesis. Thus, we can integrate the differential equation as if $A + B$ and $[A, B]$ would be scalar numbers.

We shall have:

$$F(t) = F(0)e^{(A+B)t+1/2[A, B]t^2}.$$

Putting $t = 0$, one can see that $F(0) = 1$ and therefore :

$$F(t) = e^{(A+B)t+1/2[A, B]t^2}.$$

Putting now $t = 1$, we get the final result.

Problem 1.2: Calculate the commutator $[X, D_x]$.

Solution

The calculation is performed by applying the commutator to an arbitrary function $\psi(\vec{r})$:

$$\begin{aligned} [X, D_x]\psi(\vec{r}) &= (x\frac{\partial}{\partial x} - \frac{\partial}{\partial x}x)\psi(\vec{r}) = x\frac{\partial}{\partial x}\psi(\vec{r}) - \frac{\partial}{\partial x}[x\psi(\vec{r})] \\ &= x\frac{\partial}{\partial x}\psi(\vec{r}) - \psi(\vec{r}) - x\frac{\partial}{\partial x}\psi(\vec{r}) = -\psi(\vec{r}). \end{aligned}$$

Since this relationship is satisfied for any $\psi(\vec{r})$, one can conclude that $[X, D_x] = -1$.

Problem 1.3: Check that the trace of a matrix is invariant of changes of discrete orthonormalized bases.

Solution

The sum of the diagonal elements of a matrix representation of an operator A in an arbitrary basis does not depend on the basis.

This important property can be obtained by passing from an orthonormalized discrete basis $|u_i\rangle$ to another orthonormalized discrete basis $|t_k\rangle$. We have:

$$\sum_i \langle u_i | A | u_i \rangle = \sum_i \langle u_i | (\sum_k |t_k\rangle \langle t_k|) A | u_i \rangle$$

(where we have used the completeness relationship for the states t_k). The right hand side is:

$$\sum_{i,j} \langle u_i | t_k \rangle \langle t_k | A | u_i \rangle = \sum_{i,j} \langle t_k | A | u_i \rangle \langle u_i | t_k \rangle,$$

(the change of the order in the product of two scalar numbers is allowed). Thus, we can replace $\sum_i |u_i\rangle \langle u_i|$ with unity (i.e., the completeness relationship for the states $|u_i\rangle$), in order to get finally:

$$\sum_i \langle u_i | A | u_i \rangle = \sum_k \langle t_k | A | t_k \rangle .$$

Thus, we have proved the invariance property for matriceal traces.

Problem 1.4: If for the hermitic operator N there are the hermitic operators L and M such that : $[M, N] = 0$, $[L, N] = 0$, $[M, L] \neq 0$, then the eigenfunctions of N are degenerate.

Solution

Let $\psi(x; \mu, \nu)$ be the common eigenfunctions of M and N (since they commute they are simultaneous observables). Let $\psi(x; \lambda, \nu)$ be the common eigenfunctions of L and N (again, since they commute they are simultaneous observables). The Greek parameters denote the eigenvalues of the corresponding operators. Let us consider for simplicity sake that N has a discrete spectrum. Then:

$$f(x) = \sum_{\nu} a_{\nu} \psi(x; \mu, \nu) = \sum_{\nu} b_{\nu} \psi(x; \lambda, \nu) .$$

We calculate now the matrix element $\langle f | ML | f \rangle$:

$$\langle f | ML | f \rangle = \int \sum_{\nu} \mu_{\nu} a_{\nu} \psi^*(x; \mu, \nu) \sum_{\nu'} \lambda_{\nu'} b_{\nu'} \psi(x; \lambda, \nu') dx .$$

If all the eigenfunctions of N are nondegenerate then $\langle f | ML | f \rangle = \sum_{\nu} \mu_{\nu} a_{\nu} \lambda_{\nu} b_{\nu}$. But the same result can be obtained if one calculates $\langle f | LM | f \rangle$ and the commutator would be zero. Thus, at least some of the eigenfunctions of N should be degenerate.

2. ONE DIMENSIONAL RECTANGULAR BARRIERS AND WELLS

Regions of constant potential

In the case of a rectangular potential, $V(x)$ is a constant function $V(x) = V$ in a certain region of the one-dimensional space. In such a region, the Schrödinger eq. can be written:

$$\frac{d^2}{dx^2}\psi(x) + \frac{2m}{\hbar^2}(E - V)\psi(x) = 0 \quad (1)$$

One can distinguish several cases:

(i) $E > V$

Let us introduce the positive constant k , defined by

$$k = \frac{\sqrt{2m(E - V)}}{\hbar} \quad (2)$$

Then, the solution of eq. (1) can be written:

$$\psi(x) = Ae^{ikx} + A'e^{-ikx} \quad (3)$$

where A and A' are complex constants.

(ii) $E < V$

This condition corresponds to segments of the real axis which would be prohibited to any particle from the viewpoint of classical mechanics. In this case, one introduces the positive constant q defined by:

$$q = \frac{\sqrt{2m(V - E)}}{\hbar} \quad (4)$$

and the solution of (1) can be written:

$$\psi(x) = Be^{qx} + B'e^{-qx} , \quad (5)$$

where B and B' are complex constants.

(iii) $E = V$

In this special case, $\psi(x)$ is a linear function of x .

The behaviour of $\psi(x)$ at a discontinuity of the potential

One might think that at the point $x = x_1$, where the potential $V(x)$ is discontinuous, the wavefunction $\psi(x)$ behaves in a more strange way, maybe discontinuously for example. This is not so: $\psi(x)$ and $\frac{d\psi}{dx}$ are continuous, and only the second derivative is discontinuous at $x = x_1$.

General look to the calculations

The procedure to determine the stationary states in rectangular potentials is the following: in all regions in which $V(x)$ is constant we write $\psi(x)$ in any of the two forms (3) or (5) depending on application; next, we join smoothly these functions according to the continuity conditions for $\psi(x)$ and $\frac{d\psi}{dx}$ at the points where $V(x)$ is discontinuous.

Examination of several simple cases

Let us make explicit calculations for some simple stationary states according to the proposed method.

The step potential

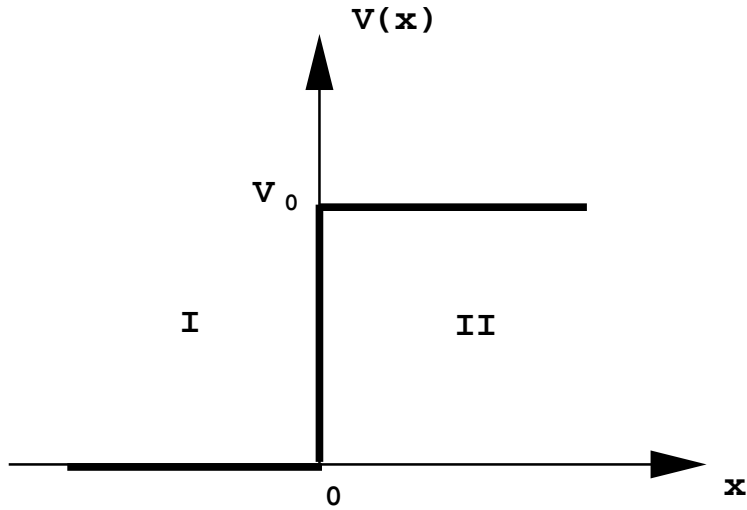


Fig. 2.1

a. $E > V_0$ case; *partial reflexion*

Let us put eq. (2) in the form:

$$k_1 = \frac{\sqrt{2mE}}{\hbar} \quad (6)$$

$$k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar} \quad (7)$$

The solution of eq. (1) has the form of eq. (3) in the regions $I(x < 0)$ and $II(x > 0)$:

$$\begin{aligned} \psi_I &= A_1 e^{ik_1 x} + A_1' e^{-ik_1 x} \\ \psi_{II} &= A_2 e^{ik_2 x} + A_2' e^{-ik_2 x} \end{aligned}$$

In region I eq. (1) takes the form

$$\psi''(x) + \frac{2mE}{\hbar^2} \psi(x) = \psi''(x) + k^2 \psi(x) = 0$$

and in the region II:

$$\psi''(x) - \frac{2m}{\hbar^2} [V_0 - E] \psi(x) = \psi''(x) - q^2 \psi(x) = 0$$

If we limit ourselves to the case of an incident particle ‘coming’ from $x = -\infty$, we have to choose $A_2' = 0$ and we can determine the ratios A_1'/A_1 and A_2/A_1 . The joining conditions give then:

- $\psi_I = \psi_{II}$, at $x = 0$:

$$A_1 + A_1' = A_2 \quad (8)$$

- $\psi_I' = \psi_{II}'$, at $x = 0$:

$$A_1 i k_1 - A_1' i k_1 = A_2 i k_2 \quad (9)$$

Substituting A_1 and A_1' from (8) in (9):

$$A_1' = \frac{A_2(k_1 - k_2)}{2k_1} \quad (10)$$

$$A_1 = \frac{A_2(k_1 + k_2)}{2k_1} \quad (11)$$

From the two expressions of the constant A_2 in (10) and (11) one gets

$$\frac{A'_1}{A_1} = \frac{k_1 - k_2}{k_1 + k_2} \quad (12)$$

and from (11) it follows:

$$\frac{A_2}{A_1} = \frac{2k_1}{k_1 + k_2} . \quad (13)$$

$\psi(x)$ is a superposition of two waves. The first (the A_1 part) corresponds to an incident wave of momentum $p = \hbar k_1$, propagating from the left to the right. The second (the A'_1 part) corresponds to a reflected particle of momentum $-\hbar k_1$ propagating in opposite direction. Since we have already chosen $A'_2 = 0$, it follows that $\psi_{II}(x)$ contains a single wave, which is associated to a transmitted particle. (We will show later how it is possible by employing the concept of probability current to define the transmission coefficient T as well as the reflection coefficient R for the step potential). These coefficients give the probability that a particle coming from $x = -\infty$ can pass through or get back from the step at $x = 0$. Thus, we obtain:

$$R = \left| \frac{A'_1}{A_1} \right|^2 , \quad (14)$$

whereas for T :

$$T = \frac{k_2}{k_1} \left| \frac{A_2}{A_1} \right|^2 . \quad (15)$$

Taking into account (12) and (13) one is led to:

$$R = 1 - \frac{4k_1k_2}{(k_1 + k_2)^2} \quad (16)$$

$$T = \frac{4k_1k_2}{(k_1 + k_2)^2} . \quad (17)$$

It is easy to check that $R + T = 1$. It is thus sure that the particle will be either transmitted or reflected. Contrary to the predictions of classical mechanics, the incident particle has a nonzero probability of not going back.

It is also easy to check using (6), (7) and (17), that if $E \gg V_0$ then $T \simeq 1$: when the energy of the particle is sufficiently big in comparison with the height of the step, everything happens as if the step does not exist for the particle.

Consider the following natural form of the solution in region I:

$$\psi_I = A_1 e^{ik_1 x} + A e^{-ik_1 x}$$

$$j = -\frac{i\hbar}{2m}(\phi^* \nabla \phi - \phi \nabla \phi^*) \quad (18)$$

with $A_1 e^{ik_1 x}$ and its conjugate $A_1^* e^{-ik_1 x}$:

$$j = -\frac{i\hbar}{2m}[(A_1^* e^{-ik_1 x})(A_1 i k_1 e^{ik_1 x}) - (A_1 e^{ik_1 x})(-A_1^* i k_1 e^{-ik_1 x})]$$

$$j = \frac{\hbar k_1}{m} |A_1|^2 .$$

Now with $A e^{-ik_1 x}$ and its conjugate $A^* e^{ik_1 x}$ one is led to:

$$j = -\frac{\hbar k_1}{m} |A|^2 .$$

In the following we wish to check the proportion of reflected current with respect to the incident current (or more exactly, we want to check the relative probability that the particle is returned back):

$$R = \frac{|j(\phi_-)|}{|j(\phi_+)|} = \frac{|\frac{-\hbar k_1}{m} |A|^2|}{|\frac{\hbar k_1}{m} |A_1|^2|} = \left| \frac{A}{A_1} \right|^2 . \quad (19)$$

Similarly, the proportion of transmission with respect to incidence (that is the probability that the particle is transmitted) is, taking now into account the solution in the region II:

$$T = \frac{|\frac{\hbar k_2}{m} |A_2|^2|}{|\frac{\hbar k_1}{m} |A_1|^2|} = \frac{k_2}{k_1} \left| \frac{A_2}{A_1} \right|^2 . \quad (20)$$

b. $E < V_0$ case; total reflection

In this case we have:

$$k_1 = \frac{\sqrt{2mE}}{\hbar} \quad (21)$$

$$q_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \quad (22)$$

In the region $I(x < 0)$, the solution of eq. (1) [written as $\psi(x)'' + k_1^2\psi(x) = 0$] has the form given in eq. (3):

$$\psi_I = A_1 e^{ik_1 x} + A_1' e^{-ik_1 x}, \quad (23)$$

whereas in the region $II(x > 0)$, the same eq. (1) [now written as $\psi(x)'' - q_2^2\psi(x) = 0$] has the form of eq. (5):

$$\psi_{II} = B_2 e^{q_2 x} + B_2' e^{-q_2 x}. \quad (24)$$

In order that the solution be kept finite when $x \rightarrow +\infty$, it is necessary that:

$$B_2 = 0. \quad (25)$$

The joining condition at $x = 0$ give now:

- $\psi_I = \psi_{II}$, at $x = 0$:

$$A_1 + A_1' = B_2' \quad (26)$$

- $\psi_I' = \psi_{II}'$, at $x = 0$:

$$A_1 i k_1 - A_1' i k_1 = -B_2' q_2. \quad (27)$$

Substituting A_1 and A_1' from (26) in (27) we get:

$$A_1' = \frac{B_2'(ik_1 + q_2)}{2ik_1} \quad (28)$$

$$A_1 = \frac{B_2'(ik_1 - q_2)}{2ik_1}. \quad (29)$$

Equating the expressions for the constant B_2' from (28) and (29) leads to:

$$\frac{A_1'}{A_1} = \frac{ik_1 + q_2}{ik_1 - q_2} = \frac{k_1 - iq_2}{k_1 + iq_2}, \quad (30)$$

so that from (29) we have:

$$\frac{B_2'}{A_1} = \frac{2ik_1}{ik_1 - q_2} = \frac{2k_1}{k_1 - iq_2}. \quad (31)$$

Therefore, the reflection coefficient R is:

$$R = \left| \frac{A'_1}{A_1} \right|^2 = \left| \frac{k_1 - iq_2}{k_1 + iq_2} \right|^2 = \frac{k_1^2 + q_2^2}{k_1^2 + q_2^2} = 1 . \quad (32)$$

As in classical mechanics, the microparticle is always reflected (total reflexion). However, there is an important difference, namely, because of the existence of the so-called evanescent wave e^{-q_2x} , the particle has a nonzero probability to find itself in a spatial region which is classically forbidden. This probability decays exponentially with x and turns to be negligible when x overcome $1/q_2$ corresponding to the evanescent wave. Notice also that A'_1/A_1 is a complex quantity. A phase difference occurs as a consequence of the reflexion, which physically is due to the fact that the particle is slowed down when entering the region $x > 0$. There is no analog phenomenon for this in classical mechanics (but there is of course such an analog in optical physics).

Rectangular barrier

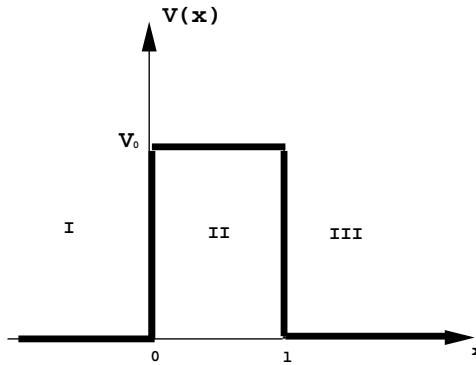


Fig. 2.2

a. $E > V_0$ case; resonances

Here we put eq. (2) in the form:

$$k_1 = \frac{\sqrt{2mE}}{\hbar} \quad (33)$$

$$k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar} . \quad (34)$$

The solution of eq. (1) is as in eq. (3) in the regions $I(x < 0)$, $II(0 < x < a)$ and $III(x > a)$:

$$\begin{aligned}\psi_I &= A_1 e^{ik_1 x} + A'_1 e^{-ik_1 x} \\ \psi_{II} &= A_2 e^{ik_2 x} + A'_2 e^{-ik_2 x} \\ \psi_{III} &= A_3 e^{ik_1 x} + A'_3 e^{-ik_1 x} .\end{aligned}$$

If we limit ourselves to the case of an incident particle coming from $x = -\infty$, we have to choose $A'_3 = 0$.

- $\psi_I = \psi_{II}$, at $x = 0$:

$$A_1 + A'_1 = A_2 + A'_2 \quad (35)$$

- $\psi'_I = \psi'_{II}$, at $x = 0$:

$$A_1 i k_1 - A'_1 i k_1 = A_2 i k_2 - A'_2 i k_2 \quad (36)$$

- $\psi_{II} = \psi_{III}$, at $x = a$:

$$A_2 e^{ik_2 a} + A'_2 e^{-ik_2 a} = A_3 e^{ik_1 a} \quad (37)$$

- $\psi'_{II} = \psi'_{III}$, at $x = a$:

$$A_2 i k_2 e^{ik_2 a} - A'_2 i k_2 e^{-ik_2 a} = A_3 i k_1 e^{ik_1 a} . \quad (38)$$

The joining conditions at $x = a$ give A_2 and A'_2 as functions of A_3 , whereas those at $x = 0$ give A_1 and A'_1 as functions of A_2 and A'_2 (thus, as functions of A_3). This procedure is shown in detail in the following.

Substituting A'_2 from eq. (37) in (38) leads to:

$$A_2 = \frac{A_3 e^{ik_1 a} (k_2 + k_1)}{2k_2 e^{ik_2 a}} . \quad (39)$$

Substituting A_2 from eq. (37) in (38) leads to:

$$A'_2 = \frac{A_3 e^{ik_1 a} (k_2 - k_1)}{2k_2 e^{-ik_2 a}} . \quad (40)$$

Substituting A_1 from eq. (35) in (36) leads to:

$$A'_1 = \frac{A_2 (k_2 - k_1) - A'_2 (k_2 + k_1)}{-2k_1} . \quad (41)$$

Substituting A'_1 from eq. (35) in (36) gives:

$$A_1 = \frac{A_2(k_2 + k_1) - A'_2(k_2 - k_1)}{2k_1} . \quad (42)$$

Now, substituting the eqs. (39) and (40) in (41), we have:

$$A'_1 = i \frac{(k_2^2 - k_1^2)}{2k_1 k_2} (\sin k_2 a) e^{ik_1 a} A_3 . \quad (43)$$

Finally, substituting the eqs. (39) and (40) in (42) we get:

$$A_1 = [\cos k_2 a - i \frac{k_1^2 + k_2^2}{2k_1 k_2} \sin k_2 a] e^{ik_1 a} A_3 . \quad (44)$$

A'_1/A_1 and A_3/A_1 [these ratios can be obtained by equating (43) and (44), and by separating, respectively, in eq. (44)] allow the calculation of the reflexion coefficient R as well as of the transmission one T . For this type of barrier, they are given by the following formulas:

$$R = |A'_1/A_1|^2 = \frac{(k_1^2 - k_2^2)^2 \sin^2 k_2 a}{4k_1^2 k_2^2 + (k_1^2 - k_2^2)^2 \sin^2 k_2 a} , \quad (45)$$

$$T = |A_3/A_1|^2 = \frac{4k_1^2 k_2^2}{4k_1^2 k_2^2 + (k_1^2 - k_2^2)^2 \sin^2 k_2 a} . \quad (46)$$

It is easy to see that they check $R + T = 1$.

b. $E < V_0$ case; *the tunnel effect*

Now, let us take the eqs. (2) and (4):

$$k_1 = \frac{\sqrt{2mE}}{\hbar} \quad (47)$$

$$q_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar} . \quad (48)$$

The solution of eq. (1) has the form given in eq. (3) in the regions $I(x < 0)$ and $III(x > a)$, while in the region $II(0 < x < a)$ has the form of eq. (5):

$$\begin{aligned} \psi_I &= A_1 e^{ik_1 x} + A'_1 e^{-ik_1 x} \\ \psi_{II} &= B_2 e^{q_2 x} + B'_2 e^{-q_2 x} \\ \psi_{III} &= A_3 e^{ik_1 x} + A'_3 e^{-ik_1 x} . \end{aligned}$$

The joining conditions at $x = 0$ and $x = a$ allow the calculation of the transmission coefficient of the barrier. As a matter of fact, it is not necessary to repeat the calculation: merely, it is sufficient to replace k_2 by $-iq_2$ in the equation obtained in the first case of this section.

Bound states in rectangular well

a. Well of finite depth

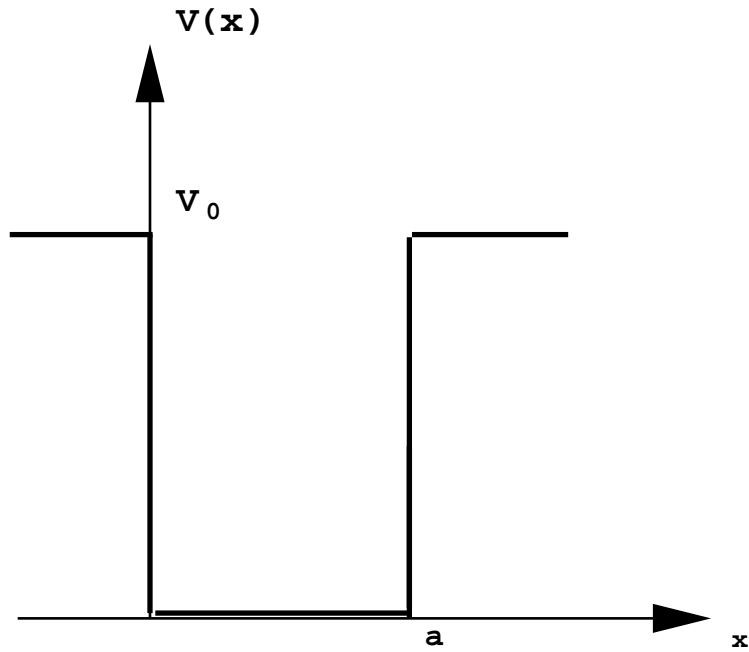


Fig. 2.3 Finite rectangular well

We first study the case $0 < E < V_0$ ($E > V_0$ is similar to the calculation in the previous section).

For the exterior regions I, ($x < 0$) and III, ($x > a$) we employ eq. (4):

$$q = \frac{\sqrt{2m(V_0 - E)}}{\hbar} . \quad (49)$$

For the central region II ($0 < x < a$) we use eq. (2):

$$k = \frac{\sqrt{2m(E)}}{\hbar} . \quad (50)$$

The solution of eq. (1) has the form of eq. (5) in the exterior regions and of eq. (3) in the central region:

$$\psi_I = B_1 e^{qx} + B_1' e^{-qx}$$

$$\begin{aligned}\psi_{II} &= A_2 e^{ikx} + A'_2 e^{-ikx} \\ \psi_{III} &= B_3 e^{qx} + B'_3 e^{-qx}\end{aligned}$$

In the region ($0 < x < a$) eq. (1) has the form:

$$\psi(x)'' + \frac{2mE}{\hbar^2} \psi(x) = \psi(x)'' + k^2 \psi(x) = 0 \quad (51)$$

while in the exterior regions:

$$\psi(x)'' - \frac{2m}{\hbar^2} [V_0 - E] \psi(x) = \psi(x)'' - q^2 \psi(x) = 0 . \quad (52)$$

Because ψ should be finite in the region I, we impose:

$$B'_1 = 0 . \quad (53)$$

The joining conditions give:

$$\psi_I = \psi_{II}, \quad \text{at } x = 0 :$$

$$B_1 = A_2 + A'_2 \quad (54)$$

$$\psi'_I = \psi'_{II}, \quad \text{at } x = 0 :$$

$$B_1 q = A_2 i k - A'_2 i k \quad (55)$$

$$\psi_{II} = \psi_{III}, \quad \text{at } x = a :$$

$$A_2 e^{ika} + A'_2 e^{-ika} = B_3 e^{qa} + B'_3 e^{-qa} \quad (56)$$

$$\psi'_{II} = \psi'_{III}, \quad \text{at } x = a :$$

$$A_2 i k e^{ika} - A'_2 i k e^{-ika} = B_3 q e^{qa} - B'_3 q e^{-qa} \quad (57)$$

Substituting the constants A_2 and A'_2 from eq. (54) in eq. (55) we get

$$\begin{aligned}A'_2 &= \frac{B_1(q - ik)}{-2ik} \\ A_2 &= \frac{B_1(q + ik)}{2ik},\end{aligned} \quad (58)$$

respectively.

Substituting the constant A_2 and the constant A'_2 from eq. (56) in eq. (57) we get

$$\begin{aligned} B'_3 e^{-qa}(ik + q) + B_3 e^{qa}(ik - q) + A'_2 e^{-ika}(-2ik) &= 0 \\ 2ikA_2 e^{ika} + B'_3 e^{-qa}(-ik + q) + B_3 e^{qa}(-ik - q) &= 0, \end{aligned} \quad (59)$$

respectively.

Equating B'_3 from eqs. (59) and taking into account the eqs (58) leads to

$$\frac{B_3}{B_1} = \frac{e^{-qa}}{4ikq} [e^{ika}(q + ik)^2 - e^{-ika}(q - ik)^2]. \quad (60)$$

Since $\psi(x)$ should be finite in region III as well, we require $B_3 = 0$. Thus

$$\left[\frac{q - ik}{q + ik} \right]^2 = \frac{e^{ika}}{e^{-ika}} = e^{2ika}. \quad (61)$$

Because q and k depend on E , eq. (1) can be satisfied for some particular values of E . The condition that $\psi(x)$ should be finite in all spatial regions imposes the quantization of the energy. Two cases are possible:

(i) if

$$\frac{q - ik}{q + ik} = -e^{ika}, \quad (62)$$

equating in both sides the real and the imaginary parts, respectively, we have

$$\tan\left(\frac{ka}{2}\right) = \frac{q}{k}. \quad (63)$$

Putting

$$k_0 = \sqrt{\frac{2mV_0}{\hbar}} = \sqrt{k^2 + q^2} \quad (64)$$

one gets

$$\frac{1}{\cos^2\left(\frac{ka}{2}\right)} = 1 + \tan^2\left(\frac{ka}{2}\right) = \frac{k^2 + q^2}{k^2} = \left(\frac{k_0}{k}\right)^2 \quad (65)$$

Eq. (63) is therefore equivalent to the system of eqs.

$$\begin{aligned} \left| \cos\left(\frac{ka}{2}\right) \right| &= \frac{k}{k_0} \\ \tan\left(\frac{ka}{2}\right) &> 0 \end{aligned} \quad (66)$$

The energy levels are determined by the intersection of a straight line of slope $\frac{1}{k_0}$ with the first set of dashed cosinusoides in fig. 2.4. Thus, we get a certain number of energy levels whose wavefunctions are even. This fact becomes clearer if we substitute (62) in (58) and (60). It is easy to check that $B'_3 = B_1$ and $A_2 = A'_2$ leading to $\psi(-x) = \psi(x)$.

(ii) if

$$\frac{q - ik}{q + ik} = e^{ika} , \quad (67)$$

a similar calculation gives

$$\begin{aligned} \left| \sin\left(\frac{ka}{2}\right) \right| &= \frac{k}{k_0} \\ \tan\left(\frac{ka}{2}\right) &< 0 . \end{aligned} \quad (68)$$

The energy levels are in this case determined by the intersection of the same straight line with the second set of dashed cosinusoides in fig. 2.4. The obtained levels are interlaced with those found in the case (i). One can easily show that the corresponding wavefunctions are odd.

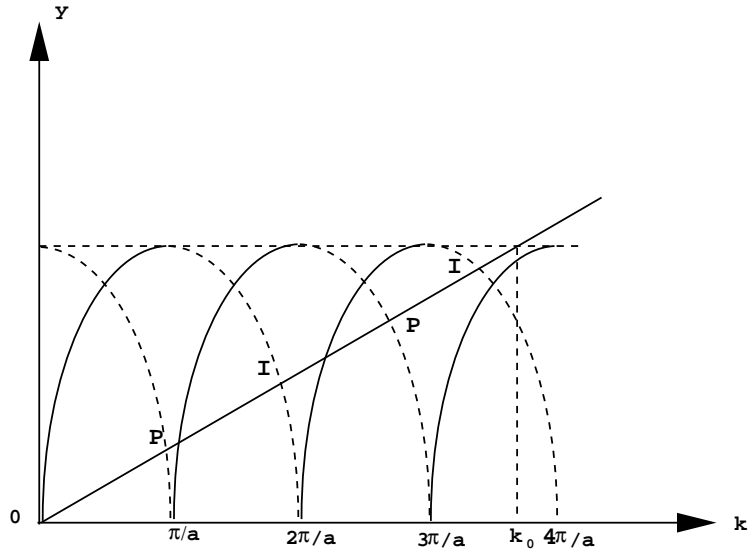


Fig. 2.4

b. Well of infinite depth

In this case it is convenient to put $V(x)$ equal to zero for $0 < x < a$ and equal to infinity for the rest of the real axis. Putting

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad (69)$$

$\psi(x)$ should be zero outside the interval $[0, a]$ and continuous at $x = 0$ and $x = a$.

For $0 \leq x \leq a$:

$$\psi(x) = Ae^{ikx} + A'e^{-ikx}. \quad (70)$$

Since $\psi(0) = 0$, one can infer that $A' = -A$, leading to:

$$\psi(x) = 2iA \sin(kx). \quad (71)$$

Moreover, $\psi(a) = 0$ and therefore

$$k = \frac{n\pi}{a}, \quad (72)$$

where n is an arbitrary positive integer. If we normalize the function (71), taking into account (72), then we obtain the stationary wavefunctions

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad (73)$$

with the energies

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}. \quad (74)$$

The quantization of the energy levels is extremely simple in this case. The stationary energies are proportional with the natural numbers squared.

2P. Problems

Problem 2.1: The attractive δ potential

Suppose we have a potential of the form:

$$V(x) = -V_0 \delta(x); \quad V_0 > 0; \quad x \in \mathfrak{R}.$$

The corresponding wavefunction $\psi(x)$ is assumed continuous.

a) Obtain the bound states ($E < 0$), if they exist, localized in this type of potential.

b) Calculate the dispersion of a plane wave falling on the δ potential and obtain the *reflection coefficient*

$$R = \frac{|\psi_{refl}|^2}{|\psi_{inc}|^2} \Big|_{x=0} ,$$

where ψ_{refl} , ψ_{inc} are the reflected and incoming waves, respectively.

Suggestion: To determine the behavior of $\psi(x)$ in $x=0$, it is better to proceed by integrating the Schrödinger equation in the interval $(-\varepsilon, +\varepsilon)$, and then to apply the limit $\varepsilon \rightarrow 0$.

Solution. a) The Schrödinger eq. is:

$$\frac{d^2}{dx^2}\psi(x) + \frac{2m}{\hbar^2}(E + V_0\delta(x))\psi(x) = 0 . \quad (75)$$

Far from the origin we have a differential eq. of the form

$$\frac{d^2}{dx^2}\psi(x) = -\frac{2mE}{\hbar^2}\psi(x). \quad (76)$$

Consequently, the wavefunctions are of the form

$$\psi(x) = Ae^{-qx} + Be^{qx} \quad \text{for} \quad x > 0 \quad \text{and} \quad x < 0, \quad (77)$$

where $q = \sqrt{-2mE/\hbar^2} \in \Re$. Since $|\psi|^2$ should be \mathcal{L}^2 integrable, we cannot accept that a part of it grows exponentially. Moreover, the wavefunction should be continuous at the origin. With these conditions, we have

$$\begin{aligned} \psi(x) &= Ae^{qx}; & (x < 0), \\ \psi(x) &= Ae^{-qx}; & (x > 0). \end{aligned} \quad (78)$$

Integrating the Schrödinger eq. between $-\varepsilon$ and $+\varepsilon$, we get

$$-\frac{\hbar^2}{2m}[\psi'(\varepsilon) - \psi'(-\varepsilon)] - V_0\psi(0) = E \int_{-\varepsilon}^{+\varepsilon} \psi(x)dx \approx 2\varepsilon E\psi(0) \quad (79)$$

Introducing now the result (78) and taking into account the limit $\varepsilon \rightarrow 0$, we have

$$-\frac{\hbar^2}{2m}(-qA - qA) - V_0A = 0 , \quad (80)$$

or $E = -m(V_0^2/2\hbar^2)$ [$-\frac{V_0^2}{4}$ in units of $\frac{\hbar^2}{2m}$]. Clearly, there is a single discrete energy. The normalization constant is found to be $A = \sqrt{mV_0/\hbar^2}$. The wavefunction of the bound state will be $\psi_o = Ae^{V_0|x|/2}$, where V_0 is in $\frac{\hbar^2}{2m}$ units.

b) Take now the wavefunction of a plane wave

$$\psi(x) = Ae^{ikx}, \quad k^2 = \frac{2mE}{\hbar^2}. \quad (81)$$

It moves from the left to the right and is reflected by the potential. If B and C are the amplitudes of the reflected and transmitted waves, respectively, then we have

$$\begin{aligned} \psi(x) &= Ae^{ikx} + Be^{-ikx}; & (x < 0), \\ \psi(x) &= Ce^{ikx}; & (x > 0). \end{aligned} \quad (82)$$

The joining conditions and the relationship $\psi'(\varepsilon) - \psi'(-\varepsilon) = -f\psi(0)$ cu $f = 2mV_0/\hbar^2$ lead to

$$\begin{aligned} A + B &= C & B &= -\frac{f}{f + 2ik}A, \\ ik(C - A + B) &= -fC & C &= \frac{2ik}{f + 2ik}A. \end{aligned} \quad (83)$$

The reflection coefficient will be

$$R = \frac{|\psi_{refl}|^2}{|\psi_{inc}|^2} \Big|_{x=0} = \frac{|B|^2}{|A|^2} = \frac{m^2V_0^2}{m^2V_0^2 + \hbar^4k^2}. \quad (84)$$

If the potential is very strong ($V_0 \rightarrow \infty$), one can see that $R \rightarrow 1$, i.e., the wave is totally reflected.

The transmission coefficient, on the other hand, will be

$$T = \frac{|\psi_{trans}|^2}{|\psi_{inc}|^2} \Big|_{x=0} = \frac{|C|^2}{|A|^2} = \frac{\hbar^4k^2}{m^2V_0^2 + \hbar^4k^2}. \quad (85)$$

Again, if the potential is very strong ($V_0 \rightarrow \infty$) then $T \rightarrow 0$, i.e., the transmitted wave fades rapidly on the other side of the potential.

In addition, $R + T = 1$ as expected, which is a check of the calculation.

Problem 2.2: Particle in a 1D potential well of finite depth

Solve the 1D Schrödinger eq. for a finite depth potential well given by

$$V(x) = \begin{cases} -V_0 & \text{dacă } |x| \leq a \\ 0 & \text{dacă } |x| > a . \end{cases}$$

Consider only the bound spectrum ($E < 0$).

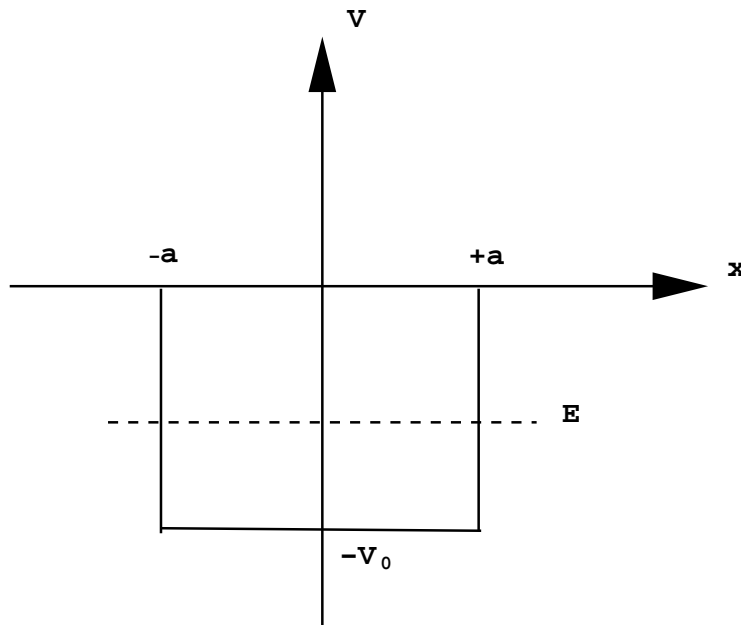


Fig. 2.5

Solution.

a) The wavefunction for $|x| < a$ and $|x| > a$.

The corresponding Schrödinger eq. is

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x) . \quad (86)$$

Defining

$$q^2 = -\frac{2mE}{\hbar^2}, \quad k^2 = \frac{2m(E + V_0)}{\hbar^2} , \quad (87)$$

we get:

- 1) for $x < -a$: $\psi_1''(x) - q^2\psi_1 = 0$, $\psi_1 = A_1e^{qx} + B_1e^{-qx}$;
- 2) for $-a \leq x \leq a$: $\psi_2''(x) + k^2\psi_2 = 0$, $\psi_2 = A_2 \cos(kx) + B_2 \sin(kx)$;
- 3) for $x > a$: $\psi_3''(x) - q^2\psi_3 = 0$, $\psi_3 = B_3e^{qx} + B_3e^{-qx}$.

b) Formulation of the boundary conditions.

The normalization of the bound states requires solutions going to zero at infinity. This means $B_1 = A_3 = 0$. Moreover, $\psi(x)$ should be continuously differentiable. All particular solutions are fixed in such a way that ψ and ψ' are continuous for that value of x corresponding to the boundary between the interior and the outside regions. The second derivative ψ'' displays the discontinuity the 'box' potential imposes. Thus we are led to:

$$\begin{aligned} \psi_1(-a) &= \psi_2(-a), & \psi_2(a) &= \psi_3(a), \\ \psi_1'(-a) &= \psi_2'(-a), & \psi_2'(a) &= \psi_3'(a). \end{aligned} \quad (88)$$

c) The eigenvalue equations.

From (88) we get four linear and homogeneous eqs for the coefficients A_1 , A_2 , B_2 and B_3 :

$$\begin{aligned} A_1e^{-qa} &= A_2 \cos(ka) - B_2 \sin(ka), \\ qA_1e^{-qa} &= A_2k \sin(ka) + B_2k \cos(ka), \\ B_3e^{-qa} &= A_2 \cos(ka) + B_2 \sin(ka), \\ -qB_3e^{-qa} &= -A_2k \sin(ka) + B_2k \cos(ka). \end{aligned} \quad (89)$$

Adding and subtracting, one gets a system of eqs. which is easier to solve:

$$\begin{aligned} (A_1 + B_3)e^{-qa} &= 2A_2 \cos(ka) \\ q(A_1 + B_3)e^{-qa} &= 2A_2k \sin(ka) \\ (A_1 - B_3)e^{-qa} &= -2B_2 \sin(ka) \\ q(A_1 - B_3)e^{-qa} &= 2B_2k \cos(ka). \end{aligned} \quad (90)$$

Assuming $A_1 + B_3 \neq 0$ and $A_2 \neq 0$, the first two eqs give

$$q = k \tan(ka), \quad (91)$$

which inserted in the last two eqs gives

$$A_1 = B_3; \quad B_2 = 0. \quad (92)$$

The result is the symmetric solution $\psi(x) = \psi(-x)$, also called of *positive parity*.

A similar calculation for $A_1 - B_3 \neq 0$ and $B_2 \neq 0$ leads to

$$q = -k \cot(ka) \quad y \quad A_1 = -B_3; \quad A_2 = 0. \quad (93)$$

The obtained wavefunction is antisymmetric, corresponding to a *negative parity*

d) Quantitative solution of the eigenvalue problem.

The equation connecting q and k , already obtained previously, gives the condition to get the eigenvalues. Using the notation

$$\xi = ka, \quad \eta = qa, \quad (94)$$

from the definition (87) we get

$$\xi^2 + \eta^2 = \frac{2mV_0a^2}{\hbar^2} = r^2. \quad (95)$$

On the other hand, using (91) and (93) we get the equations

$$\eta = \xi \tan(\xi), \quad \eta = -\xi \cot(\xi).$$

Thus, the sought energy eigenvalues can be obtained from the intersections of these two curves with the circle defined by (95) in the plane ξ - η (see fig. 2.6).

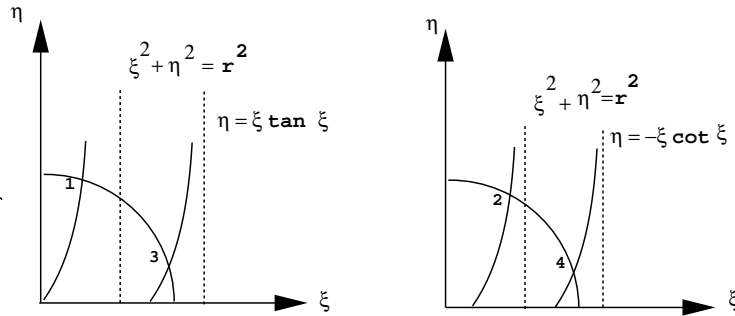


Fig. 2.6

There is at least one solution for arbitrary values of the parameter V_0 , in the positive parity case, because the tangent function passes through the

origin. For the negative parity, the radius of the circle should be greater than a certain lower bound for the two curves to intersect. Thus, the potential should have a certain depth related to a given spatial scale a and a given mass scale m , to allow for negative parity solutions. The number of energy levels grows with V_0 , a , and m . For the case in which $mVa^2 \rightarrow \infty$, the intersections are obtained from

$$\begin{aligned} \tan(ka) &= \infty &\longrightarrow & ka = \frac{2n-1}{2}\pi, \\ -\cot(ka) &= \infty &\longrightarrow & ka = n\pi, \end{aligned} \quad (96)$$

where $n = 1, 2, 3, \dots$; by combining the previous relations

$$k(2a) = n\pi. \quad (97)$$

For the energy spectrum this fact means that

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{2a} \right)^2 - V_0. \quad (98)$$

Widening the well and/or the mass of the particle m , the difference between two neighbour eigenvalues will decrease. The lowest level ($n = 1$) is not localized at $-V_0$, but slightly upper. This ‘small’ difference is called *zero point energy*.

e) The forms of the wavefunctions are shown in fig. 2.7.

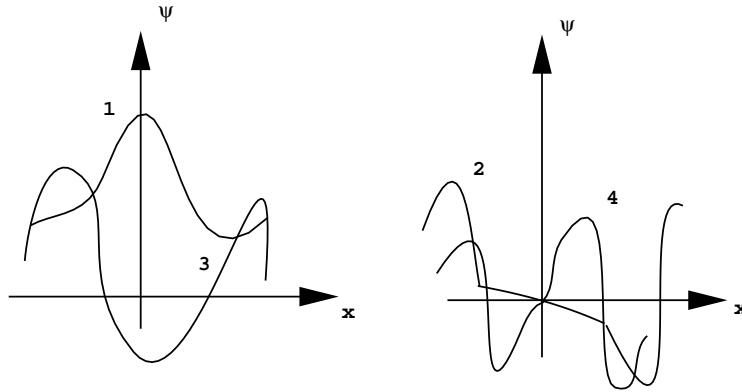


Fig. 2.7: Shapes of wave functions

Problem 2.3: Particle in 1D rectangular well of infinite depth

Solve the 1D Schrödinger eq. for a particle in a potential well of infinite depth as given by:

$$V(x) = \begin{cases} 0 & \text{for } x' < x < x' + 2a \\ \infty & \text{for } x' \geq x \text{ or } x \geq x' + 2a. \end{cases}$$

The solution in its general form is

$$\psi(x) = A \sin(kx) + B \cos(kx) , \quad (99)$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} . \quad (100)$$

Since ψ should fulfill $\psi(x') = \psi(x' + 2a) = 0$, we get:

$$A \sin(kx') + B \cos(kx') = 0 \quad (101)$$

$$A \sin[k(x' + 2a)] + B \cos[k(x' + 2a)] = 0 . \quad (102)$$

Multiplying (101) by $\sin[k(x' + 2a)]$ and (102) by $\sin(kx')$ and next subtracting the latter result from the first we get:

$$B[\cos(kx') \sin[k(x' + 2a)] - \cos[k(x' + 2a)] \sin(kx')] = 0 , \quad (103)$$

and by means of a trigonometric identity:

$$B \sin(2ak) = 0 \quad (104)$$

Multiplying (101) by $\cos[k(x' + 2a)]$ and subtracting (102) multiplied by $\cos(kx')$ leads to:

$$A[\sin(kx') \cos[k(x' + 2a)] - \sin[k(x' + 2a)] \cos(kx')] = 0 , \quad (105)$$

and by means of the same trigonometric identity:

$$A \sin[k(-2ak)] = A \sin[k(2ak)] = 0 . \quad (106)$$

Since we do not take into account the trivial solution $\psi = 0$, using (104) and (106) one has $\sin(2ak) = 0$ that takes place only if $2ak = n\pi$, with n an

integer. Accordingly, $k = n\pi/2a$ and since $k^2 = 2mE/\hbar^2$ then it comes out that the eigenvalues are given by the following expression:

$$E = \frac{\hbar^2 \pi^2 n^2}{8a^2 m} . \quad (107)$$

The energy is quantized because only for each $k_n = n\pi/2a$ one gets a well-defined energy $E_n = [n^2/2m][\pi\hbar/2a]^2$.

The general form of the solution is:

$$\psi_n = A \sin\left(\frac{n\pi x}{2a}\right) + B \cos\left(\frac{n\pi x}{2a}\right), \quad (108)$$

and it can be normalized

$$1 = \int_{x'}^{x'+2a} \psi\psi^* dx = a(A^2 + B^2), \quad (109)$$

wherefrom:

$$A = \pm \sqrt{1/a - B^2} . \quad (110)$$

Substituting this value of A in (101) one gets:

$$B = \mp \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x'}{2a}\right) , \quad (111)$$

and plugging B in (110) we get

$$A = \pm \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x'}{2a}\right) . \quad (112)$$

Using the upper signs for A and B , by substituting their values in (108) we obtain:

$$\psi_n = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi}{2a}\right)(x - x') . \quad (113)$$

Using the lower signs for A and B , one gets

$$\psi_n = -\frac{1}{\sqrt{a}} \sin\left(\frac{n\pi}{2a}\right)(x - x'). \quad (114)$$

3. ANGULAR MOMENTUM AND SPIN

Introduction

It is known from *Classical Mechanics* that the *angular momentum* \mathbf{l} for macroscopic particles is given by

$$\mathbf{l} = \mathbf{r} \times \mathbf{p}, \quad (1)$$

where \mathbf{r} and \mathbf{p} are the radius vector and the linear momentum, respectively.

However, in *Quantum Mechanics*, one can find operators of angular momentum type (OOAMT), which are not compulsory expressed only in terms of the coordinate \hat{x}_j and the momentum \hat{p}_k and acting only on the eigenfunctions in the x representation. Consequently, it is very important to settle first of all general commutation relations for the OOAMT components.

In *Quantum Mechanics* \mathbf{l} is expressed by the operator

$$\mathbf{l} = -i\hbar\mathbf{r} \times \nabla, \quad (2)$$

whose components are operators satisfying the following commutation rules

$$[l_x, l_y] = il_z, \quad [l_y, l_z] = il_x, \quad [l_z, l_x] = il_y. \quad (3)$$

Moreover, each of the components commutes with the square of the angular momentum, i.e.

$$l^2 = l_x^2 + l_y^2 + l_z^2, \quad [l_i, l^2] = 0, \quad i = 1, 2, 3. \quad (4)$$

These relations, besides being correct for the angular momentum, are fulfilled for the important OOAMT class of spin operators, which miss exact analogs in *classical mechanics*.

These commutation relations are fundamental for getting the spectra of the aforementioned operators as well as for their differential representations.

The angular momentum

For an arbitrary point of a fixed space (FS), one can introduce a function $\psi(x, y, z)$, for which let's consider two cartesian systems Σ and Σ' , where Σ' is obtained by the rotation of the z axis of Σ .

In the general case, a FS refers to a coordinate system, which is different of Σ and Σ' .

Now, let's compare the values of ψ at two points of the FS with the same coordinates (x,y,z) in Σ and Σ' , which is equivalent to the vectorial rotation

$$\psi(x', y', z') = R\psi(x, y, z) \quad (5)$$

where R is a rotation matrix in \mathbb{R}^3

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & z \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad (6)$$

Then

$$R\psi(x, y, z) = \psi(x \cos \phi - y \sin \phi, x \sin \phi + y \cos \phi, z). \quad (7)$$

On the other hand, it is important to recall that the wavefunctions are frame independent and that the transformation at rotations within the FS is achieved by means of unitary operators. Thus, to determine the form of the unitary operator $U^\dagger(\phi)$ that passes ψ to ψ' , one usually considers an infinitesimal rotation $d\phi$, keeping only the linear terms in $d\phi$ when one expands ψ' in Taylor series in the neighborhood of x

$$\begin{aligned} \psi(x', y', z') &\approx \psi(x + yd\phi, xd\phi + y, z), \\ &\approx \psi(x, y, z) + d\phi \left(y \frac{\partial \psi}{\partial x} - x \frac{\partial \psi}{\partial y} \right), \\ &\approx (1 - id\phi l_z) \psi(x, y, z), \end{aligned} \quad (8)$$

where we have used the notation¹

$$l_z = \hbar^{-1}(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x). \quad (9)$$

As one will see later, this corresponds to the projection operator onto z of the angular momentum according to the definition (2) unless the factor \hbar^{-1} . In this way, the rotations of finite angle ϕ can be represented as exponentials of the form

$$\psi(x', y', z) = e^{il_z\phi} \psi(x, y, z), \quad (10)$$

where

$$\hat{U}^\dagger(\phi) = e^{il_z\phi}. \quad (11)$$

¹The proof of (8) is displayed as problem 3.1

In order to reassert the concept of rotation, we will consider it in a more general approach with the help of the vectorial operator $\hat{\vec{A}}$ acting on ψ , assuming that \hat{A}_x , \hat{A}_y , \hat{A}_z have the same form in Σ and Σ' , that is, the mean values of $\hat{\vec{A}}$ as calculated in Σ and Σ' should be equal when they are seen from the FS

$$\begin{aligned} & \int \psi^*(\vec{r}')(\hat{A}_x \hat{i}' + \hat{A}_y \hat{j}' + \hat{A}_z \hat{k}')\psi(\vec{r}') d\vec{r}' \\ &= \int \psi^*(\vec{r})(\hat{A}_x \hat{i} + \hat{A}_y \hat{j} + \hat{A}_z \hat{k})\psi(\vec{r}) d\vec{r}, \end{aligned} \quad (12)$$

where

$$\hat{i}' = \hat{i} \cos \phi + \hat{j} \sin \phi, \quad \hat{j}' = \hat{i} \sin \phi + \hat{j} \cos \phi, \quad \hat{k}' = \hat{k}. \quad (13)$$

Thus, by combining (10), (12) and (13) we get

$$\begin{aligned} e^{il_z \phi} \hat{A}_x e^{-il_z \phi} &= \hat{A}_x \cos \phi - \hat{A}_y \sin \phi, \\ e^{il_z \phi} \hat{A}_y e^{-il_z \phi} &= \hat{A}_x \sin \phi + \hat{A}_y \cos \phi, \\ e^{il_z \phi} \hat{A}_z e^{-il_z \phi} &= \hat{A}_z. \end{aligned} \quad (14)$$

Again, considering infinitesimal rotations and expanding the left hand sides in (14), one can determine the commutation relations of \hat{A}_x , \hat{A}_y and \hat{A}_z with \hat{l}_z

$$[l_z, A_x] = iA_y, \quad [l_z, A_y] = -iA_x, \quad [l_z, A_z] = 0, \quad (15)$$

and similarly for l_x and l_y .

The basic conditions to obtain these commutation relations are

- ★ The eigenfunctions transform as in (7) when $\Sigma \rightarrow \Sigma'$.
- ★ The components \hat{A}_x , \hat{A}_y , \hat{A}_z have the same form in Σ and Σ' .
- ★ The kets corresponding to the mean values of \hat{A} in Σ and Σ' coincide (are the same) for a FS observer.

One can also use another representation in which $\psi(x, y, z)$ does not change when $\Sigma \rightarrow \Sigma'$ and the vectorial operators transform as ordinary vectors. In order to pass to such a representation when we rotate by ϕ around z one makes use of the operator $\hat{U}(\phi)$, that is

$$e^{il_z\phi}\psi'(x, y, z) = \psi(x, y, z), \quad (16)$$

and therefore

$$e^{-il_z\phi}\vec{\hat{A}}e^{il_z\phi} = \vec{\hat{A}}. \quad (17)$$

Using the relationships (14) we obtain

$$\begin{aligned} \hat{A}'_x &= \hat{A}_x \cos \phi + \hat{A}_y \sin \phi = e^{-il_z\phi} \hat{A}_x e^{il_z\phi}, \\ \hat{A}'_y &= -\hat{A}_x \sin \phi + \hat{A}_y \cos \phi = e^{-il_z\phi} \hat{A}_y e^{il_z\phi}, \\ \hat{A}'_z &= e^{-il_z\phi} \hat{A}_z e^{il_z\phi}. \end{aligned} \quad (18)$$

Since the transformations of the new representation are performed by means of unitary operators, the commutation relations do not change.

Remarks

★ The operator \hat{A}^2 is invariant at rotations, that is

$$e^{-il_z\phi} \hat{A}^2 e^{il_z\phi} = \hat{A}'^2 = \hat{A}^2. \quad (19)$$

★ It follows that

$$[\hat{l}_i, \hat{A}^2] = 0. \quad (20)$$

★ If the Hamiltonian operator is of the form

$$\hat{H} = \frac{1}{2m} \hat{p}^2 + U(|\vec{r}|), \quad (21)$$

then it remains invariant under rotations in any axis passing through the coordinate origin

$$[\hat{l}_i, \hat{H}] = 0, \quad (22)$$

where \hat{l}_i are integrals of the motion.

Definition

If \hat{A}_i are the components of a vectorial operator acting on a wavefunction depending only on the coordinates and if there are operators \hat{l}_i that satisfy the following commutation relations

$$[\hat{l}_i, \hat{A}_j] = i\varepsilon_{ijk} \hat{A}_k, \quad [\hat{l}_i, \hat{l}_j] = i\varepsilon_{ijk} \hat{l}_k, \quad (23)$$

then \hat{l}_i are known as the components of the angular momentum operator and we can infer from (20) and (23) that

$$[\hat{l}_i, \hat{l}^2] = 0. \quad (24)$$

Consequently the three operatorial components associated to the components of a classical angular momentum satisfy commutation relations of the type (23), (24). Moreover, one can prove that these relations lead to specific geometric properties of the rotations in a 3D euclidean space. This takes place if we adopt a more general point of view by defining an angular momentum operator \mathbf{J} (we shall not use the hat symbol for simplicity of writing) as any set of three observables J_x , J_y și J_z which fulfill the commutation relations

$$[J_i, J_j] = i\varepsilon_{ijk}J_k. \quad (25)$$

Moreover, let us introduce the operator

$$\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2, \quad (26)$$

the scalar square of the angular momentum \mathbf{J} . This operator is hermitic because J_x , J_y and J_z are hermitic and it is easy to show that \mathbf{J}^2 commutes with the three components of \mathbf{J}

$$[\mathbf{J}^2, J_i] = 0. \quad (27)$$

Since \mathbf{J}^2 commutes with each of the components it follows that there is a complete system of eigenfunctions, i.e.

$$\mathbf{J}^2\psi_{\gamma\mu} = f(\gamma^2)\psi_{\gamma\mu}, \quad J_i\psi_{\gamma\mu} = g(\mu)\psi_{\gamma\mu}, \quad (28)$$

where, as it will be shown in the following, the eigenfunctions depend on two subindices, which will be determined together with the form of the functions $f(\gamma)$ and $g(\mu)$. The operators J_i and J_k ($i \neq k$) do not commute, i.e. they do not have common eigenfunctions. For physical and mathematical reasons, we are interested to determine the common eigenfunctions of \mathbf{J}^2 and J_z , that is, we shall take $i = z$ in (28).

Instead of using the components J_x and J_y of the angular momentum \mathbf{J} , it is more convenient to work with the following linear combinations

$$J_+ = J_x + iJ_y, \quad J_- = J_x - iJ_y. \quad (29)$$

Contrary to the operators a and a^\dagger of the harmonic oscillator (see chapter 5), these operators are not hermitic, they are only adjunct to each other. The following properties are easy to prove

$$[J_z, J_\pm] = \pm J_\pm, \quad [J_+, J_-] = 2J_z, \quad (30)$$

$$[J^2, J_+] = [J^2, J_-] = [J^2, J_z] = 0. \quad (31)$$

$$J_z(J_\pm \psi_{\gamma\mu}) = \{J_\pm J_z + [J_z, J_\pm]\} \psi_{\gamma\mu} = (\mu \pm 1)(J_\pm \psi_{\gamma\mu}). \quad (32)$$

Therefore $J_\pm \psi_{\gamma\mu}$ are eigenfunctions of J_z corresponding to the eigenvalues $\mu \pm 1$, that is these functions are identical up to the constant factors α_μ and β_μ (to be determined)

$$\begin{aligned} J_+ \psi_{\gamma\mu-1} &= \alpha_\mu \psi_{\gamma\mu}, \\ J_- \psi_{\gamma\mu} &= \beta_\mu \psi_{\gamma\mu-1}. \end{aligned} \quad (33)$$

On the other hand

$$\alpha_\mu^* = (J_+ \psi_{\gamma\mu-1}, \psi_{\gamma\mu}) = (\psi_{\gamma\mu-1} J_- \psi_{\gamma\mu}) = \beta_\mu. \quad (34)$$

Therefore, taking a phase of the type e^{ia} (where a is real) for the function $\psi_{\gamma\mu}$ one can put α_μ real and equal to β_μ , which means

$$J_+ \psi_{\gamma,\mu-1} = \alpha_\mu \psi_{\gamma\mu}, \quad J_- \psi_{\gamma\mu} = \alpha_\mu \psi_{\gamma,\mu-1}, \quad (35)$$

and therefore

$$\begin{aligned} \gamma &= (\psi_{\gamma\mu}, [J_x^2 + J_y^2 + J_z^2] \psi_{\gamma\mu}) = \mu^2 + a + b, \\ a &= (\psi_{\gamma\mu}, J_x^2 \psi_{\gamma\mu}) = (J_x \psi_{\gamma\mu}, J_x \psi_{\gamma\mu}) \geq 0, \\ b &= (\psi_{\gamma\mu}, J_y^2 \psi_{\gamma\mu}) = (J_y \psi_{\gamma\mu}, J_y \psi_{\gamma\mu}) \geq 0. \end{aligned} \quad (36)$$

The normalization constant cannot be negative. This implies

$$\gamma \geq \mu^2, \quad (37)$$

for a fixed γ ; thus, μ has both superior and inferior limits (it takes values in a finite interval).

Let Λ and λ be these limits, respectively, for a given γ

$$J_+ \psi_{\gamma\Lambda} = 0, \quad J_- \psi_{\gamma\lambda} = 0. \quad (38)$$

Using the following operatorial identities

$$\begin{aligned} J_- J_+ &= \mathbf{J}^2 - J_z^2 + J_z = \mathbf{J}^2 - J_z(J_z - 1), \\ J_+ J_- &= \mathbf{J}^2 - J_z^2 + J_z = \mathbf{J}^2 - J_z(J_z + 1), \end{aligned} \quad (39)$$

acting on $\psi_{\gamma\Lambda}$ as well as on $\psi_{\gamma\lambda}$ one gets

$$\begin{aligned} \gamma - \Lambda^2 - \Lambda &= 0, \\ \gamma - \lambda^2 + \lambda &= 0, \\ (\lambda - \lambda + 1)(\lambda + \lambda) &= 0. \end{aligned} \quad (40)$$

In addition,

$$\Lambda \geq \lambda \rightarrow \Lambda = -\lambda = J \rightarrow \gamma = J(J + 1). \quad (41)$$

For a given γ the projection μ of the momentum takes $2J + 1$ values that differ by unity, from J to $-J$. Therefore, the difference $\Lambda - \lambda = 2J$ should be an integer and consequently the eigenvalues of J_z that are labelled by m are integer

$$m = k, \quad k = 0, \pm 1, \pm 2, \dots, \quad (42)$$

or half-integer

$$m = k + \frac{1}{2}, \quad k = 0, \pm 1, \pm 2, \dots. \quad (43)$$

A state having a given $\gamma = J(J + 1)$ presents a degeneration of order $g = 2J + 1$ with regard to the eigenvalues m (this is so because J_i, J_k commute with J^2 but do not commute between themselves).

By a ‘‘state of angular momentum J ’’ one usually understands a state of $\gamma = J(J + 1)$ having the maximum projection of its momentum, i.e. J . Quite used notations for angular momentum states are ψ_{jm} and the Dirac ket one $|jm\rangle$.

Let us now obtain the matrix elements of J_x, J_y in the representation in which J^2 and J_z are diagonal. In this case, one obtains from (35) and (39) the following relations

$$\begin{aligned} J_- J_+ \psi_{jm-1} &= \alpha_m J_- \psi_{jm} = \alpha_m \psi_{jm-1}, \\ J(J + 1) - (m - 1)^2 - (m - 1) &= \alpha_m^2, \\ \alpha_m &= \sqrt{(J + m)(J - m + 1)}. \end{aligned} \quad (44)$$

Combining (44) and (35) leads to

$$J_+ \psi_{jm-1} = \sqrt{(J+m)(J-m+1)} \psi_{jm} . \quad (45)$$

It follows that the matrix element of J_+ is

$$\langle jm | J_+ | jm-1 \rangle = \sqrt{(J+m)(J-m+1)} \delta_{nm}, \quad (46)$$

and analogously

$$\langle jn | J_- | jm \rangle = -\sqrt{(J+m)(J-m+1)} \delta_{nm-1} . \quad (47)$$

Finally, from the definitions (29) for J_+ , J_- one easily gets

$$\begin{aligned} \langle jm | J_x | jm-1 \rangle &= \frac{1}{2} \sqrt{(J+m)(J-m+1)}, \\ \langle jm | J_y | jm-1 \rangle &= \frac{-i}{2} \sqrt{(J+m)(J-m+1)}. \end{aligned} \quad (48)$$

Partial conclusions

α Properties of the eigenvalues of \mathbf{J} and J_z

If $j(j+1)\hbar^2$ and $m\hbar$ are eigenvalues of \mathbf{J} and J_z associated to the eigenvectors $|kjm\rangle$, then j and m satisfy the inequality

$$-j \leq m \leq j.$$

β Properties of the vector $J_- |kjm\rangle$

Let $|kjm\rangle$ be an eigenvector of \mathbf{J}^2 and J_z with the eigenvalues $j(j+1)\hbar^2$ and $m\hbar$

- (i) If $m = -j$, then $J_- |kj - j\rangle = 0$.
- (ii) If $m > -j$, then $J_- |kjm\rangle$ is a nonzero eigenvector of J^2 and J_z with the eigenvalues $j(j+1)\hbar^2$ and $(m-1)\hbar$.

γ Properties of the vector $J_+ |kjm\rangle$

Let $|kjm\rangle$ be a (ket) eigenvector of \mathbf{J}^2 and J_z for the eigenvalues $j(j+1)\hbar^2$ and $m\hbar$

- ★ If $m = j$, then $J_+ |kjm\rangle = 0$.
- ★ If $m < j$, then $J_+ |kjm\rangle$ is a nonzero eigenvector of \mathbf{J}^2 and J_z with the eigenvalues $j(j+1)\hbar^2$ and $(m+1)\hbar$

δ Consequences of the previous properties

$$\begin{aligned} J_z|kjm\rangle &= m\hbar|kjm\rangle, \\ J_+|kjm\rangle &= m\hbar\sqrt{j(j+1)-m(m+1)}|kjm+1\rangle, \\ J_-|kjm\rangle &= m\hbar\sqrt{j(j+1)-m(m-1)}|kjm+1\rangle. \end{aligned}$$

Applications of the orbital angular momentum

Until now we have considered those properties of the angular momentum that could be derived only from the commutation relations. Let us go back to the orbital momentum \mathbf{l} of a particle without intrinsic rotation and let us examine how one can apply the theory of the previous section in the important particular case

$$[\hat{l}_i, \hat{p}_j] = i\varepsilon_{ijk}\hat{p}_k. \quad (49)$$

First, \hat{l}_z and \hat{p}_j have a common system of eigenfunctions. On the other hand, the Hamiltonian of a free particle

$$\hat{H} = \left(\frac{\hat{\mathbf{p}}}{\sqrt{2m}} \right)^2,$$

being the square of a vectorial operator has a complete system of eigenfunctions with \hat{L}^2 and \hat{l}_z . In addition, this implies that the free particle can be found in a state of well-defined E , l , and m .

Eigenvalues and eigenfunctions of \mathbf{l}^2 and \mathbf{l}_z

It is more convenient to work in spherical coordinates because, as we will see, various angular momentum operators act only on the angle variables θ , ϕ and not on r . Thus, instead of describing r by its cartesian components x , y , z we determine the arbitrary point M of vector radius \mathbf{r} by the spherical 3D coordinates

$$x = r \cos \phi \sin \theta, \quad y = r \sin \phi \sin \theta, \quad z = r \cos \theta, \quad (50)$$

where

$$r \geq 0, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \phi \leq 2\pi.$$

Let $\Phi(r, \theta, \phi)$ and $\Phi'(r, \theta, \phi)$ be the wavefunctions of a particle in Σ and Σ' , respectively, in which the infinitesimal rotation is given by $\delta\alpha$ around the z axis

$$\begin{aligned}\Phi'(r, \theta, \phi) &= \Phi(r, \theta, \phi + \delta\alpha), \\ &= \Phi(r, \theta, \phi) + \delta\alpha \frac{\partial \Phi}{\partial \phi},\end{aligned}\quad (51)$$

or

$$\Phi'(r, \theta, \phi) = (1 + i\hat{l}_z \delta\alpha) \Phi(r, \theta, \phi). \quad (52)$$

It follows that

$$\frac{\partial \Phi}{\partial \phi} = i\hat{l}_z \Phi, \quad \hat{l}_z = -i \frac{\partial}{\partial \phi}. \quad (53)$$

For an infinitesimal rotation in x

$$\begin{aligned}\Phi'(r, \theta, \phi) &= \Phi + \delta\alpha \left(\frac{\partial \Phi}{\partial \theta} \frac{\partial \theta}{\partial \alpha} + \frac{\partial \Phi}{\partial \phi} \frac{\partial \phi}{\partial \alpha} \right), \\ &= (1 + i\hat{l}_x \delta\alpha) \Phi(r, \theta, \phi),\end{aligned}\quad (54)$$

but in this rotation

$$z' = z + y\delta\alpha; \quad z' = z + y\delta\alpha; \quad x' = x \quad (55)$$

and from (50) one gets

$$\begin{aligned}r \cos(\theta + d\theta) &= r \cos \theta + r \sin \theta \sin \phi \delta\alpha, \\ r \sin \phi \sin(\theta + d\theta) &= r \sin \theta \sin \phi + r \sin \theta \sin \phi - r \cos \theta \delta\alpha,\end{aligned}\quad (56)$$

i.e.

$$\sin \theta d\theta = \sin \theta \sin \phi \delta\alpha \rightarrow \frac{d\theta}{d\alpha} = -\sin \phi, \quad (57)$$

and

$$\begin{aligned}\cos \theta \sin \phi d\theta + \sin \theta \cos \phi d\phi &= -\cos \theta \delta\alpha, \\ \cos \phi \sin \theta \frac{d\phi}{d\alpha} &= -\cos \theta - \cos \theta \sin \phi \frac{d\theta}{d\alpha}.\end{aligned}\quad (58)$$

Substituting (57) in (56) leads to

$$\frac{d\phi}{d\alpha} = -\cot \theta \cos \phi. \quad (59)$$

With (56) and (58) substituted in (51) and comparing the right hand sides of (51) one gets

$$\hat{l}_x = i \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right). \quad (60)$$

For the rotation in y , the result is similar

$$\hat{l}_y = i \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right). \quad (61)$$

Using \hat{l}_x , \hat{l}_y one can also obtain \hat{l}_\pm , \hat{l}^2

$$\begin{aligned} \hat{l}_\pm &= \exp \left[\pm i \phi \left(\pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) \right], \\ \hat{l}^2 &= \hat{l}_- \hat{l}_+ + \hat{l}^2 + \hat{l}_z, \\ &= - \left[\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \right]. \end{aligned} \quad (62)$$

From (62) one can see that \hat{l}^2 is identical up to a constant to the angular part of the Laplace operator at a fixed radius

$$\nabla^2 f = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (63)$$

The eigenfunctions of l_z

$$\begin{aligned} \hat{l}_z \Phi_m &= m \Phi = -i \frac{\partial \Phi_m}{\partial \phi}, \\ \Phi_m &= \frac{1}{\sqrt{2\pi}} e^{im\phi}. \end{aligned} \quad (64)$$

Hermiticity conditions of \hat{l}_z

$$\int_0^{2\pi} f^* \hat{l}_z g d\phi = \left(\int_0^{2\pi} g^* \hat{l}_z f d\phi \right)^* + f^* g(2\pi) - f^* g(0). \quad (65)$$

It follows that \hat{l}_z is hermitic in the class of functions for which

$$f^* g(2\pi) = f^* g(0). \quad (66)$$

The eigenfunctions Φ_m of \hat{l}_z belong to the integrable class $\mathcal{L}^2(0, 2\pi)$ and they fulfill (66), as it happens for any function that can be expanded in $\Phi_m(\phi)$

$$\begin{aligned} F(\phi) &= \sum_k^k a_k e^{ik\phi}, & k = 0, \pm 1, \pm 2, \dots, \\ G(\phi) &= \sum_k^k b_k e^{ik\phi}, & k = \pm 1/2, \pm 3/2, \pm 5/2 \dots, \end{aligned} \quad (67)$$

with k only integers or half-integers, but not for combinations of $F(\phi)$ and $G(\phi)$. The correct choice of m is based on the common eigenfunctions of \hat{l}_z and \hat{l}^2 .

Spherical harmonics

In the $\{\vec{\mathbf{r}}\}$ representation, the eigenfunctions associated to the eigenvalues $l(l+1)\hbar^2$ of \mathbf{I}^2 and $m\hbar$ of l_z are solutions of the partial differential equations

$$\begin{aligned} -\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(r, \theta, \phi) &= l(l+1)\hbar^2\psi(r, \theta, \phi), \\ -i\frac{\partial}{\partial\phi}\psi(r, \theta, \phi) &= m\hbar\psi(r, \theta, \phi). \end{aligned} \quad (68)$$

Taking into account that the general results presented above can be applied to the orbital momentum, we infer that l can be an integer or half-integer and that, for fixed l , m can only take the values

$$-l, -l+1, \dots, l-1, l.$$

In (68), r is not present in the differential operator, so that it can be considered as a parameter. Thus, considering only the dependence on θ , ϕ of ψ , one uses the notation $Y_{lm}(\theta, \phi)$ for these common eigenfunctions of \mathbf{I}^2 and l_z , corresponding to the eigenvalues $l(l+1)\hbar^2, m\hbar$. They are known as spherical harmonics

$$\begin{aligned} \mathbf{I}^2 Y_{lm}(\theta, \phi) &= l(l+1)\hbar^2 Y_{lm}(\theta, \phi), \\ l_z Y_{lm}(\theta, \phi) &= m\hbar Y_{lm}(\theta, \phi). \end{aligned} \quad (69)$$

For more rigorousness, one should introduce one more index in order to distinguish among the various solutions of (69) corresponding to the same (l, m) pairs for particles with spin. If the spin is not taken into account,

these equations have a unique solution (up to a constant factor) for each allowed pair of (l, m) ; this is so because the subindices l, m are sufficient in this context. The solutions $Y_{lm}(\theta, \phi)$ have been found by the method of the separation of variables in spherical variables (see also the chapter *The hydrogen atom*)

$$\psi_{lm}(r, \theta, \phi) = f(r)\psi_{lm}(\theta, \phi), \quad (70)$$

where $f(r)$ is a function of r , which looks as an integration constant from the viewpoint of the partial differential equations in (68). The fact that $f(r)$ is arbitrary proves that \mathbf{L}^2 and l_z do not form a complete set of observables² in the space ε_r ³ of functions of $\vec{r}(r, \theta, \phi)$.

In order to normalize $\psi_{lm}(r, \theta, \phi)$, it is convenient to normalize $Y_{lm}(\theta, \phi)$ and $f(r)$ separately

$$\int_0^{2\pi} d\phi \int_0^\pi \sin\theta |\psi_{lm}(\theta, \phi)|^2 d\theta = 1, \quad (71)$$

$$\int_0^\infty r^2 |f(r)|^2 dr = 1. \quad (72)$$

The values of the pair (l, m)

(α): l, m should be integers

Using $l_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$, we can write (69) as follows

$$\frac{\hbar}{i} \frac{\partial}{\partial \phi} Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi). \quad (73)$$

Thus,

$$Y_{lm}(\theta, \phi) = F_{lm}(\theta, \phi) e^{im\phi}. \quad (74)$$

If $0 \leq \phi < 2\pi$, then we should tackle the condition of covering all space according to the requirement of dealing with a function continuous in any angular zone, i.e. că

$$Y_{lm}(\theta, \phi = 0) = Y_{lm}(\theta, \phi = 2\pi), \quad (75)$$

implying

$$e^{im\pi} = 1. \quad (76)$$

²By definition, the hermitic operator A is an observable if the orthogonal system of eigenvectors form a base in the space of states.

³Each quantum state of a particle is characterized by a vectorial state belonging to an abstract vectorial space ε_r .

As has been seen, m is either an integer or a half-integer; for the application to the orbital momentum, m should be an integer. ($e^{2im\pi}$ would be -1 if m is a half-integer).

(β): For a given value of l , all the corresponding Y_{lm} can be obtained by algebraic means using

$$l_+ Y_{ll}(\theta, \phi) = 0, \quad (77)$$

which combined with eq. (62) for l_+ leads to

$$\left(\frac{d}{d\theta} - l \cot \theta \right) F_{ll}(\theta) = 0. \quad (78)$$

This equation can be immediately integrated if we notice the relationship

$$\cot \theta d\theta = \frac{d(\sin \theta)}{\sin \theta}. \quad (79)$$

Its general solution is

$$F_{ll} = c_l (\sin \theta)^l, \quad (80)$$

where c_l is a normalization constant.

It follows that for any positive or zero value of l , there is a function $Y_{ll}(\theta, \phi)$, which up to a constant factor is

$$Y^{ll}(\theta, \phi) = c_l (\sin \theta)^l e^{il\phi}. \quad (81)$$

Using repeatedly the action of l_- , one can build the whole set of functions $Y_{l-1}(\theta, \phi), \dots, Y_{l_0}(\theta, \phi), \dots, Y_{l-l}(\theta, \phi)$. Next, we look at the way in which these functions can be put into correspondence with the eigenvalue pair $l(l+1)\hbar, m\hbar$ (where l is an arbitrary positive integer such that $l \leq m \leq l$). Using (78), we can make the conclusion that any other eigenfunction $Y_{lm}(\theta, \phi)$ can be unambiguously obtained from Y_{ll} .

Properties of spherical harmonics

α Iterative relationships

From the general results of this chapter, we have

$$l_{\pm} Y_{lm}(\theta, \phi) = \hbar \sqrt{l(l+1) - m(m \pm 1)} Y_{l, m \pm 1}(\theta, \phi). \quad (82)$$

Using (62) for l_{\pm} and the fact that $Y_{lm}(\theta, \phi)$ is the product of a θ -dependent function and $e^{\pm i\phi}$, one gets

$$e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} - m \cot \theta \right) Y_{lm}(\theta, \phi) = \sqrt{l(l+1) - m(m \pm 1)} Y_{lm \pm 1}(\theta, \phi) \quad (83)$$

β Orthonormalization and completeness relationships

Equation (68) determines the spherical harmonics only up to a constant factor. We shall now choose this factor such that to have the orthonormalization of $Y_{lm}(\theta, \phi)$ (as functions of the angular variables θ, ϕ)

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'} \delta_{m'm}. \quad (84)$$

In addition, any continuous function of θ, ϕ can be expressed by means of the spherical harmonics as follows

$$f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l c_{lm} Y_{lm}(\theta, \phi), \quad (85)$$

where

$$c_{lm} = \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta Y_{lm}^*(\theta, \phi) f(\theta, \phi). \quad (86)$$

The results (85), (86) are consequences of defining the spherical harmonics as an orthonormalized and complete base in the space ε_{Ω} of functions of θ, ϕ . The completeness relationship is

$$\begin{aligned} \sum_{l=0}^{\infty} \sum_{m=l}^l Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi) &= \delta(\cos \theta - \cos \theta') \delta(\phi, \phi), \\ &= \frac{1}{\sin \theta} \delta(\theta - \theta') \delta(\phi, \phi). \end{aligned} \quad (87)$$

The ‘function’ $\delta(\cos \theta - \cos \theta')$ occurs because the integral over the variable θ is performed by using the differential element $\sin \theta d\theta = -d(\cos \theta)$.

Parity operator \mathcal{P} for spherical harmonics

The behavior of \mathcal{P} in 3D is rather close to that in 1D. When it is applied to a function of cartesian coordinates $\psi(x, y, z)$ changes the sign of each of the coordinates

$$\mathcal{P}\psi(x, y, z) = \psi(-x, -y, -z). \quad (88)$$

\mathcal{P} has the properties of a hermitic operator, being also a unitary operator, as well as a projector since \mathcal{P}^2 is an identity operator

$$\begin{aligned}\langle\psi(\mathbf{r})|\mathcal{P}|\psi(\mathbf{r})\rangle &= \langle\psi(\mathbf{r})|\psi(-\mathbf{r})\rangle = \langle\psi(-\mathbf{r})|\psi(\mathbf{r}')\rangle, \\ \mathcal{P}^2|\mathbf{r}\rangle &= \mathcal{P}(\mathcal{P}|\mathbf{r}\rangle) = \mathcal{P}|-\mathbf{r}\rangle = |\mathbf{r}\rangle.\end{aligned}\quad (89)$$

Therefore

$$\mathcal{P}^2 = \hat{1}, \quad (90)$$

for which the eigenvalues are $P = \pm 1$. The eigenfunctions are called even if $P = 1$ and odd if $P = -1$. In nonrelativistic quantum mechanics, the operator \hat{H} for a conservative system is invariant with regard to discrete unitary transformations, i.e.

$$\mathcal{P}\hat{H}\mathcal{P} = \mathcal{P}^{-1}\hat{H}\mathcal{P} = \hat{H}. \quad (91)$$

Thus, \hat{H} commutes with \mathcal{P} and the parity of the state is a constant of the motion. In addition, \mathcal{P} commutes with the operators \hat{l} and \hat{l}_\pm

$$[\mathcal{P}, \hat{l}_i] = 0, \quad [\mathcal{P}, \hat{l}_\pm] = 0. \quad (92)$$

Because of all these properties, one can have the important class of wave functions which are common eigenfunctions of the triplet \mathcal{P} , \hat{l}^2 and \hat{l}_z . It follows from (92) that the parities of the states which differ only in \hat{l}_z coincide. In this way, one can identify the parity of a particle of definite orbital angular momentum \hat{l} .

In spherical coordinates, we shall consider the following change of variables

$$r \rightarrow r, \quad \theta \rightarrow \pi - \theta \quad \phi \rightarrow \pi + \phi. \quad (93)$$

Thus, using a standard base in the space of wavefunctions of a particle without 'intrinsic rotation', the radial part of the base functions $\psi_{klm}(\vec{r})$ is not changed by the parity operator. Only the spherical harmonics will change. From the trigonometric standpoint, the transformations (93) are as follows

$$\sin(\pi - \theta) \rightarrow \sin \theta, \quad \cos(\pi - \theta) \rightarrow -\cos \theta \quad e^{im(\pi + \phi)} \rightarrow (-1)^m e^{im\phi} \quad (94)$$

leading to the following transformation of the function $Y_l(\theta, \phi)$

$$Y_l(\phi - \theta, \pi + \phi) = (-1)^l Y_l(\theta, \phi). \quad (95)$$

From (95) it follows that the parity of Y_{ll} is $(-1)^l$. On the other hand, l_- (as well as l_+ is invariant to the transformations

$$\frac{\partial}{\partial(\pi-\theta)} \rightarrow -\frac{\partial}{\partial\theta}, \quad \frac{\partial}{\partial(\pi+\phi)} \rightarrow \frac{\partial}{\partial\phi} \quad e^{i(\pi+\phi)} \rightarrow -e^{i\phi} \quad \cot(\pi-\theta) \rightarrow -\cot\theta. \quad (96)$$

In other words, l_{\pm} are even. Therefore, we infer that the parity of any spherical harmonics is $(-1)^l$, that is it is invariant under azimuthal changes

$$Y_{lm}(\phi-\theta, \pi+\phi) = (-1)^l Y_{lm}(\theta, \phi). \quad (97)$$

In conclusion, the spherical harmonics are functions of well-defined parity, which is independent of m , even if l is even and odd if l is odd.

The spin operator

Some particles have not only orbital angular momentum with regard to external axes but also a *proper momentum*, which is known as *spin* denoted here by \hat{S} . This operator is not related to normal rotation with respect to ‘real’ axes in space, although it fulfills commutation relations of the same type as those of the orbital angular momentum, i.e.

$$[\hat{S}_i, \hat{S}_j] = i\varepsilon_{ijk}\hat{S}_k, \quad (98)$$

together with the following properties

- (1). For the spin operator all the formulas of the orbital angular momentum from (23) till (48) are satisfied.
- (2). The spectrum of the spin projections is a sequence of either integer or half-integer numbers differing by unity.
- (3). The eigenvalues of \hat{S}^2 are the following

$$\hat{S}^2\psi_s = S(S+1)\psi_s. \quad (99)$$

- (4). For a given S , the components S_z can take only $2S+1$ values, from $-S$ to $+S$.
- (5). Besides the usual dependence on \vec{r} and/or \vec{p} , the eigenfunctions of the particles with spin depend also on a discrete variable, (characteristic for the spin) σ denoting the projection of the spin on the z axis.

- (6). The wavefunctions $\psi(\vec{r}, \sigma)$ of a particle with spin can be expanded in eigenfunctions of given spin projection S_z , i.e.

$$\psi(\vec{r}, \sigma) = \sum_{\sigma=-S}^S \psi_\sigma(\vec{r})\chi(\sigma), \quad (100)$$

where $\psi_\sigma(\vec{r})$ is the orbital part and $\chi(\sigma)$ is the spinorial part.

- (7). The spin functions (the spinors) $\chi(\sigma_i)$ are orthogonal for any pair $\sigma_i \neq \sigma_k$. The functions $\psi_\sigma(\vec{r})\chi(\sigma)$ in the sum of (100) are the components of a wavefunction of a particle with spin.
- (8). The function $\psi_\sigma(\vec{r})$ is called the orbital part of the spinor, or shortly orbital.
- (9) The normalization of the spinors is done as follows

$$\sum_{\sigma=-S}^S \|\psi_\sigma(\vec{r})\| = 1. \quad (101)$$

The commutation relations allow to determine the explicit form of the spin operators (spin matrices) acting in the space of the eigenfunctions of definite spin projections.

Many ‘elementary’ particles, such as the electron, the neutron, the proton, etc. have a spin of $1/2$ (in units of \hbar) and therefore the projection of their spin takes only two values, ($S_z = \pm 1/2$ (in \hbar units), respectively. They belong to the fermion class because of their statistics when they form many-body systems.

On the other hand, the matrices S_x , S_y , S_z in the space of \hat{S}^2 , \hat{S}_z are

$$\begin{aligned} S_x &= \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, & S_y &= \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \\ S_z &= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, & S^2 &= \frac{3}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \end{aligned} \quad (102)$$

Definition of the Pauli matrices

The matrices

$$\sigma_i = 2S_i \quad (103)$$

are called the Pauli matrices. They are hermitic and have the same characteristic eq.

$$\lambda^2 - 1 = 0. \quad (104)$$

Therefore, the eigenvalues of σ_x , σ_y and σ_z are

$$\lambda = \pm 1. \quad (105)$$

The algebra of these matrices is the following

$$\sigma_i^2 = \hat{I}, \quad \sigma_k \sigma_j = -\sigma_j \sigma_k = i\sigma_z, \quad \sigma_j \sigma_k = i \sum_l \varepsilon_{jkl} \sigma_l + \delta_{jk} I. \quad (106)$$

In the case in which the spin system has spherical symmetry

$$\psi_1(r, +\frac{1}{2}), \quad \psi_1(r, -\frac{1}{2}), \quad (107)$$

are different solutions because of the different projections S_z . The value of the probability of one or another projection is determined by the square moduli $||\psi_1||^2$ or $||\psi_2||^2$, respectively, such that

$$||\psi_1||^2 + ||\psi_2||^2 = 1. \quad (108)$$

Since the eigenfunctions of S_z have two components, then

$$\chi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (109)$$

so that the eigenfunction of a spin one-half particle can be written as a column matrix

$$\psi = \psi_1 \chi_1 + \psi_2 \chi_2 = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}. \quad (110)$$

In the following, the orbitals will be replaced by numbers because we are interested only in the spin part.

Transformations of spinors to rotations

Let ψ be the wavefunction of a spin system in Σ . We want to determine the probability of the spin projection in a arbitrary direction in 3D space, which one can always chose as the z' of Σ' . As we have already seen in the case of the angular momentum there are two viewpoints in trying to solve this problem

- (α) ψ does not change when $\Sigma \rightarrow \Sigma'$ and the operator $\hat{\Lambda}$ transforms as a vector. We have to find the eigenfunctions of the projections S'_z and to expand ψ in these eigenfunctions. The square moduli of the coefficients give the result

$$\begin{aligned}\hat{S}'_x &= \hat{S}_x \cos \phi + \hat{S}_y \sin \phi = e^{-i\phi} \hat{S}_x e^{i\phi}, \\ \hat{S}'_y &= -\hat{S}_x \sin \phi + \hat{S}_y \cos \phi = e^{-i\phi} \hat{S}_y e^{i\phi}, \\ \hat{S}'_z &= -\hat{S}_z = e^{i\phi} \hat{S}_z,\end{aligned}\tag{111}$$

for infinitesimal rotations. Then, from the commutation relations for spin one can find

$$\hat{l} = \hat{S}_z,\tag{112}$$

where \hat{l} is the infinitesimal generator.

- (β) The second representation is: \hat{S} does not change when $\Sigma \rightarrow \Sigma'$ and the components of ψ does change. The transformation to this representation can be performed through a unitary transformation of the form

$$\begin{aligned}\hat{V}^\dagger \hat{S}' \hat{V} &= \hat{S}, \\ \begin{pmatrix} \psi'_1 \\ \psi'_2 \end{pmatrix} &= \hat{V}^\dagger \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}.\end{aligned}\tag{113}$$

Using (111) and (113) one gets

$$\begin{aligned}\hat{V}^\dagger e^{-i\hat{S}_z\phi} \hat{S} e^{i\hat{S}_z\phi} \hat{V} &= \hat{S}, \\ \hat{V}^\dagger &= e^{i\hat{S}_z\phi},\end{aligned}\tag{114}$$

and from (114) we are led to

$$\begin{pmatrix} \psi'_1 \\ \psi'_2 \end{pmatrix} = e^{i\hat{S}_z\phi} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}.\tag{115}$$

Using the explicit form of \hat{S}_z and the properties of the Pauli matrices one can find the explicit form of \hat{V}_z^\dagger , such that

$$\hat{V}_z^\dagger(\phi) = \begin{pmatrix} e^{\frac{i}{2}\phi} & 0 \\ 0 & e^{-\frac{i}{2}\phi} \end{pmatrix}.\tag{116}$$

A result of Euler

One can reach any reference frame Σ' of arbitrary orientation with regard to Σ through only three rotations; the first of angle ϕ around z , the next of angle θ around x' and the last of angle ψ_a around z' , i.e. This important result belongs to Euler. The parameters $(\varphi, \theta, \psi_a)$ are called Euler's angles. Thus

$$\hat{V}^\dagger(\varphi, \theta, \psi_a) = \hat{V}_{z'}^\dagger(\psi_a) \hat{V}_{x'}^\dagger(\theta) \hat{V}_z^\dagger(\varphi). \quad (117)$$

The matrices \hat{V}_z^\dagger are of the form (116), whereas \hat{V}_x^\dagger is of the form

$$\hat{V}_x^\dagger(\varphi) = \begin{pmatrix} \cos \frac{\theta}{2} & i \sin \frac{\theta}{2} \\ i \sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix}, \quad (118)$$

so that

$$\hat{V}^\dagger(\varphi, \theta, \psi_a) = \begin{pmatrix} e^{i\frac{\varphi+\psi_a}{2}} \cos \frac{\theta}{2} & i e^{i\frac{\psi_a-\varphi}{2}} \sin \frac{\theta}{2} \\ i e^{i\frac{\varphi-\psi_a}{2}} \sin \frac{\theta}{2} & e^{-i\frac{\varphi+\psi_a}{2}} \cos \frac{\theta}{2} \end{pmatrix}. \quad (119)$$

It comes out in this way that by the rotation of Σ , the components of the spinorial function transforms as follows

$$\begin{aligned} \psi'_1 &= \psi_1 e^{i\frac{\varphi+\psi_a}{2}} \cos \frac{\theta}{2} + i \psi_2 e^{i\frac{\psi_a-\varphi}{2}} \sin \frac{\theta}{2}, \\ \psi'_2 &= i \psi_1 e^{i\frac{\varphi-\psi_a}{2}} \sin \frac{\theta}{2} + \psi_2 e^{-i\frac{\varphi+\psi_a}{2}} \cos \frac{\theta}{2}. \end{aligned} \quad (120)$$

From (120) one can infer that there is a one-to-one mapping between any rotation in E_3 and a linear transformation of E_2 , the two-dimensional Euclidean space. This mapping is related to the two components of the spinorial wavefunction. The rotation in E_3 does not imply a rotation in E_2 , which means that

$$\langle \Phi' | \psi' \rangle = \langle \Phi | \psi \rangle = \Phi_1^* \psi_1 + \Phi_2^* \psi_2. \quad (121)$$

From (119) one finds that (121) does not hold; nevertheless there is an invariance in the transformations (119) in the space E_2 of spinorial wavefunctions

$$\{\Phi | \psi\} = \psi_1 \Phi_2 - \psi_2 \Phi_1. \quad (122)$$

The linear transformations that preserve invariant bilinear forms invariant are called binary transformations.

A physical quantity with two components for which a rotation of the coordinate system is a binary transformation is know as a *spin of first order* or shortly *spin*.

The spinors of a system of two fermions

The eigenfunctions of ${}_i\hat{s}^2 {}_i\hat{s}_z$, with $i = 1, 2$ have the following form

$${}_i|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_i, \quad {}_i|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_i. \quad (123)$$

A very used operator in a two-fermion system is the total spin

$$\hat{S} = {}_1\hat{S} + {}_2\hat{S}. \quad (124)$$

The spinors of $\hat{s}^2 \hat{s}_z$ are kets $|\hat{S}, \sigma\rangle$, which are linear combinations of ${}_i\hat{s}^2 {}_i\hat{s}_z$

$$\begin{aligned} |++\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1, & |+-\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2, \\ |-+\rangle &= \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1, & |--\rangle &= \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2. \end{aligned} \quad (125)$$

The spinorial functions in (125) are assumed orthonormalized. In E_n the ket $|++\rangle$ has $S_z = 1$ and at the same time it is an eigenfunction of the operator

$$\hat{S} = {}_1\hat{s}^2 + 2({}_1\hat{s})({}_2\hat{s}) + {}_2\hat{s}^2, \quad (126)$$

as one can see from

$$\hat{S}^2 = |++\rangle = \frac{3}{2}|++\rangle + 2({}_1\hat{s}_x \cdot {}_2\hat{s}_x + {}_1\hat{s}_y \cdot {}_2\hat{s}_y + {}_1\hat{s}_z \cdot {}_2\hat{s}_z)|++\rangle \quad (127)$$

$$\hat{S}^2 = |++\rangle = 2|++\rangle = 1(1+1)|++\rangle. \quad (128)$$

If we introduce the operator

$$\hat{S}_- = {}_1\hat{s}_- + {}_2\hat{s}_-, \quad (129)$$

one gets

$$[\hat{S}_-, \hat{S}^2] = 0. \quad (130)$$

Then $(\hat{S}_-)^k|1, 1\rangle$ can be written in terms of the eigenfunctions of the operator \hat{S}^2 , i.e.

$$\hat{S}_-|1, 1\rangle = \hat{S}_-|++\rangle = \sqrt{2}|+-\rangle + \sqrt{2}|--\rangle. \quad (131)$$

Thus, $S_z = 0$ in the state $\hat{S}_-|1, 1\rangle$. On the other hand, from the normalization condition, we have

$$|1, 0\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \quad (132)$$

$$\hat{S}_-|1, 0\rangle = |--\rangle + |- -\rangle = \alpha|1, -1\rangle. \quad (133)$$

In addition, the normalization condition gives

$$|1, -1\rangle = |--\rangle. \quad (134)$$

There is only one other linear-independent combination of functions of the type (125), which is different of $|1, 1\rangle$, $|1, 0\rangle$ and $|1, -1\rangle$, which is

$$\psi_4 = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle), \quad (135)$$

$$\hat{S}_z\psi_4 = 0, \quad \hat{S}^2\psi_4. \quad (136)$$

Therefore

$$\psi_4 = |0, 0\rangle. \quad (137)$$

ψ_4 describes the state of a system of two fermions having the total spin equal to zero. The latter type of state is called *singlet*. On the other hand, the state of two fermions of total spin one can be called *triplet* having a degree of degeneration $g = 3$.

Total angular momentum

The total angular momentum is an operator defined as the sum of the angular and spin momenta, i.e.

$$\hat{J} = \hat{l} + \hat{S}, \quad (138)$$

where \hat{l} and \hat{S} , as we have seen, act in different spaces, though the square of \hat{l} and \hat{S} commute with \hat{J}

$$[\hat{J}_i, \hat{J}_j] = i\varepsilon_{ijk}\hat{J}_k, \quad [\hat{J}_i, \hat{l}^2] = 0, \quad [\hat{J}_i, \hat{S}^2] = 0, \quad (139)$$

From (139) one finds that \hat{l}^2 and \hat{S}^2 have a common eigenfunction system with \hat{J}^2 and \hat{J}_z .

Let us determine the spectrum of the projections \hat{J}_z for a fermion. The state of maximum projection \hat{J}_z can be written

$$\bar{\psi} = \psi_U \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |l, l, +\rangle \quad (140)$$

$$\hat{j}_z \bar{\psi} = (l + \frac{1}{2})\bar{\psi}, \rightarrow j = l + \frac{1}{2}. \quad (141)$$

We introduce the operator \hat{J}_- defined as

$$\hat{J}_- = \hat{l}_- + \hat{S}_- = \hat{l}_- + \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (142)$$

On account of the normalization $\alpha = \sqrt{(J+M)(J-M+1)}$, one gets

$$\hat{J}_- \psi_U \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \sqrt{2l} |l, l-1, +\rangle + |l, l-1, -\rangle, \quad (143)$$

so that the value of the projection of \hat{j}_- in $\hat{j}_- \bar{\psi}$ will be

$$\hat{j}_z = (l-1) + \frac{1}{2} = l - \frac{1}{2}. \quad (144)$$

It follows that \hat{j}_- lowers by one unit the action of \hat{J}_z .

In the general case we have

$$\hat{j}_-^k = \hat{l}_-^k + k \hat{l}_-^{k-1} \hat{S}_-. \quad (145)$$

One can see that (145) is obtained from the binomial expansion considering that \hat{s}_-^2 and all higher-order powers of \hat{s}_- are zero.

$$\hat{j}_-^k |l, l, +\rangle = \hat{l}_-^k |l, l, +\rangle + k \hat{l}_-^{k-1} |l, l, -\rangle. \quad (146)$$

Using

$$(\hat{l}_-)^k \psi_{l,l} = \sqrt{\frac{k!(2l)!}{(2l-k)!}} \psi_{l,l-k}$$

we get

$$\hat{j}_-^k |l, l, +\rangle = \sqrt{\frac{k!(2l)!}{(2l-k)!}} |l, l-k, +\rangle + \sqrt{\frac{(k+1)!(2l)!}{(2l-k+1)!}} k |l, l-k+1, -\rangle. \quad (147)$$

Now noticing that $m = l - k$

$$\hat{j}_-^{l-m} |l, l, +\rangle = \sqrt{\frac{(l-m)!(2l)!}{(l+m)!}} |l, m, +\rangle + \sqrt{\frac{(l-m-1)!(2l)!}{(2l+m+1)!}} (l-m) |l, m+1, -\rangle. \quad (148)$$

The eigenvalues of the projections of the total angular momentum are given by the sequence of numbers differing by one unit from $j = l + \frac{1}{2}$ to $j = l - \frac{1}{2}$. All these states belong to the same eigenfunction of \hat{J} as $|l, l, +\rangle$ because $[\hat{J}_-, \hat{J}^2] = 0$:

$$\begin{aligned}\hat{J}^2|l, l, +\rangle &= (\hat{l}^2 + 2\hat{l}\hat{S} + \hat{S}^2)|l, l, +\rangle, \\ &= [l(l+1) + 2l\frac{1}{2} + \frac{3}{4}]|l, l, +\rangle\end{aligned}\quad (149)$$

where $j(j+1) = (l + \frac{1}{2})(l + \frac{3}{2})$.

In the left hand side of (149) a contribution different of zero gives only $j = \hat{l}_z \hat{S}_z$. Thus, the obtained eigenfunctions correspond to the pair $j = l + \frac{1}{2}$, $m_j = m + \frac{1}{2}$; they are of the form

$$|l + \frac{1}{2}, m + \frac{1}{2}\rangle = \sqrt{\frac{l+m+1}{2l+1}}|l, m, +\rangle + \sqrt{\frac{l-m}{2l+1}}|l, m+1, -\rangle. \quad (150)$$

The total number of linearly independent states is

$$N = (2l+1)(2s+1) = 4l+2, \quad (151)$$

of which in (150) only $(2j+1)=2l+3$ have been built. The rest of $2l-1$ eigenfunctions can be obtained from the orthonormalization condition:

$$|l - \frac{1}{2}, m - \frac{1}{2}\rangle = \sqrt{\frac{l-m}{2l+1}}|l, m, +\rangle - \sqrt{\frac{l+m+1}{2l+1}}|l, m+1, -\rangle. \quad (152)$$

If two subsystems are in interaction in such a way that each of the angular momenta \hat{j}_i is conserved, then the eigenfunctions of the total angular momentum

$$\hat{J} = \hat{j}_1 + \hat{j}_2, \quad (153)$$

can be obtained by a procedure similar to the previous one. For fixed eigenvalues of \hat{j}_1 and \hat{j}_2 there are $(2j_1+1)(2j_2+1)$ orthonormalized eigenfunctions of the projection of the total angular momentum \hat{J}_z ; the one corresponding to the maximum value of the projection \hat{J}_z , i.e. $M_J = j_1 + j_2$, can be built in a unique way and therefore $J = j_1 + j_2$ is the maximum value of the total angular momentum of the system. Applying the operator $\hat{J} = \hat{j}_1 + \hat{j}_2$ repeatedly to the function

$$|j_1 + j_2, j_1 + j_2, j_1 + j_2\rangle = |j_1, j_1\rangle \cdot |j_2, j_2\rangle, \quad (154)$$

one can obtain all the $2(j_1 + j_2) + 1$ eigenfunctions of $\hat{J} = j_1 + j_2$ with different M s:

$$-(j_1 + j_2) \leq M \leq (j_1 + j_2).$$

For example, the eigenfunction of $M = j_1 + j_2 - 1$ is

$$|j_1+j_2, j_1+j_2-1, j_1, j_2\rangle = \sqrt{\frac{j_1}{j_1+j_2}}|j_1, j_1-1, j_2, j_2\rangle + \sqrt{\frac{j_2}{j_1+j_2}}|j_1, j_1, j_2, j_2-1\rangle. \quad (155)$$

Applying iteratively the operator \hat{J}_- , all the $2(j_1 + j_2 - 1) - 1$ eigenfunctions of $J = j_1 + j_2 - 1$ can be obtained.

One can prove that

$$|j_1 - j_2| \leq J \leq j_1 + j_2 ,$$

so that

$$\sum_{\min J}^{\max J} (2J + 1) = (2J_1 + 1)(2J_2 + 1) . \quad (156)$$

Thus

$$|J, M, j_1, j_2\rangle = \sum_{m_1+m_2=M} (j_1 m_1 j_2 m_2 |JM) |j_1, m_1, j_2, m_2\rangle , \quad (157)$$

where the coefficients $(j_1 m_1 j_2 m_2 |JM)$ determine the contribution of the various kets $|j_1, m_1, j_2, m_2\rangle$ to the eigenfunctions of \hat{J}^2, \hat{J}_z having the eigenvalues $J(J + 1), M$. They are called Clebsch-Gordan coefficients.

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1. H.A. Buchdahl, "Remark concerning the eigenvalues of orbital angular momentum",
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3N. Note: 1. The operator corresponding to the Runge-Lenz vector of the classical Kepler problem is written as

$$\hat{A} = \frac{\hat{\mathbf{r}}}{r} + \frac{1}{2} \left[(\hat{l} \times \hat{p}) - (\hat{p} \times \hat{l}) \right],$$

where atomic units have been used and the case $Z = 1$ (hydrogen atom) was assumed. This operator commutes with the Hamiltonian of the atomic hydrogen $\hat{H} = \frac{\hat{p}^2}{2} - \frac{1}{r}$, that is it is an integral of the atomic quantum motion. Its components have commutators of the type $[A_i, A_j] = -2i\epsilon_{ijk}l_k \cdot H$; the commutators of the Runge-Lenz components with the components of the angular momentum are of the type $[l_i, A_j] = i\epsilon_{ijk}A_k$. Thus, they respect the conditions (23). Proving that can be a useful exercise.

3P. Problems

Problem 3.1

Show that any translation operator, for which $\psi(y + a) = T_a\psi(y)$, can be written as an exponential operator. Apply the result for $y = \vec{r}$ and for a the finite rotation α around z .

Solution

The proof can be obtained expanding $\psi(y + a)$ in Taylor series in the infinitesimal neighborhood around x , that is in powers of a

$$\psi(y + a) = \sum_{n=0}^{\infty} \frac{a^n}{n!} \frac{d^n}{dx^n} \psi(x)$$

We notice that

$$\sum_{n=0}^{\infty} \frac{a^n}{n!} \frac{d^n}{dx^n} = e^{a \frac{d}{dx}}$$

and therefore one has $T_a = e^{a \frac{d}{dx}}$ in the 1D case. In 3D, $y = \vec{r}$ and $a \rightarrow \vec{a}$. The result is $T_{\vec{a}} = e^{\vec{a} \cdot \vec{\nabla}}$.

For the finite rotation α around z we has $y = \phi$ and $a = \alpha$. It follows

$$T_{\alpha} = R_{\alpha} = e^{\alpha \frac{d}{d\phi}} .$$

Another exponential form of the rotation around z is that in terms of the angular momentum operator as was already commented in this chapter. Let $x' = x + dx$ and consider only the first order of the Taylor series

$$\begin{aligned} \psi(x', y', z') &= \psi(x, y, z) + (x' - x) \frac{\partial}{\partial x'} \psi(x', y', z') \Big|_{\vec{r}' = \vec{r}} \\ &+ (y' - y) \frac{\partial}{\partial y'} \psi(x', y', z') \Big|_{\vec{r}' = \vec{r}} \\ &+ (z' - z) \frac{\partial}{\partial z'} \psi(x', y', z') \Big|_{\vec{r}' = \vec{r}} . \end{aligned}$$

Taking into account

$$\begin{aligned} \frac{\partial}{\partial x'_i} \psi(\vec{r}') \Big|_{\vec{r}'} &= \frac{\partial}{\partial x_i} \psi(\vec{r}), \\ x' &= x - y d\phi, \quad y' = y + x d\phi, \quad z' = z, \end{aligned}$$

one can reduce the series from three to two dimensions

$$\begin{aligned}
\psi(\vec{r}') &= \psi(\vec{r}) + (x - yd\phi - x) \frac{\partial\psi(\vec{r})}{\partial x} + (y + xd\phi - y) \frac{\partial\psi(\vec{r})}{\partial y}, \\
&= \psi(\vec{r}) - yd\phi \frac{\partial\psi(\vec{r})}{\partial x} + xd\phi \frac{\partial\psi(\vec{r})}{\partial y}, \\
&= \left[1 - d\phi \left(-x \frac{\partial}{\partial y} + y \frac{\partial}{\partial x} \right) \right] \psi(\vec{r}) .
\end{aligned}$$

Since $\hat{i}l_z = \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$ it follows that $R = \left[1 - d\phi \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right]$. In the second order one can get $\frac{1}{2!}(\hat{i}l_z d\phi)^2$, and so forth. Thus, R can be written as an exponential

$$R = e^{\hat{i}l_z d\phi}.$$

Problem 3.2

Based on the expressions given in (14) show that one can get (15).

Solution

Let us consider only linear terms in the Taylor expansion (infinitesimal rotations)

$$e^{\hat{i}l_z d\phi} = 1 + \hat{i}l_z d\phi + \frac{1}{2!}(\hat{i}l_z d\phi)^2 + \dots ,$$

so that

$$\begin{aligned}
(1 + \hat{i}l_z d\phi)\hat{A}_x(1 - \hat{i}l_z d\phi) &= \hat{A}_x - \hat{A}_x d\phi, \\
(\hat{A}_x + \hat{i}l_z d\phi\hat{A}_x)(1 - \hat{i}l_z d\phi) &= \hat{A}_x - \hat{A}_x d\phi, \\
\hat{A}_x - \hat{A}_x \hat{i}l_z d\phi + \hat{i}l_z d\phi\hat{A}_x + \hat{l}_z d\phi\hat{A}_x\hat{l}_z d\phi &= \hat{A}_x - \hat{A}_x d\phi, \\
i(\hat{l}_z\hat{A}_x - \hat{A}_x\hat{l}_z)d\phi &= -\hat{A}_y d\phi.
\end{aligned}$$

We easily arrive at the conclusion

$$[\hat{l}_z, \hat{A}_x] = i\hat{A}_y .$$

In addition, $[\hat{l}_z, \hat{A}_y] = i\hat{A}_x$ can be obtained from

$$\begin{aligned}
(1 + \hat{i}l_z d\phi)\hat{A}_y(1 - \hat{i}l_z d\phi) &= \hat{A}_y d\phi - \hat{A}_y, \\
(\hat{A}_y + \hat{i}l_z d\phi\hat{A}_y)(1 - \hat{i}l_z d\phi) &= \hat{A}_y d\phi - \hat{A}_y, \\
\hat{A}_y - \hat{A}_y \hat{i}l_z d\phi + \hat{i}l_z d\phi\hat{A}_y + \hat{l}_z d\phi\hat{A}_y\hat{l}_z d\phi &= \hat{A}_y d\phi - \hat{A}_y, \\
i(\hat{l}_z\hat{A}_y - \hat{A}_y\hat{l}_z)d\phi &= -\hat{A}_x d\phi.
\end{aligned}$$

Problem 3.3

Determine the operator $\frac{d\hat{\sigma}_x}{dt}$ based on the Hamiltonian of an electron with spin in a magnetic field of induction \vec{B} .

Solution

The Hamiltonian in this case is $\hat{H}(\hat{\mathbf{p}}, \hat{\mathbf{r}}, \hat{\sigma}) = \hat{H}(\hat{\mathbf{p}}, \hat{\mathbf{r}}) + \hat{\sigma} \cdot \vec{B}$, where the latter term is the Zeeman Hamiltonian of the electron. Since $\hat{\sigma}_x$ commutes with the momenta and the coordinates, applying the Heisenberg equation of motion leads to

$$\frac{d\hat{\sigma}_x}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{\sigma}_x] = -\frac{i}{\hbar} \frac{e\hbar}{2m_e} ((\hat{\sigma}_y B_y + \hat{\sigma}_z B_z) \hat{\sigma}_x - \hat{\sigma}_x (\hat{\sigma}_y B_y + \hat{\sigma}_z B_z)) .$$

Using $[\sigma_x, \sigma_y] = i\sigma_z$, one gets :

$$\frac{d\hat{\sigma}_x}{dt} = \frac{e}{m_e} (\hat{\sigma}_y B_z - \hat{\sigma}_z B_y) = \frac{e}{m_e} (\vec{\sigma} \times \vec{B})_x .$$

4. THE WKB METHOD

In order to study more realistic potentials with regard to *rectangular barriers and wells*, it is necessary to employ approximate methods allowing to solve the Schrödinger equation for more general classes of potentials and at the same time to give very good approximations of the exact solutions.

The aim of the various approximative methods is to offer solutions of acceptable precision and simplicity that can be used for understanding the behaviour of the system in quasianalytic terms.

Within quantum mechanics, one of the oldest and efficient approximate method for getting rather good Schrödinger solutions was developed almost simulataneously by *G. Wentzel, H. A. Kramers and L. Brillouin* in 1926, hence the acronym *WKB* under which this method is known (or *JWKB* as is more correctly used by many authors, see note 4N).

It is worth mentioning that the WKB method applies to 1D Schrödinger equations and that there are serious difficulties when trying to generalize it to more dimensions.

In order to solve the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dy^2} + u(y)\psi = E\psi \quad (1)$$

with a potential of the form

$$u(y) = u_0 f\left(\frac{y}{a}\right), \quad (2)$$

we first perform the changes of notations and of variable

$$\xi^2 = \frac{\hbar^2}{2mu_0a^2} \quad (3)$$

$$\eta = \frac{E}{u_0} \quad (4)$$

$$x = \frac{y}{a}. \quad (5)$$

From eq. (5) we get

$$\frac{d}{dx} = \frac{dy}{dx} \frac{d}{dy} = a \frac{d}{dy} \quad (6)$$

$$\frac{d^2}{dx^2} = \frac{d}{dx} \left(a \frac{d}{dy} \right) = \left(a \frac{d}{dx} \right) \left(a \frac{d}{dx} \right) = a^2 \frac{d^2}{dy^2} \quad (7)$$

and the Schrödinger eq. reads

$$-\xi^2 \frac{d^2\psi}{dx^2} + f(x)\psi = \eta\psi . \quad (8)$$

Multiplying by $-1/\xi^2$ and defining $r(x) = \eta - f(x)$, it is possible to write it as follows

$$\frac{d^2\psi}{dx^2} + \frac{1}{\xi^2}r(x)\psi = 0 . \quad (9)$$

To solve (9), the following form of the solution is proposed

$$\psi(x) = \exp \left[\frac{i}{\xi} \int_a^x q(x) dx \right] . \quad (10)$$

Therefore

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= \frac{d}{dx} \left(\frac{d\psi}{dx} \right) = \frac{d}{dx} \left\{ \frac{i}{\xi} q(x) \exp \left[\frac{i}{\xi} \int_a^x q(x) dx \right] \right\} \\ \implies \frac{d^2\psi}{dx^2} &= \frac{i}{\xi} \left\{ \frac{i}{\xi} q^2(x) \exp \left[\frac{i}{\xi} \int_a^x q(x) dx \right] + \frac{\partial q(x)}{\partial x} \exp \left[\frac{i}{\xi} \int_a^x q(x) dx \right] \right\} . \end{aligned}$$

Factorizing ψ , we have

$$\frac{d^2\psi}{dx^2} = \left[-\frac{1}{\xi^2} q^2(x) + \frac{i}{\xi} \frac{dq(x)}{dx} \right] \psi . \quad (11)$$

Discarding for the time being the dependence of x , the Schrödinger eq. can be written

$$\left[-\frac{1}{\xi^2} q^2 + \frac{i}{\xi} \frac{\partial q}{\partial x} + \frac{1}{\xi^2} r \right] \psi = 0 \quad (12)$$

and since in general $\psi \neq 0$, we get:

$$i\xi \frac{dq}{dx} + r - q^2 = 0 , \quad (13)$$

which is a nonlinear differential eq. of the Riccati type whose solutions are sought in the form of expansions in powers of ξ under the assumption that ξ is very small.

More precisely, the series is taken of the form

$$q(x) = \sum_{n=0}^{\infty} (-i\xi)^n q_n(x) . \quad (14)$$

Plugging it into the Riccati eq., we get

$$i\xi \sum_{n=0}^{\infty} (-i\xi)^n \frac{dq_n}{dx} + r(x) - \sum_{\mu=0}^{\infty} (-i\xi)^\mu q_\mu \sum_{\nu=0}^{\infty} (-i\xi)^\nu q_\nu = 0 . \quad (15)$$

By a rearrangement of the terms one is led to

$$\sum_{n=0}^{\infty} (-1)^n (i\xi)^{n+1} \frac{dq_n}{dx} + r(x) - \sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty} (-i\xi)^{\mu+\nu} q_\mu q_\nu = 0 . \quad (16)$$

Double series have the following important property

$$\sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty} a_{\mu\nu} = \sum_{n=0}^{\infty} \sum_{m=0}^n a_{m,n-m} ,$$

where $\mu = n - m$, $\nu = m$.

Thus

$$\sum_{n=0}^{\infty} (-1)^n (i\xi)^{n+1} \frac{dq_n}{dx} + r(x) - \sum_{n=0}^{\infty} \sum_{m=0}^n (-i\xi)^{n-m+m} q_m q_{n-m} = 0 . \quad (17)$$

Let us see explicitly the first several terms in each of the series in eq. (17):

$$\sum_{n=0}^{\infty} (-1)^n (i\xi)^{n+1} \frac{dq_n}{dx} = i\xi \frac{dq_0}{dx} + \xi^2 \frac{dq_1}{dx} - i\xi^3 \frac{dq_2}{dx} + \dots \quad (18)$$

$$\sum_{n=0}^{\infty} \sum_{m=0}^n (-i\xi)^n q_m q_{n-m} = q_0^2 - i2\xi q_0 q_1 + \dots \quad (19)$$

Asking that the first terms in both series contain $i\xi$, one should write them as

$$\sum_{n=1}^{\infty} (-1)^{n-1} (i\xi)^n \frac{dq_{n-1}}{dx} + r(x) - q_0^2 - \sum_{n=1}^{\infty} \sum_{m=0}^n (-i\xi)^n q_m q_{n-m} = 0 ,$$

which leads to

$$\sum_{n=1}^{\infty} \left[- (-i\xi)^n \frac{dq_{n-1}}{dx} - \sum_{m=0}^n (-i\xi)^n q_m q_{n-m} \right] + \left[r(x) - q_0^2 \right] = 0 . \quad (20)$$

In order that this equation be right the following conditions should be satisfied

$$r(x) - q_0^2 = 0 \quad \Rightarrow \quad q_0 = \pm\sqrt{r(x)} \quad (21)$$

$$\begin{aligned} & -(-i\xi)^n \frac{dq_{n-1}}{dx} - \sum_{m=0}^n (-i\xi)^n q_m q_{n-m} = 0 \\ \Rightarrow & \quad \frac{dq_{n-1}}{dx} = - \sum_{m=0}^n q_m q_{n-m} \quad n \geq 1 . \end{aligned} \quad (22)$$

The latter is a recurrence relationship, which occurs naturally in the WKB method. Recalling that we have defined $r(x) = \eta - f(x)$, $\eta = \frac{E}{u_0}$ & $f(x) = \frac{u}{u_0}$, by means of eq. (21) we get

$$q_0 = \pm\sqrt{\eta - f(x)} = \pm\sqrt{\frac{E}{u_0} - \frac{u}{u_0}} = \pm\sqrt{\frac{2m(E - u)}{2mu_0}} . \quad (23)$$

This clearly indicates the classical nature of the WKB momentum of the particle of energy E in the potential u and units of $\sqrt{2mu_0}$. Thus

$$q_0 = p(x) = \sqrt{\eta - f(x)}$$

is not an operator. If we approximate till the second order, we get

$$q(x) = q_0 - i\xi q_1 - \xi^2 q_2$$

and using the WKB recurrence relationship (22) we calculate q_1 and q_2

$$\begin{aligned} \frac{dq_0}{dx} = -2q_0 q_1 \quad \Rightarrow \quad q_1 &= -\frac{1}{2} \frac{\frac{dq_0}{dx}}{q_0} = -\frac{1}{2} \frac{d}{dx} (\ln |q_0|) \\ \Rightarrow \quad q_1 &= -\frac{1}{2} \frac{d}{dx} (\ln |p(x)|) \end{aligned} \quad (24)$$

$$\frac{dq_1}{dx} = -2q_0 q_2 - q_1^2 \quad \Rightarrow \quad q_2 = -\frac{\frac{dq_1}{dx} - q_1^2}{2q_0} . \quad (25)$$

A glance to eq. (24), affords us to consider q_1 as the slope, up to a change of sign, of $\ln |q_0|$; when q_0 is very small, then $q_1 \ll 0 \Rightarrow -\xi q_1 \gg 0$ and therefore the series diverges. To avoid this the following **WKB condition** is imposed

$$|q_0| \gg |-\xi q_1| = \xi |q_1| .$$

It is worth noting that this WKB condition WKB is not fulfilled at those points x_k where

$$q_0(x_k) = p(x_k) = 0 .$$

Since $q_0 = p = \sqrt{\frac{2m(E-u)}{2mu_0}}$ the previous equation leads us to

$$E = u(x_k) . \quad (26)$$

In classical mechanics the points x_k that satisfies (26) are called **turning points** because the change of the sense of the motion of a macroscopic particle takes place there.

By means of these arguments, we can say that q_0 is a classical solution of the problem under examination; also that the quantities q_1 & q_2 are the first and the second quantum corrections, respectively, in the WKB problem.

To obtain the WKB wavefunctions we shall consider only the classical solution and the first quantum correction that we plug in the WKB form of ψ

$$\begin{aligned} \psi &= \exp \left[\frac{i}{\xi} \int_a^x q(x) dx \right] = \exp \left[\frac{i}{\xi} \int_a^x (q_0 - i\xi q_1) dx \right] \\ \Rightarrow \quad \psi &= \exp \left(\frac{i}{\xi} \int_a^x q_0 dx \right) \cdot \exp \left(\int_a^x q_1 dx \right) . \end{aligned}$$

For the second factor, we get

$$\begin{aligned} \exp \left(\int_a^x q_1 dx \right) &= \exp \left[-\frac{1}{2} \int_a^x \frac{d}{dx} (\ln |p(x)|) dx \right] = \\ &= \exp \left[-\frac{1}{2} (\ln |p(x)|) \Big|_a^x \right] = \frac{A}{\sqrt{p(x)}} , \end{aligned}$$

where A is a constant, whereas for the first factor we get

$$\exp \left(\frac{i}{\xi} \int_a^x q_0 dx \right) = \exp \left[\pm \frac{i}{\xi} \int_a^x p(x) dx \right] .$$

Thus, we can write ψ in the following form

$$\psi^\pm = \frac{1}{\sqrt{p(x)}} \exp \left[\pm \frac{i}{\xi} \int_a^x p(x) dx \right] . \quad (27)$$

The latter are known as the *WKB solutions of the 1D Schrödinger equation*. The general WKB solution in the region in which the WKB condition is satisfied is written down as

$$\psi = a_+ \psi^+ + a_- \psi^- . \quad (28)$$

As already mentioned there is no WKB solution at the turning points. This raises the question of the manner in which one has to do the passing from $\psi(x < x_k)$ to $\psi(x > x_k)$. The solution of this difficulty is achieved by introducing the WKB connection formulas.

The connection formulas

We have already seen that the WKB solutions are singular at the classical turning points; however, these solutions are correct both on the left and right side of these turning points x_k . A natural question is how do we change $\psi(x < x_k)$ in $\psi(x > x_k)$ when passing through the turning points. The explicit answer is given by the connection formulas.

From the theory of differential equations of complex variable it can be proved that really there are such connection formulas and that they are the following

$$\begin{aligned} \psi_1(x) &= \frac{1}{[-r(x)]^{\frac{1}{4}}} \exp\left(-\int_x^{x_k} \sqrt{-r(x)} dx\right) \rightarrow \\ &\rightarrow \frac{2}{[r(x)]^{\frac{1}{4}}} \cos\left(\int_{x_k}^x \sqrt{r(x)} dx - \frac{\pi}{4}\right) , \end{aligned} \quad (29)$$

where $\psi_1(x)$ has only an attenuated exponential behavior for $x < x_k$. The first connection formula shows that the function $\psi(x)$, which at the left of the turning point behaves exponentially decaying, turns at the right of x_k into a cosinusoide of phase $\phi = \frac{\pi}{4}$ and double amplitude with regard to the amplitude of the exponential.

In the case of a more general function $\psi(x)$, such as a function with both rising and decaying exponential behavior, the connection formula is

$$\begin{aligned} \sin\left(\phi + \frac{\pi}{4}\right) \frac{1}{[-r(x)]^{\frac{1}{4}}} \exp\left(\int_x^{x_k} \sqrt{-r(x)} dx\right) \leftarrow \\ \leftarrow \frac{1}{[r(x)]^{\frac{1}{4}}} \cos\left(\int_{x_k}^x \sqrt{r(x)} dx + \phi\right) , \end{aligned} \quad (30)$$

under the condition that ϕ sã do not take a value that is too close to $-\frac{\pi}{4}$. The reason is that if $\phi = -\frac{\pi}{4}$, then the sinus function is zero . The latter connection formula means that a function whose behavior is of the cosinusoid type at the right of a turning point changes into a growing exponential with sinusoid-modulated amplitude at the right of that point.

In order to study the details of the procedure of getting the connection formulas we recommend the book *Mathematical Methods of Physics* by J. Mathews & R.L. Walker.

Estimation of the WKB error

We have found the solution of the Schrödinger equation in the regions where the WKB condition is satisfied. However, the WKB solutions are divergent at the turning points. We thus briefly analyze the error introduced by using the WKB approximation and tackling the *connection formulas* in a close neighbourhood of the turning points.

Considering $x = x_k$ as a turning point, we have $q_0(x_k) = p(x_k) = 0 \Rightarrow E = u(x_k)$. At the left of x_k , that is on the ‘half-line’ $x < x_k$, we shall assume $E < u(x)$ leading to the WKB solution

$$\begin{aligned} \psi(x) = & \frac{a}{\left[\frac{u(x)-E}{u_0}\right]^{\frac{1}{4}}} \exp\left(-\frac{1}{\xi} \int_x^{x_k} \sqrt{\frac{u(x)-E}{u_0}} dx\right) + \\ & + \frac{b}{\left[\frac{u(x)-E}{u_0}\right]^{\frac{1}{4}}} \exp\left(\frac{1}{\xi} \int_x^{x_k} \sqrt{\frac{u(x)-E}{u_0}} dx\right). \end{aligned} \quad (31)$$

Similarly, at the right of x_k (on the ‘half-line’ $x > x_k$) we assume $E > u(x)$; therefore the WKB solution in the latter region will be

$$\begin{aligned} \psi(x) = & \frac{c}{\left[\frac{E-u(x)}{u_0}\right]^{\frac{1}{4}}} \exp\left(\frac{i}{\xi} \int_{x_k}^x \sqrt{\frac{E-u(x)}{u_0}} dx\right) + \\ & + \frac{d}{\left[\frac{E-u(x)}{u_0}\right]^{\frac{1}{4}}} \exp\left(-\frac{i}{\xi} \int_{x_k}^x \sqrt{\frac{E-u(x)}{u_0}} dx\right). \end{aligned} \quad (32)$$

If $\psi(x)$ is a real function, it will have this property both at the right and the left of x_k . It is usually called the “*reality condition*”. It means that if $a, b \in \Re$, then $c = d^*$.

Our problem consists in connecting the approximations on the two sides of x_k such that they refer to the same solution. This means to find c and d if one knows a and b , as well as viceversa. To achieve this connection, we have to use an approximate solution, which should be correct along a contour connecting the regions on the two sides of x_k , where the WKB solutions are also correct. A method proposed by *Zwann* and *Kemble* is very useful in this case. It consists in going out from the real axis in the neighbourhood of x_k on a contour around x_k in the complex plane. It is assumed that on this contour the WKB solutions are still correct. Here, we shall use this method as a means of getting the estimation of the error produced by the WKB method.

The estimation of the error is always an important matter for any approximate solutions. In the case of the WKB procedure, it is more significant because it is an approximation on large intervals of the real axis that can lead to the acculation of the errors as well as to some artefacts due to the phase shifts that can be introduced in this way.

Let us define *the associated WKB functions* as follows

$$W_{\pm} = \frac{1}{\left[\frac{E-u(x)}{u_0}\right]^{\frac{1}{4}}} \exp\left(\pm \frac{i}{\xi} \int_{x_k}^x \sqrt{\frac{E-u(x)}{u_0}} dx\right), \quad (33)$$

that we consider as functions of complex variable. We shall use cuts in order to avoid the discontinuities in the zeros of $r(x) = \frac{E-u(x)}{u_0}$. These functions satisfy the differential equation that is obtained by differentiating with respect to x , leading to

$$\begin{aligned} W'_{\pm} &= \left(\pm \frac{i}{\xi} \sqrt{r} - \frac{1}{4} \frac{r'}{r}\right) W_{\pm} \\ W''_{\pm} + \left[\frac{r}{\xi^2} + \frac{1}{4} \frac{r''}{r} - \frac{5}{16} \left(\frac{r'}{r}\right)^2\right] W_{\pm} &= 0. \end{aligned} \quad (34)$$

Let us notice that

$$s(x) = \frac{1}{4} \frac{r''}{r} - \frac{5}{16} \left(\frac{r'}{r}\right)^2, \quad (35)$$

then W_{\pm} are exact solutions of the equation

$$W_{\pm}'' + \left[\frac{1}{\xi^2} r(x) + s(x) \right] W_{\pm} = 0 , \quad (36)$$

although they satisfy only approximately the Schrödinger equation, which is a regular equation in $x = x_k$, whereas the same equation for the associate WKB functions is singular at that point.

We shall now define the functions $\alpha_{\pm}(x)$ satisfying the following two relationships

$$\psi(x) = \alpha_+(x)W_+(x) + \alpha_-(x)W_-(x) \quad (37)$$

$$\psi'(x) = \alpha_+(x)W'_+(x) + \alpha_-(x)W'_-(x) , \quad (38)$$

where $\psi(x)$ is a solution of the Schrödinger equation. Solving the previous equations for α_{\pm} , we get

$$\alpha_+ = \frac{\psi W'_- - \psi' W_-}{W_+ W'_- - W'_+ W_-} \quad \alpha_- = -\frac{\psi W'_+ - \psi' W_+}{W_+ W'_- - W'_+ W_-} ,$$

where the numerator is just the *Wronskian* of W_+ and W_- . It is not difficult to prove that this takes the value $-\frac{2}{\xi}i$, so that α_{\pm} simplifies to the following form

$$\alpha_+ = \frac{\xi}{2}i (\psi W'_- - \psi' W_-) \quad (39)$$

$$\alpha_- = \frac{-\xi}{2}i (\psi W'_+ - \psi' W_+) . \quad (40)$$

Doing the derivative in x in the eqs. (39) and (40), we have

$$\frac{d\alpha_{\pm}}{dx} = \frac{\xi}{2}i (\psi' W'_{\mp} + \psi W''_{\mp} - \psi'' W_{\mp} - \psi' W'_{\mp}) . \quad (41)$$

In the brackets, the first and the fourth terms are zero; recalling that

$$\psi'' + \frac{1}{\xi^2} r(x)\psi = 0 \quad \& \quad W_{\pm}'' + \left[\frac{1}{\xi^2} r(x) + s(x) \right] W_{\pm} = 0 ,$$

we can write eq. (41) in the form

$$\begin{aligned} \frac{d\alpha_{\pm}}{dx} &= \frac{\xi}{2}i \left[-\psi \left(\frac{r}{\xi^2} + s \right) W_{\mp} + \frac{r}{\xi^2} \psi W_{\mp} \right] \\ \frac{d\alpha_{\pm}}{dx} &= \mp \frac{\xi}{2}i s(x)\psi(x)W_{\mp}(x) , \end{aligned} \quad (42)$$

which based on eqs. (33) and (37) becomes

$$\frac{d\alpha_{\pm}}{dx} = \mp \frac{\xi}{2} i \frac{s(x)}{[r(x)]^{\frac{1}{2}}} \left[\alpha_{\pm} + \alpha_{\mp} \exp \left(\mp \frac{2}{\xi} i \int_{x_k}^x \sqrt{r(x)} dx \right) \right]. \quad (43)$$

Eqs. (42) and (43) are useful for estimating the WKB error in the 1D case.

The reason for which $\frac{d\alpha_{\pm}}{dx}$ can be considered as a measure of the WKB errors is that in the eqs. (31) and (32) the constants a , b and c , d , respectively, give only approximate solutions ψ , while the functions α_{\pm} when introduced in the eqs. (37) and (38) produce exact ψ solutions. From the geometrical viewpoint the derivative gives the slope of the tangent to these functions and indicates the measure in which α_{\pm} deviates from the constants a , b , c and d .

4N. Note: The original (J)WKB papers are the following:

G. Wentzel, “Eine Verallgemeinerung der Wellenmechanik”, [“A generalization of wave mechanics”],
Zeitschrift für Physik **38**, 518-529 (1926) [received on 18 June 1926]

L. Brillouin, “La mécanique ondulatoire de Schrödinger: une méthode générale de résolution par approximations successives”, [“Schrödinger’s wave mechanics: a general method of solving by successive approximations”],
Comptes Rendus Acad. Sci. Paris **183**, 24-26 (1926) [received on 5 July 1926]

H.A. Kramers, “Wellenmechanik und halbzahlige Quantisierung”, [“Wave mechanics and half-integer quantization”],
Zf. Physik **39**, 828-840 (1926) [received on 9 Sept. 1926]

H. Jeffreys, “On certain approx. solutions of linear diff. eqs. of the second order”,
Proc. Lond. Math. Soc. **23**, 428-436 (1925)

4P. Problems

Problem 4.1

Employ the WKB method for a particle of energy E moving in a potential $u(x)$ of the form shown in fig. 4.1.

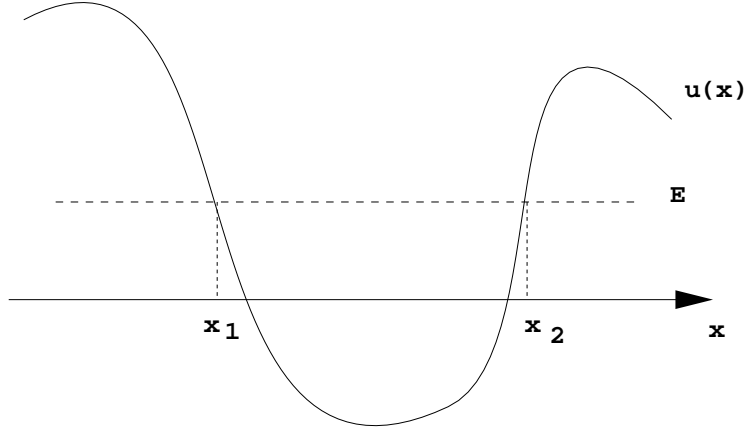


Fig. 4.1

Solution

The Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - u(x)] \psi = 0 . \quad (44)$$

As one can see, we have

$$r(x) = \frac{2m}{\hbar^2} [E - u(x)] \quad \begin{cases} \text{is positive for } a < x < b \\ \text{is negative for } x < a, x > b. \end{cases}$$

If $\psi(x)$ corresponds to the region $x < a$, when passing to the interval $a < x < b$, the connection formula is given by eq. (29) telling us that

$$\psi(x) \approx \frac{A}{[E - u]^{\frac{1}{4}}} \cos \left(\int_a^x \sqrt{\frac{2m}{\hbar^2} (E - u)} dx - \frac{\pi}{4} \right) , \quad (45)$$

where A is an arbitrary constant.

When $\psi(x)$ corresponds to the region $x > b$, when passing to the segment $a < x < b$, we have in a similar way

$$\psi(x) \approx -\frac{B}{[E - u]^{\frac{1}{4}}} \cos \left(\int_x^b \sqrt{\frac{2m}{\hbar^2} (E - u)} dx - \frac{\pi}{4} \right) , \quad (46)$$

where B is another arbitrary constant. The reason why the connection formula is again given by eq. (29) is easily understood examining what happens when the particle reaches the second classical turning point at $x = b$. This produces the inversion of the direction of motion. Thus, the particle appears to come from the right toward the left. In other words, we are in the first case (from the left to the right), only that as seen in a mirror placed at the point $x = a$.

These two expressions should be the same, independently of the constants A and B , so that

$$\begin{aligned} \cos \left(\int_a^x \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} \right) &= -\cos \left(\int_x^b \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} \right) \\ \Rightarrow \cos \left(\int_a^x \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} \right) &+ \cos \left(\int_x^b \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} \right) = 0 . \end{aligned} \quad (47)$$

Recalling that

$$\cos A + \cos B = 2 \cos \left(\frac{A+B}{2} \right) \cos \left(\frac{A-B}{2} \right) ,$$

eq. (47) can be written

$$\begin{aligned} 2 \cos \left[\frac{1}{2} \left(\int_a^x \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} + \int_x^b \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} \right) \right] \\ \cdot \cos \left[\frac{1}{2} \left(\int_a^x \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} - \int_x^b \sqrt{\frac{2m}{\hbar^2}(E-u)} dx + \frac{\pi}{4} \right) \right] = 0 , \end{aligned} \quad (48)$$

which implies that the arguments of the cosinusoids are integer multiples of $\frac{\pi}{2}$. On the other hand, the argument of the second cosinusoid do not lead to a nontrivial result. Therefore, we pay attention only to the argument of the first cosinusoid, which prove to be essential for getting an important result

$$\begin{aligned} \frac{1}{2} \left(\int_a^x \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} + \int_x^b \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{4} \right) &= \frac{n}{2} \pi \quad \text{for } n \text{ odd} \\ \Rightarrow \int_a^b \sqrt{\frac{2m}{\hbar^2}(E-u)} dx - \frac{\pi}{2} &= n\pi \end{aligned}$$

$$\begin{aligned}
&\Rightarrow \int_a^b \sqrt{\frac{2m}{\hbar^2}(E - u)} dx = (n + \frac{1}{2})\pi \\
&\Rightarrow \int_a^b \sqrt{2m(E - u)} dx = (n + \frac{1}{2})\pi\hbar . \tag{49}
\end{aligned}$$

This result is very similar to the *Bohr - Sommerfeld quantization rules*.

We recall that Bohr's postulate says that the orbital angular momentum of an electron moving on an "allowed atomic orbit" is quantized as $L = n\hbar$, $n = 1, 2, 3, \dots$. We also recall that the Wilson - Sommerfeld quantization rules assert that any coordinate of a system that varies periodically in time should satisfy the 'quantum' condition: $\oint p_q dq = n_q h$, where q is a periodic coordinate, p_q is the associated momentum, n_q is an integer, and h is Planck's constant. One can see that the WKB result is indeed very similar.

Problem 4.2

Estimate the error of the WKB solution WKB at a point $x_1 \neq x_k$, where x_k is a classical turning point for the differential equation $y'' + xy = 0$. *The solution of this problem is of importance in the study of uniform fields, such as the gravitational and electric fields generated by large planes.*

Solution:

For this differential equation we have

$$\xi = 1, \quad r(x) = x \quad \& \quad s(x) = -\frac{5}{16}x^{-2} .$$

$r(x) = x$ has a single zero at $x_k = 0$, therefore for $x \gg 0$:

$$W_{\pm} = x^{-\frac{1}{4}} \exp\left(\pm i \int_0^x \sqrt{x} dx\right) = x^{-\frac{1}{4}} \exp\left(\pm \frac{2}{3}ix^{\frac{3}{2}}\right) . \tag{50}$$

Derivating W_{\pm} up to the second derivative in x , we realize that the following differential equation is satisfied

$$W_{\pm}'' + (x - \frac{5}{16}x^{-2})W_{\pm} = 0 . \tag{51}$$

The exact solution $y(x)$ of the latter differential equation can be written as a linear combination of W_{\pm} , as it has been shown in the corresponding

section where the WKB error has been tackled; recall that the following form of the linear combination was proposed therein

$$y(x) = \alpha_+(x)W_+(x) + \alpha_-(x)W_-(x)$$

For large x , the general solution of the differential equation can be written in the WKB approximation as follows

$$y(x) = Ax^{-\frac{1}{4}} \cos\left(\frac{2}{3}x^{\frac{3}{2}} + \delta\right) \quad \text{for } x \rightarrow \infty. \quad (52)$$

Thus, $\alpha_+ \rightarrow \frac{A}{2}e^{i\delta}$ and $\alpha_- \rightarrow \frac{A}{2}e^{-i\delta}$ for $x \rightarrow \infty$. We want to calculate the error due to these WKB solutions. A simple measure of this error is the deviation of α_+ and of α_- relative to the constants A . Using the equation

$$\frac{d\alpha_{\pm}}{dx} = \mp \frac{\xi}{2} i \frac{s(x)}{\sqrt{r(x)}} \left[\alpha_{\pm} + \alpha_{\mp} \exp\left(\mp 2i \int_{x_k}^x \sqrt{r(x)} dx\right) \right]$$

and doing the corresponding substitutions, one gets

$$\frac{d\alpha_{\pm}}{dx} = \mp \frac{i}{2} \left(-\frac{5}{16}x^{-2}\right) x^{-\frac{1}{2}} \left[\frac{A}{2}e^{\pm i\delta} + \frac{A}{2}e^{\mp i\delta} \exp\left(\mp 2i \frac{2}{3}x^{\frac{3}{2}}\right) \right]. \quad (53)$$

Taking $\Delta\alpha_{\pm}$ as the changes displayed by α_{\pm} when x varies between x_1 and ∞ , we can do the required calculation by means of

$$\begin{aligned} \frac{\Delta\alpha_{\pm}}{A/2} &= \frac{2}{A} \int_{x_1}^{\infty} \frac{d\alpha_{\pm}}{dx} dx = \\ &= \pm i \frac{5}{32} e^{\pm i\delta} \left[\frac{2}{3} x_1^{-\frac{3}{2}} + e^{\mp 2i\delta} \int_{x_1}^{\infty} x^{-\frac{5}{2}} \exp\left(\mp i \frac{4}{3} x^{\frac{3}{2}}\right) dx \right]. \end{aligned} \quad (54)$$

The second term in the parentheses is less important than the first one because the complex exponential oscillates between 1 and -1 and therefore $x^{-\frac{5}{2}} < x^{-\frac{3}{2}}$. Consequently

$$\frac{\Delta\alpha_{\pm}}{A/2} \approx \pm \frac{5}{48} i e^{\pm i\delta} x_1^{-\frac{3}{2}}, \quad (55)$$

and as we can see the error introduced by the WKB approximation is indeed small if we take into account that the complex exponential oscillates between -1 and 1 , while $x_1^{-\frac{3}{2}}$ is also small.

5. THE HARMONIC OSCILLATOR (HO)

The solution of the Schrödinger eq. for HO

The HO can be considered as a paradigm of Physics. Its utility is manifest in many areas from classical physics until quantum electrodynamics and theories of gravitational collapse.

From classical mechanics we know that many complicated potentials can be well approximated near their equilibrium positions by HO potentials

$$V(x) \sim \frac{1}{2}V''(a)(x-a)^2 . \quad (1)$$

This is a 1D case. For this case, the classical Hamiltonian function of a particle of mass m , oscillating at the frequency ω has the following form:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 \quad (2)$$

and the quantum Hamiltonian corresponding to the space of configurations is given by

$$\hat{H} = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2 + \frac{1}{2}m\omega^2x^2 \quad (3)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2 . \quad (4)$$

Since we consider a time-independent potential, the eigenfunctions Ψ_n and the eigenvalues E_n are obtained by means of the time-independent Schrödinger equation

$$\hat{H}\Psi_n = E_n\Psi_n . \quad (5)$$

For the HO Hamiltonian, the Schrödinger eq. is

$$\frac{d^2\Psi}{dx^2} + \left[\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2}x^2\right]\Psi = 0 . \quad (6)$$

We canceled the subindices of E and Ψ because they are not of any importance here. Defining

$$k^2 = \frac{2mE}{\hbar^2} \quad (7)$$

$$\lambda = \frac{m\omega}{\hbar} , \quad (8)$$

the Schrödinger eq. becomes

$$\frac{d^2\Psi}{dx^2} + [k^2 - \lambda^2 x^2]\Psi = 0 , \quad (9)$$

which is known as Weber's differential equation in mathematics. We shall make now the transformation

$$y = \lambda x^2 . \quad (10)$$

In general, by changing the variable from x to y , the differential operators take the form

$$\frac{d}{dx} = \frac{dy}{dx} \frac{d}{dy} \quad (11)$$

$$\frac{d^2}{dx^2} = \frac{d}{dx} \left(\frac{dy}{dx} \frac{d}{dy} \right) = \frac{d^2 y}{dx^2} \frac{d}{dy} + \left(\frac{dy}{dx} \right)^2 \frac{d^2}{dy^2} . \quad (12)$$

Applying this obvious rule to the proposed transformation we obtain the following differential eq. in the y variable

$$y \frac{d^2\Psi}{dy^2} + \frac{1}{2} \frac{d\Psi}{dy} + \left[\frac{k^2}{4\lambda} - \frac{1}{4} y \right] \Psi = 0 , \quad (13)$$

and, by definind :

$$\kappa = \frac{k^2}{2\lambda} = \frac{\bar{k}^2}{2m\omega} = \frac{E}{\hbar\omega} , \quad (14)$$

we get

$$y \frac{d^2\Psi}{dy^2} + \frac{1}{2} \frac{d\Psi}{dy} + \left[\frac{\kappa}{2} - \frac{1}{4} y \right] \Psi = 0 . \quad (15)$$

Let us try to solve this equation by first doing its asymptotic analysis in the limit $y \rightarrow \infty$. We first rewrite the previous equation in the form

$$\frac{d^2\Psi}{dy^2} + \frac{1}{2y} \frac{d\Psi}{dy} + \left[\frac{\kappa}{2y} - \frac{1}{4} \right] \Psi = 0 . \quad (16)$$

We notice that in the limit $y \rightarrow \infty$ the equation behaves as follows

$$\frac{d^2\Psi_\infty}{dy^2} - \frac{1}{4} \Psi_\infty = 0 . \quad (17)$$

This equation has as solution

$$\Psi_\infty(y) = A \exp \frac{y}{2} + B \exp \frac{-y}{2} . \quad (18)$$

Taking $A = 0$, we eliminate $\exp \frac{y}{2}$ since it diverges in the limit $y \rightarrow \infty$, keeping only the attenuated exponential. We can now suggest that Ψ has the following form

$$\Psi(y) = \exp \frac{-y}{2} \psi(y) . \quad (19)$$

Plugging it in the differential equation for y (eq. 15) one gets:

$$y \frac{d^2 \psi}{dy^2} + \left(\frac{1}{2} - y \right) \frac{d\psi}{dy} + \left(\frac{\kappa}{2} - \frac{1}{4} \right) \psi = 0 . \quad (20)$$

The latter is a confluent hypergeometric equation ⁴ :

$$z \frac{d^2 y}{dz^2} + (c - z) \frac{dy}{dz} - ay = 0 . \quad (21)$$

The general solution of this equation is

$$y(z) = A {}_1F_1(a; c, z) + B z^{1-c} {}_1F_1(a - c + 1; 2 - c, z) , \quad (22)$$

where the confluent hypergeometric equation is defined by

$${}_1F_1(a; c, z) = \sum_{n=0}^{\infty} \frac{(a)_n x^n}{(c)_n n!} . \quad (23)$$

Comparing now our equation with the standard confluent hypergeometric equation, one can see that the general solution of the first one is

$$\psi(y) = A {}_1F_1\left(a; \frac{1}{2}, y\right) + B y^{\frac{1}{2}} {}_1F_1\left(a + \frac{1}{2}; \frac{3}{2}, y\right) , \quad (24)$$

where

$$a = -\left(\frac{\kappa}{2} - \frac{1}{4} \right) . \quad (25)$$

If we keep these solutions in their present form, the normalization condition is not satisfied for the wavefunction because from the asymptotic behaviour of the confluent hypergeometric function ⁵ it follows (taking into account only the dominant exponential behavior) :

$$\Psi(y) = e^{\frac{-y}{2}} \psi(y) \rightarrow \text{const. } e^{\frac{y}{2}} y^{a - \frac{1}{2}} . \quad (26)$$

⁴It is also known as Kummer's differential equation.

⁵ The asymptotic behavior for $|x| \rightarrow \infty$ is

$${}_1F_1(a; c, z) \rightarrow \frac{\Gamma(c)}{\Gamma(c-a)} e^{-ia\pi} x^{-a} + \frac{\Gamma(c)}{\Gamma(a)} e^x x^{a-c} .$$

The latter approximation leads to a divergence in the normalization integral, which physically is not acceptable. What one does in this case is to impose the termination condition for the series ⁶, that is, the series has only a finite number of terms and therefore it is a polynomial of n order.

We thus notice that asking for a finite normalization constant (as already known, a necessary condition for the physical interpretation in terms of probabilities), leads us to the truncation of the series, which simultaneously generates the quantization of energy.

In the following we consider the two possible cases

1) $a = -n$ and $B = 0$

$$\frac{\kappa}{2} - \frac{1}{4} = n. \quad (27)$$

The eigenfunctions are given by

$$\Psi_n(x) = D_n \exp \frac{-\lambda x^2}{2} {}_1F_1(-n; \frac{1}{2}, \lambda x^2) \quad (28)$$

and the energy is:

$$E_n = \hbar\omega(2n + \frac{1}{2}). \quad (29)$$

2) $a + \frac{1}{2} = -n$ and $A = 0$

$$\frac{\kappa}{2} - \frac{1}{4} = n + \frac{1}{2}. \quad (30)$$

The eigenfunctions are now

$$\Psi_n(x) = D_n \exp \frac{-\lambda x^2}{2} x {}_1F_1(-n; \frac{3}{2}, \lambda x^2), \quad (31)$$

whereas the stationary energies are

$$E_n = \hbar\omega[(2n + 1) + \frac{1}{2}]. \quad (32)$$

The polynomials obtained by this truncation of the confluent hypergeometric series are called Hermite polynomials and in hypergeometric notation they are

$$H_{2n}(\eta) = (-1)^n \frac{(2n)!}{n!} {}_1F_1(-n; \frac{1}{2}, \eta^2) \quad (33)$$

⁶The truncation condition of the confluent hypergeometric series ${}_1F_1(a; c, z)$ is $a = -n$, where n is a nonnegative integer (i.e., zero included).

$$H_{2n-1}(\eta) = (-1)^n \frac{2(2n+1)!}{n!} \eta {}_1F_1\left(-n; \frac{3}{2}, \eta^2\right). \quad (34)$$

We can now combine the obtained results (because some of them give us the even cases and the others the odd ones) in a single expression for the eigenvalues and eigenfunctions

$$\Psi_n(x) = D_n \exp\left(-\frac{\lambda x^2}{2}\right) H_n(\sqrt{\lambda}x) \quad (35)$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad n = 0, 1, 2 \dots \quad (36)$$

The HO energy spectrum is equidistant, i.e., there is the same energy difference $\hbar\omega$ between any consecutive neighbour levels. Another remark refers to the minimum value of the energy of the oscillator; somewhat surprisingly it is not zero. This is considered by many people to be a pure quantum result because it is zero when $\hbar \rightarrow 0$. It is known as *the zero point energy* and the fact that it is different of zero is the main characteristic of all confining potentials.

The normalization constant is easy to calculate

$$D_n = \left[\sqrt{\frac{\lambda}{\pi}} \frac{1}{2^n n!} \right]^{\frac{1}{2}}. \quad (37)$$

Thus, one gets the following normalized eigenfunctions of the 1D operator

$$\Psi_n(x) = \left[\sqrt{\frac{\lambda}{\pi}} \frac{1}{2^n n!} \right]^{\frac{1}{2}} \exp\left(-\frac{\lambda x^2}{2}\right) H_n(\sqrt{\lambda}x). \quad (38)$$

Creation and annihilation operators: \hat{a}^\dagger and \hat{a}

There is another approach to deal with the HO besides the conventional one of solving the Schrödinger equation. It is the algebraic method, also known as the method of creation and annihilation (ladder) operators. This is a very efficient procedure, which can be successfully applied to many quantum-mechanical problems, especially when dealing with discrete spectra.

Let us define two nonhermitic operators a and a^\dagger :

$$a = \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{ip}{m\omega} \right) \quad (39)$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(x - \frac{ip}{m\omega} \right) . \quad (40)$$

These operators are known as *annihilation operator* and *creation operator*, respectively (the reason of this terminology will be seen in the following, though one can claim that it comes from quantum field theories). Let us calculate the commutator of these operators

$$[a, a^\dagger] = \frac{m\omega}{2\hbar} \left[x + \frac{ip}{m\omega}, x - \frac{ip}{m\omega} \right] = \frac{1}{2\hbar} (-i[x, p] + i[p, x]) = 1 , \quad (41)$$

where we have used the commutator

$$[x, p] = i\hbar . \quad (42)$$

Therefore the annihilation and creation operators do not commute, since we have

$$[a, a^\dagger] = 1 . \quad (43)$$

Let us also introduce the very important *number operator* \hat{N} :

$$\hat{N} = a^\dagger a . \quad (44)$$

This operator is hermitic as one can readily prove using $(AB)^\dagger = B^\dagger A^\dagger$:

$$\hat{N}^\dagger = (a^\dagger a)^\dagger = a^\dagger (a^\dagger)^\dagger = a^\dagger a = \hat{N} . \quad (45)$$

Considering now that

$$a^\dagger a = \frac{m\omega}{2\hbar} \left(x^2 + \frac{p^2}{m^2\omega^2} \right) + \frac{i}{2\hbar} [x, p] = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2} \quad (46)$$

we notice that the Hamiltonian can be written in a quite simple form as a function of the number operator

$$\hat{H} = \hbar\omega \left(\hat{N} + \frac{1}{2} \right) . \quad (47)$$

The number operator bears this name because its eigenvalues are precisely the subindices of the eigenfunctions on which it acts

$$\hat{N} | n \rangle = n | n \rangle , \quad (48)$$

where we have used the notation

$$Psi_n = | n \rangle . \quad (49)$$

Applying this fact to (47), we get

$$\hat{H} | n \rangle = \hbar\omega(n + \frac{1}{2}) | n \rangle . \quad (50)$$

On the other hand, from the Schrödinger equation we know that $\hat{H} | n \rangle = E | n \rangle$. In this way, it comes out that the energy eigenvalues are given by

$$E_n = \hbar\omega(n + \frac{1}{2}) . \quad (51)$$

This result is identical (as it should be) to the result (36). We go ahead and show why the operators a and a^\dagger bear the names they have. For this, we calculate the commutators

$$[\hat{N}, a] = [a^\dagger a, a] = a^\dagger [a, a] + [a^\dagger, a]a = -a , \quad (52)$$

which can be obtained from $[a, a] = 0$ and (43). Similarly, let us calculate

$$[\hat{N}, a^\dagger] = [a^\dagger a, a^\dagger] = a^\dagger [a, a^\dagger] + [a^\dagger, a^\dagger]a = a^\dagger . \quad (53)$$

Using these two commutators, we can write

$$\begin{aligned} \hat{N}(a^\dagger | n \rangle) &= ([\hat{N}, a^\dagger] + a^\dagger \hat{N}) | n \rangle \\ &= (a^\dagger + a^\dagger \hat{N}) | n \rangle \\ &= a^\dagger(1 + n) | n \rangle = (n + 1)a^\dagger | n \rangle . \end{aligned} \quad (54)$$

By a similar procedure, one can also obtain

$$\hat{N}(a | n \rangle) = ([\hat{N}, a] + a \hat{N}) | n \rangle = (n - 1)a | n \rangle . \quad (55)$$

The expression (54) implies that one can consider the ket $a^\dagger | n \rangle$ as an eigenket of that number operator for which the eigenvalue is raised by one unit. In physical terms, this means that an energy quanta has been produced by the action of a^\dagger on the ket. This already explains the name of creation operator. Similar comments with corresponding conclusion can be inferred for the operator a , originating the name of annihilation operator (an energy quanta is eliminated from the system when this operator is put in action). Moreover, eq. (54) implies the proportionality of the kets $a^\dagger | n \rangle$ and $| n + 1 \rangle$:

$$a^\dagger | n \rangle = c | n + 1 \rangle , \quad (56)$$

where c is a constant that should be determined. Considering in addition

$$(a^\dagger | n \rangle)^\dagger = \langle n | a = c^* \langle n + 1 | , \quad (57)$$

one can perform the following calculation

$$\langle n | a(a^\dagger | n \rangle) = c^* \langle n + 1 | (c | n + 1 \rangle) \quad (58)$$

$$\langle n | aa^\dagger | n \rangle = c^* c \langle n + 1 | n + 1 \rangle \quad (59)$$

$$\langle n | aa^\dagger | n \rangle = |c|^2 . \quad (60)$$

But from the commutation relation for the operators a and a^\dagger

$$[a, a^\dagger] = aa^\dagger - a^\dagger a = aa^\dagger - \hat{N} = 1 , \quad (61)$$

we have

$$aa^\dagger = \hat{N} + 1 . \quad (62)$$

Substituting in (60), we get

$$\langle n | \hat{N} + 1 | n \rangle = \langle n | n \rangle + \langle n | \hat{N} | n \rangle = n + 1 = |c|^2 . \quad (63)$$

Asking conventionally for a positive and real c , the following value is obtained

$$c = \sqrt{n + 1} . \quad (64)$$

Consequently, we have

$$a^\dagger | n \rangle = \sqrt{n + 1} | n + 1 \rangle . \quad (65)$$

For the annihilation operator, following the same procedure one can get the following relation

$$a | n \rangle = \sqrt{n} | n - 1 \rangle . \quad (66)$$

Let us show now that the values of n should be nonnegative integers. For this, we employ the positivity requirement for the norm, applying it to the state vector $a | n \rangle$. The latter condition tells us that the interior product of the vector with its adjunct $((a | n \rangle)^\dagger = \langle n | a^\dagger)$ should always be nonnegative

$$(\langle n | a^\dagger) \cdot (a | n \rangle) \geq 0 . \quad (67)$$

This relationship is nothing else but

$$\langle n | a^\dagger a | n \rangle = \langle n | \hat{N} | n \rangle = n \geq 0 . \quad (68)$$

Thus, n cannot be negativ. It should be an integer since were it not by applying iteratively the annihilation operator we would be lead to negative values of n , which would be a contradiction to the previous statement. It is possible to express the state n ($|n\rangle$) directly as a function of the ground state ($|0\rangle$) using the creation operator. Let us see how proceeds this important iteration

$$|1\rangle = a^\dagger |0\rangle \quad (69)$$

$$|2\rangle = \left[\frac{a^\dagger}{\sqrt{2}}\right] |1\rangle = \left[\frac{(a^\dagger)^2}{\sqrt{2!}}\right] |0\rangle \quad (70)$$

$$|3\rangle = \left[\frac{a^\dagger}{\sqrt{3}}\right] |2\rangle = \left[\frac{(a^\dagger)^3}{\sqrt{3!}}\right] |0\rangle \quad (71)$$

⋮

$$|n\rangle = \left[\frac{(a^\dagger)^n}{\sqrt{n!}}\right] |0\rangle . \quad (72)$$

One can also apply this method to get the eigenfunctions in the configuration space. To achieve this, we start with the ground state

$$a |0\rangle = 0 . \quad (73)$$

In the x representation, we have

$$\hat{a}\Psi_0(x) = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right)\Psi_0(x) = 0 . \quad (74)$$

Recalling the form of the momentum operator in the x representation, we can obtain a differential equation for the wavefunction of the ground state. Moreover, introducing the definition $x_0 = \sqrt{\frac{\hbar}{m\omega}}$, we have

$$\left(x + x_0^2 \frac{d}{dx}\right)\Psi_0 = 0 . \quad (75)$$

The latter equation can be readily solved, and normalizing (its integral from $-\infty$ to ∞ should be equal to unity), we obtain the wavefunction of the ground state

$$\Psi_0(x) = \left(\frac{1}{\sqrt{\sqrt{\pi}x_0}}\right)e^{-\frac{1}{2}\left(\frac{x}{x_0}\right)^2} . \quad (76)$$

The rest of the eigenfunctions, which describe the HO excited states, can be obtained employing the creation operator. The procedure is the following

$$\Psi_1 = a^\dagger \Psi_0 = \left(\frac{1}{\sqrt{2}x_0}\right)(x - x_0^2 \frac{d}{dx})\Psi_0 \quad (77)$$

$$\Psi_2 = \frac{1}{\sqrt{2}}(a^\dagger)^2 \Psi_0 = \frac{1}{\sqrt{2!}}\left(\frac{1}{\sqrt{2}x_0}\right)^2(x - x_0^2 \frac{d}{dx})^2 \Psi_0 . \quad (78)$$

By mathematical induction, one can show that

$$\Psi_n = \frac{1}{\sqrt{\sqrt{\pi}2^n n!}} \frac{1}{x_0^{n+\frac{1}{2}}} (x - x_0^2 \frac{d}{dx})^n e^{-\frac{1}{2}(\frac{x}{x_0})^2} . \quad (79)$$

Time evolution of the oscillator

In this section we shall illustrate on the HO example the way of working with the Heisenberg representation in which the states are fixed in time and only the operators evolve. Thus, we shall consider the operators as functions of time and obtain explicitly the time evolution of the HO position and momentum operators, a and a^\dagger , respectively. The Heisenberg equations of the motion for p and x are

$$\frac{d\hat{p}}{dt} = -\frac{\partial}{\partial \hat{x}} V(\hat{\mathbf{x}}) \quad (80)$$

$$\frac{d\hat{x}}{dt} = \frac{\hat{p}}{m} . \quad (81)$$

Hence the equations of the motion for x and p in the HO case are the following

$$\frac{d\hat{p}}{dt} = -m\omega^2 \hat{x} \quad (82)$$

$$\frac{d\hat{x}}{dt} = \frac{\hat{p}}{m} . \quad (83)$$

These are a pair of coupled equations, which are equivalent to a pair of *uncoupled* equations for the creation and annihilation operators. Explicitly, we have

$$\frac{da}{dt} = \sqrt{\frac{m\omega}{2\hbar}} \frac{d}{dt} \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right) \quad (84)$$

$$\frac{da}{dt} = \sqrt{\frac{m\omega}{2\hbar}} \left(\frac{d\hat{x}}{dt} + \frac{i}{m\omega} \frac{d\hat{p}}{dt} \right) . \quad (85)$$

Substituting (82) and (83) in (85), we get

$$\frac{da}{dt} = \sqrt{\frac{m\omega}{2\hbar}} \left(\frac{\hat{p}}{m} - i\omega\hat{x} \right) = -i\omega a . \quad (86)$$

Similarly, one can obtain a differential equation for the creation operator

$$\frac{da^\dagger}{dt} = i\omega a^\dagger . \quad (87)$$

The differential evolution equations for the creation and annihilation operators can be immediately integrated leading to the explicit evolution of these operators as follows

$$a(t) = a(0)e^{-i\omega t} \quad (88)$$

$$a^\dagger(t) = a^\dagger(0)e^{i\omega t} . \quad (89)$$

It is worth noting based on these results and eqs. (44) and (47) that both the Hamiltonian and the number operator are not time dependent. Using the latter two results, we can obtain the position and momentum operators as functions of time as far as they are expressed in terms of the creation and annihilation operators

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger) \quad (90)$$

$$\hat{p} = i\sqrt{\frac{m\hbar\omega}{2}} (a^\dagger - a) . \quad (91)$$

Substituting them, one gets

$$\hat{x}(t) = \hat{x}(0) \cos \omega t + \frac{\hat{p}(0)}{m\omega} \sin \omega t \quad (92)$$

$$\hat{p}(t) = -m\omega\hat{x}(0) \sin \omega t + \hat{p}(0) \cos \omega t . \quad (93)$$

The time evolution of these operators is the same as for the classical equations of the motion.

Thus, we have shown here the explicit evolution form of the four HO basic operators, and also we illustrated the effective way of working in the Heisenberg representation.

The 3D HO

We commented on the importance in physics of the HO at the very beginning of our analysis of the quantum HO. If we will consider a 3D analog, we would be led to study a Taylor expansion in three variables⁷ retaining the terms up to the second order, we get a quadratic form in the most general case. The problem at hand in this approximation is not as simple as it might look from the examination of the corresponding potential

$$V(x, y, z) = ax^2 + by^2 + cz^2 + dxy + exz + fyz . \quad (94)$$

There are however many systems with spherical symmetry or for which this symmetry is sufficiently exact. In acest caz:

$$V(x, y, z) = K(x^2 + y^2 + z^2) , \quad (95)$$

which is equivalent to saying that the second unmixed partial derivatives have all the same value, denoted by K in our case). We can add that this is a good approximation in the case in which the values of the mixed second partial derivatives are small in comparison to the unmixed ones.

When these conditions are satisfied and the potential is given by (95), we say that the system is a *3D spherically symmetric HO*.

The Hamiltonian in this case is of the form

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + \frac{m\omega^2}{2} r^2 , \quad (96)$$

where the Laplace operator is given in spherical coordinates and r is the spherical radial coordinate.

Since the potential is time independent the energy is conserved. In addition, because of the spherical symmetry the orbital momentum is also conserved. having two conserved quantities, we may say that to each of it one can associate a quantum number. Thus, we can assume that the eigenfunctions depend on two quantum numbers (even though for this case we shall see that another one will occur). Taking care of these comments, the equation of interest is

⁷It is possible to express the Taylor series in the neighbourhood of \mathbf{r}_0 as an exponential operator

$$e^{[(x-x_0)+(y-y_0)+(z-z_0)](\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z})} f(\mathbf{r}_0) .$$

$$\hat{H}\Psi_{nl} = E_{nl}\Psi_{nl} . \quad (97)$$

The Laplace operator in spherical coordinates reads

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2} \quad (98)$$

and can be also inferred from the known fact

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] . \quad (99)$$

The eigenfunctions of \hat{L}^2 are the spherical harmonics, i.e.

$$\hat{L}^2 Y_{lm_l}(\theta, \varphi) = -\hbar^2 l(l+1) Y_{lm_l}(\theta, \varphi) \quad (100)$$

The fact that the spherical harmonics ‘wear’ the quantum number m_l introduces it in the total wavefunction Ψ_{nlm_l} .

In order to achieve the separation of the variables and functions, the following substitution is proposed

$$\Psi_{nlm_l}(r, \theta, \varphi) = \frac{R_{nl}(r)}{r} Y_{lm_l}(\theta, \varphi) . \quad (101)$$

Once this is plugged in the Schrödinger equation, the spatial part is separated from the angular one; the latter is identified with an operator that is proportional to the square of the orbital momentum, for which the eigenfunctions are the spherical harmonics, whereas for the spatial part the following equation is obtained

$$R''_{nl} + \left(\frac{2mE_{nl}}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2} r^2 - \frac{l(l+1)}{r^2} \right) R_{nl}(r) = 0 . \quad (102)$$

Using the definitions (7) and (8), the previous equation is precisely of the form (9), unless the angular momentum term, which is commonly known as the unghiular, care în mod comun se cunoaște ca *angular momentum barrier*

$$R''_{nl} + \left(k^2 - \lambda^2 r^2 - \frac{l(l+1)}{r^2} \right) R_{nl} = 0 . \quad (103)$$

To solve this equation, we shall start with its asymptotic analysis. If we shall consider first $r \rightarrow \infty$, we notice that the orbital momentum term is negligible, so that in this limit the asymptotic behavior is similar to that of (9), leading to

$$R_{nl}(r) \sim \exp \frac{-\lambda r^2}{2} \quad \text{for } \lim r \rightarrow \infty . \quad (104)$$

If now we pass to the behavior close to zero, we can see that the dominant term is that of the orbital momentum, i.e., the differential equation (102) in this limit turns into

$$R_{nl}'' - \frac{l(l+1)}{r^2} R_{nl} = 0 . \quad (105)$$

This is a differential equation of the Euler type ⁸, whose two independent solutions are

$$R_{nl}(r) \sim r^{l+1} \text{ or } r^{-l} \quad \text{for } \lim r \rightarrow 0 . \quad (106)$$

The previous arguments lead to proposing the substitution

$$R_{nl}(r) = r^{l+1} \exp \frac{-\lambda r^2}{2} \phi(r) . \quad (107)$$

One can also use another substitution

$$R_{nl}(r) = r^{-l} \exp \frac{-\lambda r^2}{2} v(r) , \quad (108)$$

which, however, produces the same solutions as (107) (showing this is a helpful exercise). Substituting (107) in (103), the following differential equation for ϕ is obtained

$$\phi'' + 2\left(\frac{l+1}{r} - \lambda r\right)\phi' - [\lambda(2l+3) - k^2]\phi = 0 . \quad (109)$$

Using now the change of variable $w = \lambda r^2$, one gets

$$w\phi'' + \left(l + \frac{3}{2} - w\right)\phi' - \left[\frac{1}{2}\left(l + \frac{3}{2}\right) - \frac{\kappa}{2}\right]\phi = 0 , \quad (110)$$

⁸An equation of the Euler type has the form

$$x^n y^{(n)}(x) + x^{n-1} y^{(n-1)}(x) + \dots + xy'(x) + y(x) = 0 .$$

Its solutions are of the type x^α that are plugged in the equation obtaining a polynomial in α .

where $\kappa = \frac{k^2}{2\lambda} = \frac{E}{\hbar\omega}$ has been introduced. We see that we found again a differential equation of the confluent hypergeometric type having the solutions (see (21) and (22))

$$\phi(r) = A {}_1F_1\left[\frac{1}{2}\left(l + \frac{3}{2} - \kappa\right); l + \frac{3}{2}, \lambda r^2\right] + B r^{-(2l+1)} {}_1F_1\left[\frac{1}{2}\left(-l + \frac{1}{2} - \kappa\right); -l + \frac{1}{2}, \lambda r^2\right]. \quad (111)$$

The second particular solution cannot be normalized because diverges strongly in zero. This forces one to take $B = 0$, therefore

$$\phi(r) = A {}_1F_1\left[\frac{1}{2}\left(l + \frac{3}{2} - \kappa\right); l + \frac{3}{2}, \lambda r^2\right]. \quad (112)$$

Using the same arguments as in the 1D HO case, that is, imposing a regular solution at infinity, leads to the truncation of the series, which implies the quantization of the energy. The truncation is explicitly

$$\frac{1}{2}\left(l + \frac{3}{2} - \kappa\right) = -n, \quad (113)$$

where introducing κ we get the energy spectrum

$$E_{nl} = \hbar\omega\left(2n + l + \frac{3}{2}\right). \quad (114)$$

One can notice that for the 3D spherically symmetric HO there is a zero point energy $\frac{3}{2}\hbar\omega$.

The unnormalized eigenfunctions are

$$\Psi_{nlm}(r, \theta, \varphi) = r^l e^{-\frac{\lambda r^2}{2}} {}_1F_1\left(-n; l + \frac{3}{2}, \lambda r^2\right) Y_{lm}(\theta, \varphi). \quad (115)$$

5P. Problems

Problem 5.1

Determine the eigenvalues and eigenfunctions of the HO in the momentum space.

The quantum HO Hamiltonian reads

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2.$$

In the momentum space, the operators \hat{x} and \hat{p} have the following form

$$\hat{p} \rightarrow p$$

$$\hat{x} \rightarrow i\hbar \frac{\partial}{\partial p} .$$

Thus, the HO quantum Hamiltonian in the momentum representation is

$$\hat{H} = \frac{p^2}{2m} - \frac{1}{2}m\omega^2\hbar^2 \frac{d^2}{dp^2} .$$

We have to solve the eigenvalue problem (i.e., to get the eigenfunctions and the eigenvalues) given by (5), which, with the previous Hamiltonian, turns into the following differential equation

$$\frac{d^2\Psi(p)}{dp^2} + \left(\frac{2E}{m\hbar^2\omega^2} - \frac{p^2}{m^2\hbar^2\omega^2} \right) \Psi(p) = 0 . \quad (116)$$

One can see that this equation is identical, up to some constants, with the differential equation in the space of configurations (eq. (6)). Just to show another way of solving it, we define two parameters, which are analogous to those in (7) and (8)

$$k^2 = \frac{2E}{m\hbar^2\omega^2} \quad \lambda = \frac{1}{m\hbar\omega} . \quad (117)$$

With these definitions, we get the differential eq. (9) and therefore the solution sought for (after performing the asymptotic analysis) is of the form

$$\Psi(y) = e^{-\frac{1}{2}y} \phi(y) , \quad (118)$$

where $y = \lambda p^2$ and λ is defined in (117). Substitute (118) in (116) taking care to put (118) in the variable p . One gets a differential equation in the variable ϕ

$$\frac{d^2\phi(p)}{dp^2} - 2\lambda p \frac{d\phi(p)}{dp} + (k^2 - \lambda)\phi(p) = 0 . \quad (119)$$

We shall now make the change of variable $u = \sqrt{\lambda}p$ that finally leads us to the Hermite equation

$$\frac{d^2\phi(u)}{du^2} - 2u \frac{d\phi(u)}{du} + 2n\phi(u) = 0 , \quad (120)$$

where n is a nonnegative integer and where we have put

$$\frac{k^2}{\lambda} - 1 = 2n .$$

From here and the definitions given in (117) one can easily conclude that the eigenvalues are given by

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

The solutions for (120) are the Hermite polynomials $\phi(u) = H_n(u)$ and the unnormalized eigenfunctions are

$$\Psi(p) = Ae^{-\frac{\lambda}{2}p^2} H_n(\sqrt{\lambda}p) .$$

Problem 5.2

Prove that the Hermite polynomials can be expressed in the following integral representation

$$H_n(x) = \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{\infty} (x + iy)^n e^{-y^2} dy . \quad (121)$$

This representation of Hermite polynomials is not really usual, though it can prove useful in many cases. In order to accomplish the proof, we shall expand expand the integral and next prove that what we've got is identical to the series expansion of the Hermite polynomials that reads

$$\sum_{k=0}^{\lfloor \frac{n}{2} \rfloor} \frac{(-1)^k n!}{(n-2k)!k!} (2x)^{n-2k} , \quad (122)$$

where the symbol $\lfloor c \rfloor$, indicating where the series terminates, denotes the greatest integer less or equal to c .

The first thing we shall do is to expand the binomial in the integral by using the well-known binomial theorem

$$(x + y)^n = \sum_{m=0}^n \frac{n!}{(n-m)!m!} x^{n-m} y^m .$$

Thus

$$(x + iy)^n = \sum_{m=0}^n \frac{n!}{(n-m)!m!} i^m x^{n-m} y^m , \quad (123)$$

which plugged in the integral leads to

$$\frac{2^n}{\sqrt{\pi}} \sum_{m=0}^n \frac{n!}{(n-m)!m!} i^m x^{n-m} \int_{-\infty}^{\infty} y^m e^{-y^2} dy . \quad (124)$$

Inspecting of the integrand we realize that the integral is not zero when m is even, whereas it is zero when m is odd. Using the even notation $m = 2k$, we get

$$\frac{2^n}{\sqrt{\pi}} \sum_{k=0}^{\lfloor \frac{n}{2} \rfloor} \frac{n!}{(n-2k)!(2k)!} i^{2k} x^{n-2k} 2 \int_0^{\infty} y^{2k} e^{-y^2} dy . \quad (125)$$

Under the change of variable $u = y^2$, the integral turns into a gamma function

$$\frac{2^n}{\sqrt{\pi}} \sum_{k=0}^{\lfloor \frac{n}{2} \rfloor} \frac{n!}{(n-2k)!(2k)!} i^{2k} x^{n-2k} \int_0^{\infty} u^{k-\frac{1}{2}} e^{-u} du , \quad (126)$$

more precisely $\Gamma(k + \frac{1}{2})$, which can be expressed in terms of factorials (of course for k an integer)

$$\Gamma(k + \frac{1}{2}) = \frac{(2k)!}{2^{2k} k!} \sqrt{\pi} .$$

Plugging this expression in the sum and using $i^{2k} = (-1)^k$, one gets

$$\sum_{k=0}^{\lfloor \frac{n}{2} \rfloor} \frac{(-1)^k n!}{(n-2k)! k!} (2x)^{n-2k} , \quad (127)$$

which is identical to (122), hence completing the proof.

Problem 5.3

Show that Heisenberg's uncertainty relation is satisfied by doing the calculation using the HO eigenfunctions .

We have to show that for any Ψ_n , we have

$$\langle (\Delta p)^2 (\Delta x)^2 \rangle \geq \frac{\hbar^2}{4} , \quad (128)$$

where the notation $\langle \rangle$ means the mean value.

We shall separately calculate $\langle (\Delta p)^2 \rangle$ and $\langle (\Delta x)^2 \rangle$, where each of these expressions is

$$\langle (\Delta p)^2 \rangle = \langle (p - \langle p \rangle)^2 \rangle = \langle p^2 - 2p \langle p \rangle + \langle p \rangle^2 \rangle = \langle p^2 \rangle - \langle p \rangle^2 ,$$

$$\langle (\Delta x)^2 \rangle = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x \langle x \rangle + \langle x \rangle^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 .$$

First of all, we shall prove that both the mean of x as well as of p are zero. For the mean of x , we have

$$\langle x \rangle = \int_{-\infty}^{\infty} x [\Psi_n(x)]^2 dx .$$

This integral is zero because the integrand is odd. Thus

$$\langle x \rangle = 0 . \quad (129)$$

The same argument holds for the mean of p , if we do the calculation in the momentum space, employing the functions obtained in problem 1. It is sufficient to notice that the functional form is the same (only the symbol does change). Thus

$$\langle p \rangle = 0 . \quad (130)$$

Let us now calculate the mean of x^2 . We shall use the virial theorem⁹. We first notice that

$$\langle V \rangle = \frac{1}{2} m \omega^2 \langle x^2 \rangle .$$

Therefore, it is possible to relate the mean of x^2 directly to the mean of the potential for this case (implying the usage of the virial theorem).

$$\langle x^2 \rangle = \frac{2}{m \omega^2} \langle V \rangle . \quad (131)$$

We also need the total energy

$$\langle H \rangle = \langle T \rangle + \langle V \rangle ,$$

⁹We recall that the virial theorem in quantum mechanics asserts that

$$2 \langle T \rangle = \langle \mathbf{r} \cdot \nabla V(\mathbf{r}) \rangle .$$

For a potential of the form $V = \lambda x^n$, the virial theorem gives

$$2 \langle T \rangle = n \langle V \rangle ,$$

where T is the kinetic energy and V is the potential energy.

for which again one can make use of the virial theorem (for $n = 2$)

$$\langle H \rangle = 2 \langle V \rangle . \quad (132)$$

Thus, we obtain

$$\langle x^2 \rangle = \frac{\langle H \rangle}{m\omega^2} = \frac{\hbar\omega(n + \frac{1}{2})}{m\omega^2} \quad (133)$$

$$\langle x^2 \rangle = \frac{\hbar}{m\omega} (n + \frac{1}{2}) . \quad (134)$$

Similarly, the mean of p^2 can be readily calculated

$$\langle p^2 \rangle = 2m \langle \frac{p^2}{2m} \rangle = 2m \langle T \rangle = m \langle H \rangle = m\hbar\omega(n + \frac{1}{2}) . \quad (135)$$

Employing (133) and (135), we have

$$\langle (\Delta p)^2 (\Delta x)^2 \rangle = (n + \frac{1}{2})^2 \hbar^2 . \quad (136)$$

Based on this result, we come to the conclusion that in the HO stationary states that actually have not been directly used, Heisenberg's uncertainty relation is satisfied and it is at the minimum for the ground state, $n = 0$.

Problem 5.4

Obtain the matrix elements of the operators a , a^\dagger , \hat{x} , and \hat{p} .

Let us first find the matrix elements for the creation and annihilation operators, which are very helpful for all the other operators.

We shall use the relationships (65) and (66), leading to

$$\langle m | a | n \rangle = \sqrt{n} \langle m | n - 1 \rangle = \sqrt{n} \delta_{m,n-1} . \quad (137)$$

Similarly for the creation operator we have the result

$$\langle m | a^\dagger | n \rangle = \sqrt{n+1} \langle m | n + 1 \rangle = \sqrt{n+1} \delta_{m,n+1} . \quad (138)$$

Let us proceed now with the calculation of the matrix elements of the position operator. For this, let us express this operator in terms of creation

and annihilation operators. Using the definitions (39) and (40), one can immediately prove that the position operator is given by

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) . \quad (139)$$

Employing this result, the matrix elements of the operator \hat{x} can be readily calculated

$$\begin{aligned} \langle m | \hat{x} | n \rangle &= \langle m | \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) | n \rangle \\ &= \sqrt{\frac{\hbar}{2m\omega}}[\sqrt{n}\delta_{m,n-1} + \sqrt{n+1}\delta_{m,n+1}] . \end{aligned} \quad (140)$$

Following the same procedure we can calculate the matrix elements of the momentum operator, just by taking into account that \hat{p} is given in terms of the creation and annihilation operators as follows

$$\hat{p} = i\sqrt{\frac{m\hbar\omega}{2}}(a^\dagger - a) . \quad (141)$$

This leads us to

$$\langle m | \hat{p} | n \rangle = i\sqrt{\frac{m\hbar\omega}{2}}[\sqrt{n+1}\delta_{m,n+1} - \sqrt{n}\delta_{m,n-1}] . \quad (142)$$

One can realize the ease of the calculations when the matrix elements of the creation and annihilation operators are used. Finally, we remark on the nondiagonality of the obtained matrix elements. This is not so much of a surprise because the employed representation is that of the number operator and none of the four operators do not commute with it.

Problem 5.5

Find the mean values of \hat{x}^2 and \hat{p}^2 for the 1D HO and use them to calculate the mean (expectation) values of the kinetic and potential energies. Compare the result with the virial theorem.

First of all, let us obtain the mean value of \hat{x}^2 . For this, we use eq. (139) that leads us to

$$\hat{x}^2 = \frac{\hbar}{2m\omega}(a^2 + (a^\dagger)^2 + a^\dagger a + a a^\dagger) . \quad (143)$$

Recall that the creation and annihilation operators do not commute. Based on (143), we can calculate the mean value of \hat{x}^2

$$\begin{aligned} \langle \hat{x}^2 \rangle &= \langle n | \hat{x}^2 | n \rangle \\ &= \frac{\hbar}{2m\omega} [\sqrt{n(n-1)}\delta_{n,n-2} + \sqrt{(n+1)(n+2)}\delta_{n,n+2} \\ &\quad + n\delta_{n,n} + (n+1)\delta_{n,n}], \end{aligned} \quad (144)$$

which shows that

$$\langle \hat{x}^2 \rangle = \langle n | \hat{x}^2 | n \rangle = \frac{\hbar}{2m\omega}(2n+1). \quad (145)$$

In order to calculate the mean value of \hat{p}^2 we use (141) that helps us to express this operator in terms of the creation and annihilation operators

$$\hat{p}^2 = -\frac{m\hbar\omega}{2}(a^2 + (a^\dagger)^2 - aa^\dagger - a^\dagger a). \quad (146)$$

This leads us to

$$\langle \hat{p}^2 \rangle = \langle n | \hat{p}^2 | n \rangle = \frac{m\hbar\omega}{2}(2n+1). \quad (147)$$

The latter result practically gives us the mean kinetic energy

$$\langle \hat{T} \rangle = \langle \frac{\hat{p}^2}{2m} \rangle = \frac{1}{2m} \langle \hat{p}^2 \rangle = \frac{\hbar\omega}{4}(2n+1). \quad (148)$$

On the other hand, the mean value of the potential energy

$$\langle \hat{V} \rangle = \langle \frac{1}{2}m\omega^2\hat{x}^2 \rangle = \frac{1}{2}m\omega^2 \langle \hat{x}^2 \rangle = \frac{\hbar\omega}{4}(2n+1), \quad (149)$$

where (145) has been used.

We can see that these mean values are equal for any n , which confirms the quantum virial theorem, telling us that for a quadratic (HO) potential, the mean values of the kinetic and potential energies should be equal and therefore be half of the mean value of the total energy.

6. THE HYDROGEN ATOM

Introduction

In this chapter we shall study the hydrogen atom by solving the time-independent Schrödinger equation for the potential due to two charged particles, the electron and the proton, and the Laplacian operator in spherical coordinates. From the mathematical viewpoint, the method of separation of variables will be employed, and a physical interpretation of the wavefunction as solution of the Schrödinger equation in this important case will be provided, together with the interpretation of the quantum numbers and of the probability densities.

The very small spatial scale of the hydrogen atom is a clue that the related physical phenomena enter the domain of applicability of the quantum mechanics, for which the atomic processes have been a successful area since the early days of the quantum approaches. Quantum mechanics, as any other theoretical framework, gives relationships between observable quantities. Since the uncertainty principle leads to a substantial change in the understanding of observables at the conceptual level, it is important to have a clear idea on the notion of atomic observable. As a matter of fact, the real quantities on which quantum mechanics offers explicit answers and connections are always probabilities. Instead of saying, for example, that the radius of the electron orbit in the fundamental state of the hydrogen atom is always 5.3×10^{-11} m, quantum mechanics asserts that this is a truly mean radius (not in the measurable sense). Thus, if one performs an appropriate experiment, one gets, precisely as in the case of the common arrangement of macroscopic detectors probing macroscopic properties of the matter, random values around the mean value 5.3×10^{-11} m. In other words, from the viewpoint of the experimental errors there is no essential difference with regard to the classical physics. The fundamental difference is in the procedure of calculating the mean values within the theoretical framework.

As is known, for performing quantum-mechanical calculations, one needs a corresponding wave function Ψ . Although Ψ has no direct physical interpretation, the square modulus $|\Psi|^2$ calculated at an arbitrary position and given moment is proportional to the probability to find the particle in the infinitesimal neighbourhood of that point at the given time. The purpose of quantum mechanics is to determine Ψ for a specified particle in the prepared experimental conditions.

Before proceeding with the rigorous approaches of getting Ψ for the hydrogen electron, we will argue on several general requirements regarding the wave function. First, the integral of $|\Psi|^2$ over all space should be finite if we really want to deal with a localizable electron. In addition, if

$$\int_{-\infty}^{\infty} |\Psi|^2 dV = 0 , \quad (1)$$

then the particle does not exist. $|\Psi|^2$ cannot be negative or complex because of simple mathematical reasons. In general, it is convenient to identify $|\Psi|^2$ with the probability P not just the proportionality. In order that $|\Psi|^2$ be equal to P one imposes

$$\int_{-\infty}^{\infty} |\Psi|^2 dV = 1 , \quad (2)$$

because

$$\int_{-\infty}^{\infty} P dV = 1 \quad (3)$$

is the mathematical way of saying that the particle exists at a point in space at any given moment. A wave function respecting eq. 2 is said to be normalized. Besides this, Ψ should be single valued, because P has a unique value at a given point and given time. Another condition is that Ψ and its partial first derivatives $\frac{\partial \Psi}{\partial x}$, $\frac{\partial \Psi}{\partial y}$, $\frac{\partial \Psi}{\partial z}$ should be continuous at any arbitrary point.

The Schrödinger equation is considered as the fundamental equation of nonrelativistic quantum mechanics in the same sense in which Newton's force law is the fundamental equation of motion of newtonian mechanics. Notice however that we have now a wave equation for a function Ψ which is not directly measurable.

Once the potential energy is given, one can solve the Schrödinger equation for Ψ , implying the knowledge of the probability density $|\Psi|^2$ as a function of x, y, z, t . In many cases of interest, the potential energy does not depend on time. Then, the Schrödinger equation simplifies considerably. Notice, for example, that for a 1D free particle the wave function can be written

$$\begin{aligned} \Psi(x, t) &= Ae^{(-i/\hbar)(Et-px)} \\ &= Ae^{-(iE/\hbar)t} e^{(ip/\hbar)x} \\ &= \psi(x)e^{-(iE/\hbar)t} , \end{aligned} \quad (4)$$

i.e., $\Psi(x, t)$ is the product of a time-dependent phase $e^{-(iE/\hbar)t}$ and a stationary wave function $\psi(x)$.

In the general case, the stationary Schrödinger equation can be solved, under the aforementioned requirements, only for certain values of the energy E . This is not a mathematical difficulty, but merely a fundamental physical feature. To solve the Schrödinger equation for a given system means to get the wave function ψ , as a solution for which certain physical boundary conditions hold and, in addition, as already mentioned, it is continuous together with its first derivative everywhere in space, is finite, and single valued. Thus, the quantization of energy occurs as a natural theoretical element in wave mechanics, whereas in practice as a universal phenomenon, characteristic for all stable microscopic systems.

Schrödinger equation for the hydrogen atom

In this section, we shall apply the Schrödinger equation to the hydrogen atom, about which one knows that it is formed of a positive nucleus/proton of charge $+e$ and an electron of charge $-e$. The latter, being 1836 times smaller in mass than the proton, is by far more dynamic.

If the interaction between two particles is of the type $u(r) = u(|\vec{r}_1 - \vec{r}_2|)$, the problem of the motion is reduced both classically and quantum to the motion of a single particle in a field of spherical symmetry. Indeed, the Lagrangian

$$L = \frac{1}{2}m_1\dot{r}_1^2 + \frac{1}{2}m_2\dot{r}_2^2 - u(|\vec{r}_1 - \vec{r}_2|) \quad (5)$$

is transformed, using

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \quad (6)$$

and

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}, \quad (7)$$

in the Lagrangian

$$L = \frac{1}{2}M\dot{R}^2 + \frac{1}{2}\mu\dot{r}^2 - u(r), \quad (8)$$

where

$$M = m_1 + m_2 \quad (9)$$

and

$$\mu = \frac{m_1m_2}{m_1 + m_2}. \quad (10)$$

On the other hand, the momentum is introduced through the Lagrange formula

$$\vec{P} = \frac{\partial L}{\partial \dot{\vec{R}}} = M \dot{\vec{R}} \quad (11)$$

and

$$\vec{p} = \frac{\partial L}{\partial \dot{\vec{r}}} = m \dot{\vec{r}}, \quad (12)$$

that allows to write the classical Hamilton function in the form

$$H = \frac{P^2}{2M} + \frac{p^2}{2m} + u(r). \quad (13)$$

Thus, one can obtain the hamiltonian operator for the corresponding quantum problem with commutators of the type

$$[P_i, P_k] = -i\hbar\delta_{ik} \quad (14)$$

and

$$[p_i, p_k] = -i\hbar\delta_{ik}. \quad (15)$$

These commutators implies a Hamiltonian operator of the form

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 + u(r), \quad (16)$$

which is fundamental for the study of the hydrogen atom by means of the stationary Schrödinger equation

$$\hat{H}\psi = E\psi. \quad (17)$$

This form does not include relativistic effects, i.e., electron velocities close to the velocity of light in vacuum.

The potential energy $u(r)$ is the electrostatic one

$$u = -\frac{e^2}{4\pi\epsilon_0 r} \quad (18)$$

There are two possibilities. The first is to express u as a function of the cartesian coordinates x, y, z , substituing r by $\sqrt{x^2 + y^2 + z^2}$. The second is to write the Schrödinger equation in spherical polar coordinates r, θ, ϕ . Because of the obvious spherical symmetry of this case, we shall deal with the latter approach, which leads to considerable mathematical simplifications.

In spherical coordinates, the Schrödinger equation reads

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - u) \psi = 0 \quad (19)$$

Substituting (18), and multiplying the whole equation by $r^2 \sin^2 \theta$, one gets

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \psi = 0. \quad (20)$$

This equation is a partial differential equation for the electron wavefunction $\psi(r, \theta, \phi)$ ‘within’ the atomic hydrogen. Together with the various conditions that the wavefunction $\psi(r, \theta, \phi)$ should fulfill [for example, $\psi(r, \theta, \phi)$ should have a unique value at any spatial point (r, θ, ϕ)], this equation specifies in a complete manner the behavior of the hydrogen electron. To see the explicit behavior, we shall solve eq. 20 for $\psi(r, \theta, \phi)$ and we shall interpret appropriately the obtained results.

Separation of variables in spherical coordinates

The real usefulness of writing the hydrogen Schrödinger equation in spherical coordinates consists in the easy way of achieving the separation procedure in three independent equations, each of them being one-dimensional. The separation procedure is to seek the solutions for which the wavefunction $\psi(r, \theta, \phi)$ has the form of a product of three functions, each of one of the three spherical variables, namely $R(r)$, depending only on r ; $\Theta(\theta)$ depending only on θ , and $\Phi(\phi)$ that depends only on ϕ . This is quite similar to the separation of the Laplace equation. Thus

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi). \quad (21)$$

The $R(r)$ function describes the differential variation of the electron wavefunction ψ along the vector radius coming out from the nucleus, with θ and ϕ assumed to be constant. The differential variation of ψ with the polar angle θ along a meridian of an arbitrary sphere centered in the nucleus is described only by the function $\Theta(\theta)$ for constant r and ϕ . Finally, the function $\Phi(\phi)$ describes how ψ varies with the azimuthal angle ϕ along a parallel of an arbitrary sphere centered at the nucleus, under the conditions that r and θ are kept constant.

Using $\psi = R\Theta\Phi$, one can see that

$$\frac{\partial\psi}{\partial r} = \Theta\Phi \frac{dR}{dr} , \quad (22)$$

$$\frac{\partial\psi}{\partial\theta} = R\Phi \frac{d\Theta}{d\theta} , \quad (23)$$

$$\frac{\partial\psi}{\partial\phi} = R\Theta \frac{d\Phi}{d\phi} . \quad (24)$$

Obviously, the same type of formulas are maintained for the unmixed higher-order derivatives. Substituting them in eq. 20, and after deviding by $R\Theta\Phi$, we get

$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} + \frac{2mr^2 \sin^2\theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = 0 . \quad (25)$$

The third term of this equation is a function of the angle ϕ only, while the other two terms are functions of r and θ . We rewrite now the previous equation in the form

$$\frac{\sin^2\theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin\theta}{\Theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{2mr^2 \sin^2\theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} . \quad (26)$$

This equation can be correct only if the two sides are equal to the same constant, because they are functions of different variables. It is convenient to denote this (separation) constant by m_l^2 . The differential equation for the Φ function is

$$-\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} = m_l^2 . \quad (27)$$

If one substitutes m_l^2 in the right hand side of eq. 26 and devides the resulting equation by $\sin^2\theta$, after regrouping the terms, the flowing result is obtained

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) . \quad (28)$$

Once again, we end up with an equation in which different variables occur in the two sides, thus forcing at equating of both sides to the same constant.

For reasons that will become clear later on, we shall denote this constant by $l(l+1)$. The equations for the functions $\Theta(\theta)$ and $R(r)$ reads

$$\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) = l(l+1) \quad (29)$$

and

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = l(l+1) . \quad (30)$$

The equations 27, 29 and 30 are usually written in the form

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0 , \quad (31)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 , \quad (32)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 . \quad (33)$$

Each of these equations is an ordinary differential equation for a function of a single variable. In this way, the Schrödinger equation for the hydrogen electron, which initially was a partial differential equation for a function ψ of three variables, got a simple form of three 1D ordinary differential equations for unknown functions of one variable.

Interpreting the separation constants: the quantum numbers

The solution for the azimuthal part

Eq. 31 is readily solved leading to the following solution

$$\Phi(\phi) = A_\phi e^{im_l\phi} , \quad (34)$$

where A_ϕ is the integration constant. One of the conditions that any wavefunctions should fulfill is to have a unique value for any point in space. This applies to Φ as a component of the full wavefunction ψ . One should notice that ϕ and $\phi + 2\pi$ are identical in the same meridional plane. Therefore, one should have $\Phi(\phi) = \Phi(\phi + 2\pi)$, i.e., $A_\phi e^{im_l\phi} = A_\phi e^{im_l(\phi+2\pi)}$. This can be fulfilled only if m_l is zero or a positive or negative integer ($\pm 1, \pm 2, \pm 3, \dots$).

m_l is known as the magnetic quantum number of the atomic electron and is related to the direction of the projection of the orbital momentum L_z . It comes into play whenever the effects of axial magnetic fields on the electron may show up. There is also a deep connection between m_l and the orbital quantum number l , which in turn determines the modulus of the orbital momentum of the electron.

The interpretation of the orbital number l does not miss some problems. Let us examine eq. 33 that corresponds to the radial wavefunction $R(r)$. This equation rules only the radial motion of the electron, i.e., with the relative distance with respect to the nucleus along some guiding ellipses. However, the total energy of the electron E is also present. This energy includes the kinetic energy in its orbital motion that is not related to the radial motion. This contradiction can be eliminated by the following argument. The kinetic energy T has two parts: T_{radial} due to the radial oscillatory motion and $T_{orbital}$, which is due to the closed orbital motion. The potential energy V of the electron is the electrostatic energy. Therefore, its total energy is

$$E = T_{radial} + T_{orbital} - \frac{e^2}{4\pi\epsilon_0 r} . \quad (35)$$

Substituting this expression of E in eq. 33 we get with some regrouping of the terms

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[T_{radial} + T_{orbital} - \frac{\hbar^2 l(l+1)}{2mr^2} \right] R = 0 . \quad (36)$$

If the last two terms in parentheses compensates between themselves, we get a differential equation for the pure radial motion. Thus, we impose the condition

$$T_{orbital} = \frac{\hbar^2 l(l+1)}{2mr^2} . \quad (37)$$

However, the orbital kinetic energy of the electron is

$$T_{orbital} = \frac{1}{2} m v_{orbital}^2 \quad (38)$$

and since the orbital momentum of the electron L is

$$L = m v_{orbital} r , \quad (39)$$

we can express the orbital kinetic energy in the form

$$T_{orbital} = \frac{L^2}{2mr^2} . \quad (40)$$

Therefore, we have

$$\frac{L^2}{2mr^2} = \frac{\hbar^2 l(l+1)}{2mr^2} \quad (41)$$

and consequently

$$L = \sqrt{l(l+1)}\hbar . \quad (42)$$

The interpretation of this result is that since the orbital quantum number l is constrained to take the values $l = 0, 1, 2, \dots, (n - 1)$, the electron can only have orbital momenta L specified by means of eq. 42. As in the case of the total energy E , the angular momentum is conserved and gets quantized. Its natural unit in quantum mechanics is $\hbar = h/2\pi = 1.054 \times 10^{-34}$ J.s.

In the macroscopic planetary motion (putting aside the many-body features), the orbital quantum number is so large that any direct experimental detection is impossible. For example, an electron with $l = 2$ has an angular momentum $L = 2.6 \times 10^{-34}$ J.s., whereas the terrestrial angular momentum is 2.7×10^{40} J.s.!

A common notation for the angular momentum states is by means of the letter s for $l = 0$, p for $l = 1$, d for $l = 2$, and so on. This alphabetic code comes from the empirical spectroscopic classification in terms of the so-called series, which was in use before the advent of quantum mechanics.

The combination of the principal quantum number with the latter corresponding to the angular momentum is another frequently used notation in atomic and molecular physics.. For example, a state for which $n = 2$ and $l = 0$ is a state $2s$, while a state $n = 4$ and $l = 2$ is a state $4d$.

On the other hand, for the interpretation of the magnetic quantum number, we shall take into account, as we did for the linear momentum, that the orbital momentum is a vector operator and therefore one has to specify its direction, sense, and modulus. L , being a vector product, is perpendicular on the plane of rotation. The geometric rules of the vectorial products still hold, in particular the rule of the right hand: its direction and sense are given by the right thumb whenever the other four fingers point at the direction of rotation.

But what significance can be associated to a direction and sense in the limited space of the atomic hydrogen ? The answer may be quick if we think that the rotating electron is nothing but a one-electron loop current that considered as a magnetic dipole has a corresponding magnetic field. Consequently, an atomic electron will always interact with an applied magnetic B . The magnetic quantum number m_l specifies the spatial direction of L , which is determined by the component of L along the direction of the

external magnetic field. This effect is commonly known as the quantization of the space in a magnetic field.

If we choose the direction of the magnetic field as the z axis, the component of L along this direction is

$$L_z = m_l \hbar . \quad (43)$$

The possible values of m_l for a given value of l , go from $+l$ to $-l$, passing through zero, so that there are $2l + 1$ possible orientations of the angular momentum L in a magnetic field. When $l = 0$, L_z can be only zero; when $l = 1$, L_z can be \hbar , 0 , or $-\hbar$; when $l = 2$, L_z takes only one of the values $2\hbar$, \hbar , 0 , $-\hbar$, or $-2\hbar$, and so forth. It is worth mentioning that L cannot be put exactly parallel or anti-parallel to B , because L_z is always smaller than the modulus $\sqrt{l(l+1)}\hbar$ of the total orbital momentum.

The spatial quantization of the orbital momentum for the hydrogen atom is shown in fig. 6.1 in a particular case.

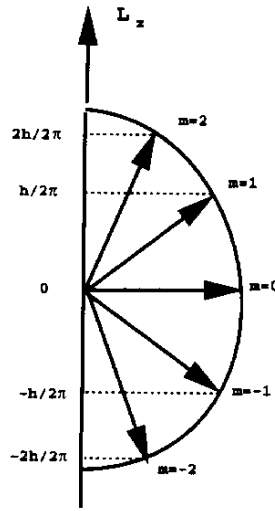


Fig. 6.1: The spatial quantization of the electron angular momentum for states $l = 2$, $L = \sqrt{6}\hbar$.

One should consider the atom/electron characterized by a given m_l as having the orientation of its angular momentum L determined relative to the external applied magnetic field.

In the absence of the external magnetic field, the direction of the z axis is fully arbitrary. Therefore, the component of L in any arbitrary chosen

direction is $m_l\hbar$; the external magnetic field offers a preferred reference direction from the experimental viewpoint.

Why is quantized only the component L_z ? The answer is related to the fact that L cannot be put along a direction in an arbitrary way. Its ‘vectorial arrow’ moves always along a cone centered on the quantization axis such that its projection L_z is $m_l\hbar$. The reason why such a phenomenon occurs is due to the uncertainty principle. If L would be fixed in space, in such a way that L_x , L_y and L_z would have well-defined values, the electron would have to be confined to a well-defined plane. For example, if L would be fixed along the z direction, the electron tends to maintain itself in the plane xy (fig. 6.2a).

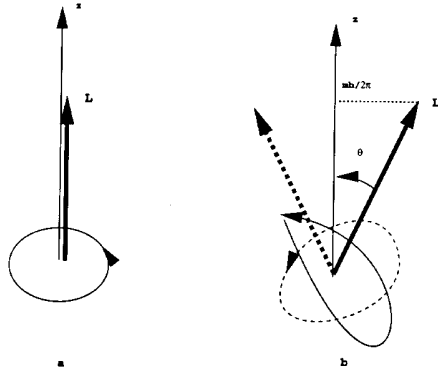


Fig. 6.2: The uncertainty principle forbids a fixed direction in space of the angular momentum.

This can occur only in the case in which the component p_z of the electron momentum is ‘infinitely’ uncertain. This is however impossible if the electron is part of the hydrogen atom. But since in reality just the component L_z of L together with L^2 have well-defined values and $|L| > |L_z|$, the electron is not constrained to a single plane (fig. 6.2b). If this would be the case, an uncertainty would exist in the coordinate z of the electron. The direction of L changes continuously (see fig. 6.3), so that the mean values of L_x and L_y are zero, although L_z keeps all the time its value $m_l\hbar$.

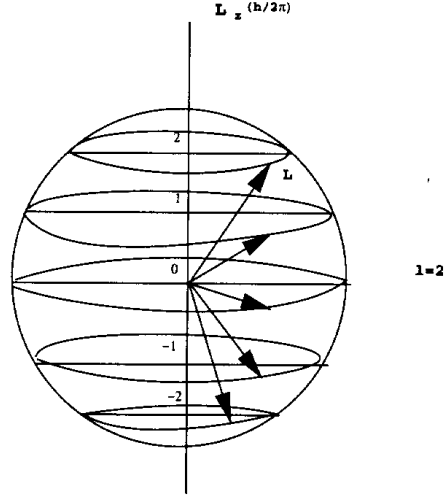


Fig. 6.3: The angular momentum displays a constant precession around the z axis.

The solution for Φ should also fulfill the normalization condition given by eq. 2. Thus, we have

$$\int_0^{2\pi} |\Phi|^2 d\phi = 1 \quad (44)$$

and substituting Φ , one gets

$$\int_0^{2\pi} A_\phi^2 d\phi = 1 . \quad (45)$$

It follows that $A_\phi = 1/\sqrt{2\pi}$, and therefore the normalized Φ is

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi} . \quad (46)$$

Solution for the polar part

The solution of the $\Theta(\theta)$ equation is more complicated. It is expressed in terms of the associated Legendre polynomials

$$P_l^{m_l}(x) = (-1)^{m_l} (1-x^2)^{m_l/2} \frac{d^{m_l}}{dx^{m_l}} P_l(x) = (-1)^{m_l} \frac{(1-x^2)^{m_l/2}}{2^l l!} \frac{d^{m_l+l}}{dx^{m_l+l}} (x^2-1)^l . \quad (47)$$

Their orthogonality relationship is

$$\int_{-1}^1 [P_l^{m_l}(\cos\theta)]^2 d\cos\theta = \frac{2}{2l+1} \frac{(l+m_l)!}{(l-m_l)!} . \quad (48)$$

For the case of quantum mechanics, $\Theta(\theta)$ is given by the normalized associated Legendre polynomials. Thus, if

$$\Theta(\theta) = A_\theta P_l^{m_l}(\cos\theta) , \quad (49)$$

then the normalization condition is

$$\int_{-1}^1 A_\theta^2 [P_l^{m_l}(\cos\theta)]^2 d\cos\theta = 1 . \quad (50)$$

Therefore, the normalization constant for the polar part is given by

$$A_\theta = \sqrt{\frac{2l+1}{2} \frac{(l-m_l)!}{(l+m_l)!}} \quad (51)$$

and consequently, the function $\Theta(\theta)$ already normalized reads

$$\Theta(\theta) = \sqrt{\frac{2l+1}{2} \frac{(l-m_l)!}{(l+m_l)!}} P_l^{m_l}(\cos\theta) . \quad (52)$$

For our purposes here, the most important property of these functions is that they exist only when the constant l is an integer number greater or at least equal to $|m_l|$, which is the absolute value of m_l . This condition can be written in the form of the set of values available for m_l

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l . \quad (53)$$

Unification of the azimuthal and polar parts: spherical harmonics

The solutions of the azimuthal and polar parts can be unified within spherical harmonics functions that depend on both ϕ and θ . This simplifies the algebraic manipulations of the full wave functions $\psi(r, \theta, \phi)$. Spherical harmonics are introduced as follows

$$Y_l^{m_l}(\theta, \phi) = (-1)^{m_l} \sqrt{\frac{2l+1}{4\pi} \frac{(l-m_l)!}{(l+m_l)!}} P_l^{m_l}(\cos\theta) e^{im_l\phi} . \quad (54)$$

The supplementary factor $(-1)^{m_l}$ does not produce any problem because the Schrödinger equation is linear and homogeneous. This factor is added for the sake of convenience in angular momentum studies. It is known as the Condon-Shortley phase factor and its effect is to introduce an alternance of the signs \pm for the spherical harmonics.

Solution for the radial part

The solution for the radial part $R(r)$ of the wave function ψ of the hydrogen atom is somewhat more complicated. It is here where significant differences with respect to the electrostatic Laplace equation do occur. The final result is expressed analytically in terms of the associated Laguerre polynomials (Schrödinger 1926). The radial equation can be solved in exact way only when E is positive or for one of the following negative values E_n (in which cases, the electron is in a bound stationary state within atomic hydrogen)

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \left(\frac{1}{n^2}\right), \quad (55)$$

where n is an integer number called the principal quantum number. It gives the quantization of the electron energy in the hydrogen atom. This discrete atomic spectrum has been first obtained in 1913 by Bohr using semi-empirical quantization methods and next by Pauli and Schrödinger almost simultaneously in 1926.

Another condition that should be satisfied to solve the radial equation is that n have to be strictly bigger than l . Its lowest value is $l + 1$ for a given l . Vice versa, the condition on l is

$$l = 0, 1, 2, \dots, (n - 1) \quad (56)$$

for given n .

The radial equation can be written in the form

$$r^2 \frac{d^2 R}{dr^2} + 2r \frac{dR}{dr} + \left[\frac{2mE}{\hbar^2} r^2 + \frac{2me^2}{4\pi\epsilon_0\hbar^2} r - l(l+1) \right] R = 0, \quad (57)$$

Dividing by r^2 and using the substitution $\chi(r) = rR$ to eliminate the first derivative $\frac{dR}{dr}$, one gets the standard form of the radial Schrödinger equation displaying the effective potential $U(r) = -\text{const}/r + l(l+1)/r^2$ (actually, electrostatic potential plus quantized centrifugal barrier). These are necessary mathematical steps in order to discuss a new boundary condition,

since the spectrum is obtained by means of the R equation. The difference between a radial Schrödinger equation and a full-line one is that a supplementary boundary condition should be imposed at the origin ($r = 0$). The coulombian potential belongs to a class of potentials that are called weak singular for which $\lim_{r \rightarrow 0} U(r)r^2 = 0$. In these cases, one tries solutions of the type $\chi \propto r^\nu$, implying $\nu(\nu - 1) = l(l + 1)$, so that the solutions are $\nu_1 = l + 1$ and $\nu_2 = -l$, just as in electrostatics. The negative solution is eliminated for $l \neq 0$ because it leads to a divergent normalization constant, nor did it respect the normalization at the delta function for the continuous part of the spectrum. On the other hand, the particular case $\nu_2 = 0$ is eliminated because the mean kinetic energy is not finite. The final conclusion is that $\chi(0) = 0$ for any l .

Going back to the analysis of the radial equation for R , first thing to do is to write it in nondimensional variables. This is performed by noticing that the only space and time scales that one can form on combining the three fundamental constants entering this problem, namely e^2 , m_e and \hbar are the Bohr radius $a_0 = \hbar^2/me^2 = 0.529 \cdot 10^{-8}$ cm. and $t_0 = \hbar^3/me^4 = 0.24210^{-16}$ sec., usually known as atomic units. Employing these units, one gets

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left[2E + \frac{2}{r} - \frac{l(l+1)}{r^2} \right] R = 0, \quad (58)$$

where we are especially interested in the discrete part of the spectrum ($E < 0$). The notations $n = 1/\sqrt{-E}$ and $\rho = 2r/n$ leads us to

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[\frac{n}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] R = 0. \quad (59)$$

For $\rho \rightarrow \infty$, this equation reduces to $\frac{d^2 R}{d\rho^2} = \frac{R}{4}$, having solutions $R \propto e^{\pm\rho/2}$. Because of the normalization condition only the decaying exponential is acceptable. On the other hand, the asymptotics at zero, as we already commented on, should be $R \propto \rho^l$. Therefore, we can write R as a product of three radial functions $R = \rho^l e^{-\rho/2} F(\rho)$, of which the first two give the asymptotic behaviors, whereas the third is the radial function in the intermediate region. The latter function is of most interest because its features determine the energy spectrum. The equation for F is

$$\rho \frac{d^2 F}{d\rho^2} + (2l + 2 - \rho) \frac{dF}{d\rho} + (n - l - 1)F = 0. \quad (60)$$

This is a particular case of confluent hypergeometric equation for which the two ‘hyper’geometric parameters depend on the pair of quantum numbers n, l . It can be identified as the equation for the associated Laguerre polynomials $L_{n+l}^{2l+1}(\rho)$. Thus, the normalized form of R is

$$R_{nl}(r) = -\frac{2}{n^2} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho), \quad (61)$$

where the following Laguerre normalization condition has been used

$$\int_0^\infty e^{-\rho} \rho^{2l} [L_{n+l}^{2l+1}(\rho)]^2 \rho^2 d\rho = \frac{2n[(n+l)!]^3}{(n-l-1)!}. \quad (62)$$

We have now the solutions of all the equations depending on a single variable and therefore we can build the wave function for any electronic state of the hydrogen atom. The full wave function reads

$$\psi(r, \theta, \phi) = \mathcal{N}_H(\alpha r)^l e^{-\alpha r/2} L_{n+l}^{2l+1}(\alpha r) P_l^{m_l}(\cos\theta) e^{im_l\phi}, \quad (63)$$

where $\mathcal{N}_H = -\frac{2}{n^2} \sqrt{\frac{2l+1}{4\pi} \frac{(l-m_l)! (n-l-1)!}{(l+m_l)! [(n+l)!]^3}}$ and $\alpha = 2/na_0$.

Using the spherical harmonics, the solution is written as follows

$$\psi(r, \theta, \phi) = -\frac{2}{n^2} \sqrt{\frac{(n-l-1)!}{[(n+l)!]^3}} (\alpha r)^l e^{-\alpha r/2} L_{n+l}^{2l+1}(\alpha r) Y_l^{m_l}(\theta, \phi). \quad (64)$$

The latter formula may be considered as the final result for the Schrödinger solution of the hydrogen atom for any stationary electron state. Indeed, one can see explicitly both the asymptotic dependence and the two orthogonal and complete sets of functions, i.e., the associated Laguerre polynomials and the spherical harmonics that correspond to this particular case of linear partial second-order differential equation. The parabolic coordinates $[\xi = r(1 - \cos\theta), \eta = r(1 + \cos\theta), \phi = \phi]$, are another coordinate system in which the Schrödinger hydrogen equation is separable (E. Schrödinger, *Ann. Physik* **80**, 437, 1926; P.S. Epstein, *Phys. Rev.* **28**, 695, 1926; I. Waller, *Zf. Physik* **38**, 635, 1926). The final solution in this case is expressed as the product of factors of asymptotic nature, azimuthal harmonics, and two sets of associate Laguerre polynomials in the variables ξ and η , respectively. The energy spectrum ($-1/n^2$) and the degeneracy (n^2) of course do not depend on the coordinate system.

Electronic probability density

In the Bohr model of the hydrogen atom, the electron rotates around the nucleus on circular or elliptic trajectories. It is possible to think of appropriate experiments allowing to “see” that the electron moves within experimental errors at the predicted radii $r = n^2 a_0$ (where n is the principal quantum number labeling the orbit and $a_0 = 0.53 \text{ \AA}$ is the Bohr radius) in the equatorial plane $\theta = 90^\circ$, whereas the azimuthal angle may vary according to the specific experimental conditions.

The more rigorous quantum theory changes the conclusions of the Bohr model in at least two important aspects. First, one cannot speak about exact values of r, θ, ϕ , but only of relative probabilities to find the electron within an infinitesimal given region of space. This feature is a consequence of the wave nature of the electron. Secondly, the electron does not move around the nucleus in the classical conventional way because the probability density $|\psi|^2$ does not depend on time but can vary substantially as a function of the relative position of the infinitesimal region.

The hydrogenic electron wave function ψ is $\psi = R\Theta\Phi$, where $R = R_{nl}(r)$ describes the way ψ changes with r when the principal and orbital quantum numbers have the values n and l , respectively. $\Theta = \Theta_{lm_l}(\theta)$ describes in turn how ψ varies with θ when the orbital and magnetic quantum numbers have the values l and m_l , respectively. Finally, $\Phi = \Phi_{m_l}(\phi)$ gives the change of ψ with ϕ when the magnetic quantum number has the value m_l . The probability density $|\psi|^2$ can be written

$$|\psi|^2 = |R|^2 |\Theta|^2 |\Phi|^2 . \quad (65)$$

Notice that the probability density $|\Phi|^2$, which measures the possibility to find the electron at a given azimuthal angle ϕ , is a constant (does not depend on ϕ). Therefore, the electronic probability density is symmetric with respect to the z axis and independent on the magnetic substates (at least until an external magnetic field is applied). Consequently, the electron has an equal probability to be found in any azimuthal direction. The radial part R of the wave function, contrary to Φ , not only varies with r , but it does it differently for any different combination of quantum numbers n and l . Fig. 6.4 shows plots of R as a function of r for the states $1s$, $2s$, and $2p$. R is maximum at the center of the nucleus ($r = 0$) for all the s states, whereas it is zero at $r = 0$ for all the states of nonzero angular momentum.

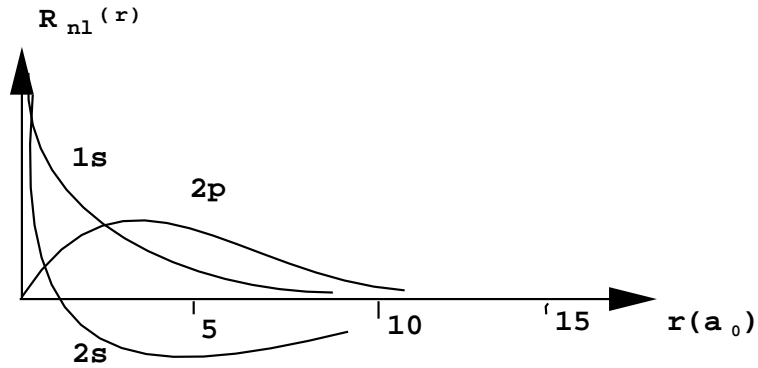


Fig. 6.4: Approximate plots of the radial functions R_{1s} , R_{2s} , R_{2p} ; ($a_0 = 0.53 \text{ \AA}$).

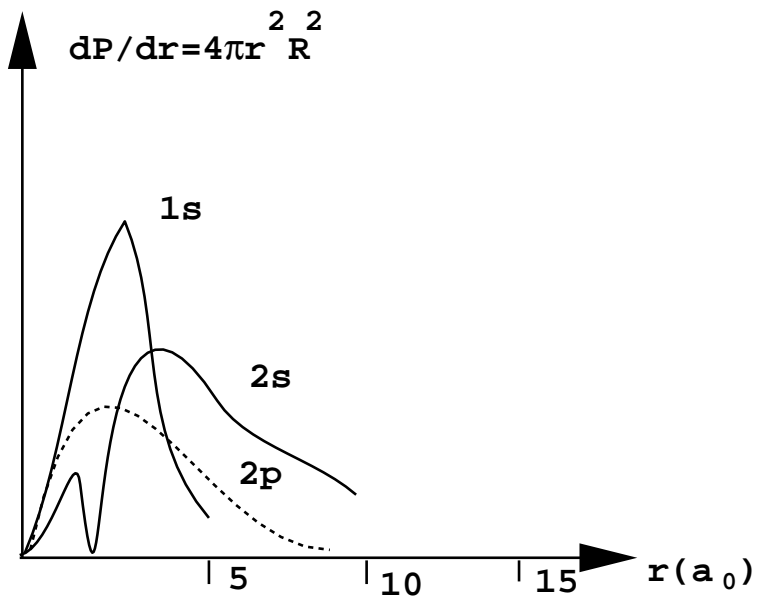


Fig. 6.5: Probability density of finding the hydrogenic electron between r and $r + dr$ with respect to the nucleus for the states $1s$, $2s$, $2p$.

The electronic probability density at the point r, θ, ϕ is proportional to $|\psi|^2$, but the real probability in the infinitesimal volume element dV is $|\psi|^2 dV$. In spherical coordinates

$$dV = r^2 \sin \theta dr d\theta d\phi, \quad (66)$$

and since Θ and Φ are normalized functions, the real numerical probability $P(r)dr$ to find the electron at a relative distance with respect to the nucleus between r and $r + dr$ is

$$\begin{aligned} P(r)dr &= r^2 |R|^2 dr \int_0^\pi |\Theta|^2 \sin\theta d\theta \int_0^{2\pi} |\Phi|^2 d\phi \\ &= r^2 |R|^2 dr \end{aligned} \quad (67)$$

$P(r)$ is displayed in fig. 6.5 for the same states for which the radial functions R appear in fig. 6.4. In principle, the curves are quite different. We immediately see that $P(r)$ is not maximal in the nucleus for the states s , as happens for R . Instead, their maxima are encountered at a finite distance from the nucleus. The most probable value of r for a $1s$ electron is exactly a_0 , the Bohr radius. However, the mean value of r for a $1s$ electron is $1.5a_0$. At first sight this might look strange, because the energy levels are the same both in quantum mechanics and in Bohr's model. This apparent unmatching is eliminated if one takes into account that the electron energy depends on $1/r$ and not on r , and the mean value of $1/r$ for a $1s$ electron is exactly $1/a_0$.

The function Θ varies with the polar angle θ for all the quantum numbers l and m_l , unless $l = m_l = 0$, which are the s states. The probability density $|\Theta|^2$ for a s state is a constant ($1/2$). This means that since $|\Phi|^2$ is also a constant, the electronic probability density $|\psi|^2$ has the same value for a given r value, not depending on the direction. In other states, the electrons present an angular behavior that in many cases may be quite complicated. This can be seen in fig.6.5, where the electronic probability densities for different atomic states are displayed as a function of r and θ . (The plotted term is $|\psi|^2$ and not $|\psi|^2 dV$). Because $|\psi|^2$ is independent of ϕ , a three-dimensional representation of $|\psi|^2$ can be obtained by rotating a particular representation around a vertical axis. This can prove that the probability densities for the s states have spherical symmetry, while all the other states do not possess it. In this way, one can get more or less pronounced lobes of characteristic forms depending on state. These lobes are quite important in chemistry for specifying the atomic interaction in the molecular bulk.

6N. Note:

1. In 1933, E. Schrödinger has been awarded the Nobel Prize in Physics (together with Dirac) for the "discovery of new productive forms of atomic theory". Schrödinger wrote a remarkable series of four papers "Quantisierung

als Eigenwertproblem” [“Quantization as an eigenvalue problem”] (I-IV, received by Annalen der Physik on 27 January, 23 February, 10 May and 21 June 1926, respectively).

6P. Problems

Problem 6.1 - Obtain the formulas for the stable orbits and the energy levels of the electron in the atomic hydrogen using only arguments based on the de Broglie wavelength associated to the electron and the empirical value $5.3 \cdot 10^{-11}$ m for the Bohr radius.

Solution: The electron wavelength is given by $\lambda = \frac{h}{mv}$, whereas if we equate the electric force and the centripetal force $\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$ we obtain the electron ‘velocity’ $v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}}$. Thus, the wavelength of the electron is $\lambda = \frac{h}{e} \sqrt{\frac{4\pi\epsilon_0 r}{m}}$. If we now use the value 5.3×10^{-11} m for the radius r of the electron orbit, we can see that the wavelength of the electron is $\lambda = 33 \times 10^{-11}$ m. But this is exactly the same value as of the circumference of the orbit, $2\pi r = 33 \times 10^{-11}$ m. One may say that the electron orbit in the atomic hydrogen corresponds to a wave “closing into itself” (i.e., stationary). This fact can be compared to the vibrations of a metallic ring. If the wavelengths are multiples of the circumference, the ring goes on with its vibrations for a long time with very small dissipation. If, on the other hand, the number of wavelengths making a circumference is not an integer, the interference of the waves is negative and they disappear in a short period of time. One may say that the electron will rotate around the nucleus without radiating its energy for an infinite time as far as its orbit contains an integer number of de Broglie wavelengths. Thus, the stability/stationary condition is

$$n\lambda = 2\pi r_n ,$$

where r_n is the radius of the electron orbit containing n wavelengths. Substituting λ , we have

$$\frac{nh}{e} \sqrt{\frac{4\pi\epsilon_0 r_n}{m}} = 2\pi r_n ,$$

and therefore the stationary electron orbits are

$$r_n = \frac{n^2 \hbar^2 \epsilon_0}{\pi m e^2} .$$

To get the energy levels, we use $E = T + V$ and substituting the kinetic and potential energies leads to

$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} ,$$

or equivalently

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n} .$$

Plugging the value of r_n into the latter equation, we get

$$E_n = -\frac{me^4}{8\epsilon_0^2\hbar^2} \left(\frac{1}{n^2} \right) .$$

Problem 6.2 - Unsöld's theorem tells that for any value of the orbital number l , the probability densities, summed over all possible substates, from $m_l = -l$ to $m_l = +l$ give a constant that is independent of the angles θ and ϕ , i.e.

$$\sum_{m_l=-l}^{+l} |\Theta_{lm_l}|^2 |\Phi_{m_l}|^2 = ct .$$

This theorem shows that any atom or ion with closed (occupied) sublevels has a spherically-symmetric charge distribution. Check Unsöld's theorem for $l = 0$, $l = 1$, and $l = 2$.

Solution: For $l = 0$, $\Theta_{00} = 1/\sqrt{2}$ and $\Phi_0 = 1/\sqrt{2\pi}$, so that

$$|\Theta_{0,0}|^2 |\Phi_0|^2 = \frac{1}{4\pi} .$$

For $l = 1$, we have

$$\sum_{m_l=-1}^{+1} |\Theta_{lm_l}|^2 |\Phi_{m_l}|^2 = |\Theta_{1,-1}|^2 |\Phi_{-1}|^2 + |\Theta_{1,0}|^2 |\Phi_0|^2 + |\Theta_{1,1}|^2 |\Phi_1|^2 .$$

On the other hand, the wave functions are given by $\Theta_{1,-1} = (\sqrt{3}/2)\sin\theta$, $\Phi_{-1} = (1/\sqrt{2\pi})e^{-i\phi}$, $\Theta_{1,0} = (\sqrt{6}/2)\cos\theta$, $\Phi_0 = 1/\sqrt{2\pi}$, $\Theta_{1,1} = (\sqrt{3}/2)\sin\theta$, $\Phi_1 = (1/\sqrt{2\pi})e^{i\phi}$, which plugged into the previous equation give

$$\sum_{m_l=-1}^{+1} |\Theta_{lm_l}|^2 |\Phi_{m_l}|^2 = \frac{3}{8\pi}\sin^2\theta + \frac{3}{4\pi}\cos^2\theta + \frac{3}{8\pi}\sin^2\theta = \frac{3}{4\pi}$$

and again we've got a constant.

For $l = 2$, we have

$$\sum_{m_l=-2}^{+2} |\Theta_{lm_l}|^2 |\Phi_{m_l}|^2 = |\Theta_{2,-2}|^2 |\Phi_{-2}|^2 + |\Theta_{2,-1}|^2 |\Phi_{-1}|^2 \\ + |\Theta_{2,0}|^2 |\Phi_0|^2 + |\Theta_{2,1}|^2 |\Phi_1|^2 + |\Theta_{2,2}|^2 |\Phi_2|^2 ,$$

and the wave functions are $\Theta_{2,-2} = (\sqrt{15}/4)\sin^2\theta$, $\Phi_{-2} = (1/\sqrt{2\pi})e^{-2i\phi}$, $\Theta_{2,-1} = (\sqrt{15}/2)\sin\theta\cos\theta$, $\Phi_{-1} = (1/\sqrt{2\pi})e^{-i\phi}$, $\Theta_{2,0} = (\sqrt{10}/4)(3\cos^2\theta - 1)$, $\Phi_0 = 1/\sqrt{2\pi}$, $\Theta_{2,1} = (\sqrt{15}/2)\sin\theta\cos\theta$, $\Phi_1 = (1/\sqrt{2\pi})e^{i\phi}$, $\Theta_{2,2} = (\sqrt{15}/4)\sin^2\theta$, $\Phi_2 = (1/\sqrt{2\pi})e^{2i\phi}$. Plugging them into the previous equation give

$$\sum_{m_l=-2}^{+2} |\Theta_{lm_l}|^2 |\Phi_{m_l}|^2 = \frac{5}{4\pi} ,$$

which again fulfills Unsöld's theorem.

Problem 6.3 - The probability to find an atomic electron whose radial wave functions is that of the ground state $R_{10}(r)$ outside a sphere of Bohr radius a_0 centered on the nucleus is

$$\int_{a_0}^{\infty} |R_{10}(r)|^2 r^2 dr .$$

Obtain the probability to find the electron in the ground state at a distance from the nucleus bigger than a_0 .

Solution: The radial wave function corresponding to the ground state is

$$R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0} .$$

Substituting it in the integral, we get $\int_{a_0}^{\infty} |R(r)|^2 r^2 dr = \frac{4}{a_0^3} \int_{a_0}^{\infty} r^2 e^{-2r/a_0} dr$, or

$$\int_{a_0}^{\infty} |R(r)|^2 r^2 dr = \frac{4}{a_0^3} \left[-\frac{a_0}{2} r^2 e^{-2r/a_0} - \frac{a_0^2}{2} r e^{-2r/a_0} - \frac{a_0^3}{4} e^{-2r/a_0} \right]_{a_0}^{\infty} .$$

This leads us to

$$\int_{a_0}^{\infty} |R(r)|^2 r^2 dr = \frac{5}{e^2} \approx 68\% !! ,$$

which is the result asked for in this problem.

7. QUANTUM SCATTERING

Introduction

One usually begins the quantum theory of scattering by referring to results already known from the classical scattering in central fields with some simplifying assumptions helping to avoid unnecessary calculations in getting basic results. It is generally known that studying scatterings in the laboratory provides information on the distribution of matter in the target and other details of the interaction between the incident beam and the target. The hypotheses that we shall assume correct in the following are

i) The particles are spinless. This, of course, does not mean that spin effects are not important in quantum scatterings.

ii) We shall study only elastic scattering for which the internal structure of the particles is not taken into account.

iii) The target is sufficiently thin to neglect multiple scatterings.

iv) The interactions are described by a potential that depends only on the relative distance between the particles (central potential).

These hypotheses eliminate some quantum effects that are merely details. They also represent conditions for getting the quantum analogs of basic classical results. We now define

$$\frac{d\sigma}{d\Omega} \propto \frac{I(\theta, \varphi)}{I_0}, \quad (1)$$

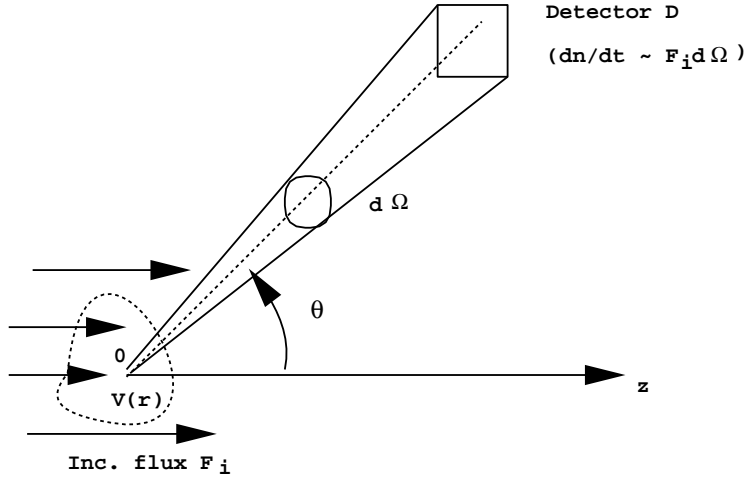
where $d\Omega$ is the solid angle infinitesimal element, I_0 is the number of incident particles per unit transverse area, and $I d\Omega$ is the number of scattered particles in the solid angle element.

Employing these well-known concepts, together with the asymptotic notion of *impact parameter* b associated to each classical incident particle, one gets in classical mechanics the following important formula

$$\frac{d\sigma}{d\Omega} = \frac{b}{\sin\theta} \left| \frac{db}{d\theta} \right|. \quad (2)$$

If one wants to study the scattering phenomenology in quantum terminology, one should investigate the time evolution of a ‘scattering’ wave packet. Let F_i be the flux of incident particles, i.e., the number of particles per unit of time passing through the unit of transverse surface onto the propagation axis. An appropriate detector configuration is usually placed

far away from the effective interaction region, ‘seeing’ a solid angle $d\Omega$ of that region. In general, the number of particles dn/dt scattered per unit of time in $d\Omega$ in the direction (θ, φ) is detected.



dn/dt is proportional to $d\Omega$ and F_i . Let us call $\sigma(\theta, \varphi)$ the coefficient of proportionality between dn and $F_i d\Omega$:

$$dn = \sigma(\theta, \varphi) F_i d\Omega , \quad (3)$$

which is by definition the differential cross section.

The number of particles per unit of time reaching the detector is equal to the number of particles crossing the surface $\sigma(\theta, \varphi) d\Omega$, which is perpendicular to the beam axis. The total section is by definition

$$\sigma = \int \sigma(\theta, \varphi) d\Omega . \quad (4)$$

To further simplify the calculation, we choose the z axis along the incident beam direction.

On the negative side of the axis, for large negative t , the particle is practically free: it is not affected by $V(\mathbf{r})$ and its state can be represented by plane waves. Therefore, the wave function contains terms of the form e^{ikz} , where k is the constant occurring in the Helmholtz equation. By analogy with optics, the form of the scattered wave is

$$f(r) = \frac{e^{ikr}}{r} . \quad (5)$$

Indeed

$$(\nabla^2 + k^2)e^{ikr} \neq 0 \quad (6)$$

and

$$(\nabla^2 + k^2)\frac{e^{ikr}}{r} = 0 \quad (7)$$

for $r > r_0$, where r_0 is any positive number.

We assume that the motion of the particle is described by the Hamiltonian

$$H = \frac{\mathbf{p}^2}{2\mu} + V = H_0 + V . \quad (8)$$

V is different of zero only in a small neighbourhood close to the origin. A wave packet at $t = 0$ can be written

$$\psi(\mathbf{r}, 0) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int \varphi(\mathbf{k}) \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0)] d^3\mathbf{k} , \quad (9)$$

where ψ is a function that is nonzero in a ‘width’ $\Delta\mathbf{k}$ centered on \mathbf{k}_0 . We also assume that \mathbf{k}_0 is antiparallel to \mathbf{r}_0 . In order to see quantitatively what happens to the wave packet when scatters the target, one can use the expansion of $\psi(\mathbf{r}, 0)$ in the eigenfunctions $\psi_n(\mathbf{r})$ of H , i.e., $\psi(\mathbf{r}, 0) = \sum_n c_n \psi_n(\mathbf{r})$. Thus, the wave packet at time t is

$$\psi(\mathbf{r}, t) = \sum_n c_n \varphi_n(\mathbf{r}) \exp\left(-\frac{i}{\hbar} E_n t\right) . \quad (10)$$

This is an eigenfunction of the operator H_0 , not of H , but we can substitute these eigenfunctions by eigenfunctions of H , which we denote by $\psi_k^{(+)}(\mathbf{r})$. The asymptotic form of the latter is

$$\psi_k^{(+)}(\mathbf{r}) \simeq \mathbf{e}^{i\mathbf{k}\cdot\mathbf{r}} + \mathbf{f}(\mathbf{r}) \frac{\mathbf{e}^{i\mathbf{k}\cdot\mathbf{r}}}{|\mathbf{r}|} , \quad (11)$$

where, as usually $\mathbf{p} = \hbar\mathbf{k}$ and $E = \frac{\hbar^2 k^2}{2m}$.

This corresponds to a plane wave of the incident beam type and a divergent spherical wave resulting from the interaction between the incident beam and the target. One can expand $\psi(\mathbf{r}, 0)$ in plane waves and $\psi_k(\mathbf{r})$

$$\psi(\mathbf{r}, 0) = \int \varphi(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}_0) \psi_k(\mathbf{r}) d^3k , \quad (12)$$

where $\hbar\omega = \frac{\hbar^2 k^2}{2m}$. The divergent spherical wave does not contribute to the initial wave packet because it is an additive part.

Scattering of a wave packet

Any wave is dispersed during its propagation. This is why one cannot ignore the effect of the divergent wave from this viewpoint. One can make use of the following trick

$$\omega = \frac{\hbar}{2m}k^2 = \frac{\hbar}{2m}[\mathbf{k}_0 + (\mathbf{k} - \mathbf{k}_0)]^2 = \frac{\hbar}{2m}[2\mathbf{k}_0 \cdot \mathbf{k} - \mathbf{k}_0^2 + (\mathbf{k} - \mathbf{k}_0)^2], \quad (13)$$

pentru a neglija ultimul termen în paranteze. Substituting ω in ψ , we ask that $\frac{\hbar}{2m}(\mathbf{k} - \mathbf{k}_0)^2 T \ll 1$, where $T \simeq \frac{2mr_0}{\hbar k_0}$. Therefore

$$\frac{(\Delta k)^2 r_0}{k_0} \ll 1. \quad (14)$$

This condition tells us that the wave packet does not disperse significantly even when it moves over a macroscopic distance r_0 .

Choosing the direction of the vector \mathbf{k} of the incident wave along one of the three cartesian directions (we use the z one), we can write in spherical coordinates the following important formula

$$\psi_k(r, \theta, \varphi) \simeq e^{ikz} + \frac{f(k, \theta, \varphi)e^{ikr}}{r}.$$

Since the Hamiltonian H , up to now not considered as an operator (the class of the results presented are the same both at the classical and quantum level), is invariant under z rotations, we can choose boundary conditions of spherical symmetry too. Thus

$$\psi_k(r, \theta, \varphi) \simeq e^{ikz} + \frac{f(\theta)e^{ikr}}{r}.$$

This type of functions are known as scattering wave functions. The coefficient $f(\theta)$ of the spherical wave is known as the scattering amplitude. It is a basic concept in the formal theory of quantum scatterings.

Probability amplitude in scattering

We write the Schrödinger equation as follows

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r}, t)\psi. \quad (15)$$

Recall that the expression

$$P(\mathbf{r}, t) = \psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2 \quad (16)$$

can be interpreted, cf. Max Born, as a probability density under normalization conditions of the type

$$\int |\psi(\mathbf{r}, t)|^2 d^3r = 1 . \quad (17)$$

This normalization integral should be time independent. This can be noted by writing

$$I = \frac{\partial}{\partial t} \int_{\Omega} P(\mathbf{r}, t) d^3r = \int_{\Omega} (\psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t} \psi) d^3r , \quad (18)$$

and from Schrödinger's equation

$$\frac{\partial \psi}{\partial t} = \frac{i\hbar}{2m} \nabla^2 \psi - \frac{i}{\hbar} V(\mathbf{r}, t) \psi \quad (19)$$

one gets

$$\begin{aligned} I &= \frac{i\hbar}{2m} \int_{\Omega} [\psi^* \nabla^2 - (\nabla^2 \psi^*) \psi] d^3r = \frac{i\hbar}{2m} \int_{\Omega} \nabla \cdot [\psi^* \nabla \psi - (\nabla \psi^*) \psi] d^3r = \\ &= \frac{i\hbar}{2m} \int_A [\psi^* \nabla \psi - (\nabla \psi^*) \psi]_n dA , \end{aligned} \quad (20)$$

where the Green theorem has been used to evaluate the volume integral. dA is the infinitesimal surface element on the boundary of the integration region and $[]_n$ denotes the component along the normal direction to the surface element dA .

Defining

$$\mathbf{S}(\mathbf{r}, t) = \frac{\hbar}{2im} [\psi^* \nabla \psi - (\nabla \psi^*) \psi] , \quad (21)$$

we get

$$I = \frac{\partial}{\partial t} \int_{\Omega} P(\mathbf{r}, t) d^3r = - \int_{\Omega} \nabla \cdot \mathbf{S} d^3r = - \int_A S_n dA , \quad (22)$$

for well-behaved wave packets (not funny asymptotically) so that the normalization integral converges. The surface integral is zero when Ω covers the whole space. One can prove (see P. Dennery & A. Krzywicki, *Mathematical methods for physicists*) that the surface integral is zero. Therefore, the normalization integral is constant in time and the initial condition holds. From the same equation for \mathbf{S} , we get

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{S}(\mathbf{r}, t) = 0 , \quad (23)$$

which is the continuity equation for the density flux P and the current density \mathbf{S} in the absence of any type of sources or sinks. If we interpret $\frac{\hbar}{im}\nabla$ as a sort of velocity ‘operator’ (as for time, it is difficult to speak rigorously about a velocity operator in quantum mechanics!), then

$$\mathbf{S}(\mathbf{r}, t) = \text{Re}(\psi^* \frac{\hbar}{im} \nabla \psi) . \quad (24)$$

To calculate the quantum current density for a scattering wave function is a tricky and inspiring (not illustrative) exercise! The final result is $j_r = \frac{\hbar k}{mr^2} |f(\theta)|^2$, where the direction $\theta = 0$ should not be included.

Green’s function in scattering theory

Another way of writing the Schrödinger equation at hand is $(-\frac{\hbar^2}{2m}\nabla^2 + V)\psi = E\psi$, or $(\nabla^2 + k^2)\psi = U\psi$, where $k^2 = \frac{2mE}{\hbar^2}$, si $U = \frac{2mV}{\hbar^2}$.

It follows that it is more convenient to put this equation in an integral form. This can be done if we consider $U\psi$ in the right hand side of the equation as a inhomogeneity. This allows to build the solution by means of Green’s function (integral kernel), which, by definition, is the solution of

$$(\nabla^2 + k^2)G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') . \quad (25)$$

One can write now the Schrödinger solution as the sum of the homogeneous equation and the inhomogeneous one of Green’s type

$$\psi(\mathbf{r}) = \lambda(\mathbf{r}) - \int \mathbf{G}(\mathbf{r}, \mathbf{r}') \mathbf{U}(\mathbf{r}') \psi(\mathbf{r}') d^3\mathbf{r}' . \quad (26)$$

We seek now a G function in the form of a product of linear independent functions, for example, plane waves

$$G(\mathbf{r}, \mathbf{r}') = \int A(\mathbf{q}) e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} dq . \quad (27)$$

Using eq. 25, we have

$$\int A(\mathbf{q})(k^2 - q^2) e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} dq = \delta(\mathbf{r} - \mathbf{r}') , \quad (28)$$

which turns in an identity if

$$A(\mathbf{q}) = (2\pi)^{-3} (k^2 - q^2)^{-1} . \quad (29)$$

Thus

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^3} \int \frac{e^{iqR}}{k^2 - q^2} d^3q, \quad (30)$$

where $R = |\mathbf{r} - \mathbf{r}'|$. After performing a calculation of complex variable ¹⁰, we get

$$G(r) = -\frac{1}{4\pi} \frac{e^{ikr}}{r}. \quad (31)$$

This function is not determined univoquely since the Green function can be any solution of the eq. 25. The right particular solution is chosen by imposing boundary conditions on the eigenfunctions $\psi_k(\mathbf{r})$.

The Green function obtained in this way is

$$G(\mathbf{r}, \mathbf{r}') = -\left(\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|} \right). \quad (32)$$

Thus, we finally get the integral equation for the scattering wave function

$$\psi(k, \mathbf{r}) = \varphi(k, \mathbf{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} U(\mathbf{r}') \psi(k, \mathbf{r}') d^3r', \quad (33)$$

where φ is a solution of the Helmholtz equation. Noticing that $|\mathbf{r} - \mathbf{r}'| = R$, then

$$(\nabla^2 + k^2)\psi = (\nabla^2 + k^2)[\varphi + \int G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') \psi(\mathbf{r}') d^3r'] \quad (34)$$

and assuming that we can change the order of operations and put the ∇ operator inside the integral, we get

$$(\nabla^2 + k^2)\psi = \int (\nabla^2 + k^2)G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') \psi(\mathbf{r}') d^3r' = U(\mathbf{r})\psi(\mathbf{r}), \quad (35)$$

which shows us that $G(R) = \frac{1}{4\pi} \frac{e^{ikR}}{R}$ is indeed a solution.

Optical theorem

The total cross section is given by

$$\sigma_{tot}(k) = \int \frac{d\sigma}{d\Omega} d\Omega. \quad (36)$$

¹⁰See problem 7.1.

Let us express now $f(\theta)$ as a function of the phase shift $S_l(k) = e^{2i\delta_l(k)}$ in the form

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l(k)} \sin \delta_l(k) P_l(\cos \theta) . \quad (37)$$

Then

$$\begin{aligned} \sigma_{tot} &= \int \left[\frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l(k)} \sin \delta_l(k) P_l(\cos \theta) \right] \\ &\quad \left[\int \left[\frac{1}{k} \sum_{l'=0}^{\infty} (2l'+1) e^{i\delta_{l'}(k)} \sin \delta_{l'}(k) P_{l'}(\cos \theta) \right] \right] . \end{aligned} \quad (38)$$

Using now $\int P_l(\cos \theta) P_{l'}(\cos \theta) = \frac{4\pi}{2l+1} \delta_{ll'}$, we get

$$\sigma_{tot} = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l(k) . \quad (39)$$

Of interest is the relationship

$$\begin{aligned} \text{Im} f(0) &= \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) \text{Im} [e^{i\delta_l(k)} \sin \delta_l(k)] P_l(1) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l(k) = \\ &\quad \frac{k}{4\pi} \sigma_{tot} , \end{aligned} \quad (40)$$

which is known as the *optical theorem*. Its physical significance is related to the fact that the interference of the incident wave with the dispersed wave at zero/forward angle produces the “getting out” of the particle from the incident wave, allowing in this way the conservation of the probability.

Born approximation

Let us consider the situation of Fig. 7.2:

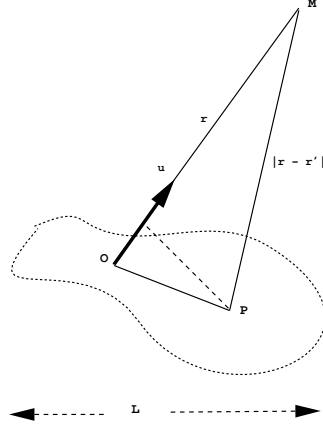


Fig. 7.2

The observation point M is far away from P , which is in the range of the potential U . The geometrical conditions are $r \gg L$, $r' \ll l$. The segment MP that corresponds to $|\mathbf{r} - \mathbf{r}'|$ is in the aforementioned geometrical conditions approximately equal to the projection of MP onto MO

$$|\mathbf{r} - \mathbf{r}'| \simeq r - \mathbf{u} \cdot \mathbf{r}' , \quad (41)$$

where \mathbf{u} is a unit vector (versor) in the \mathbf{r} direction. Then, for large r

$$G = -\frac{1}{4\pi} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \simeq_{r \rightarrow \infty} -\frac{1}{4\pi} \frac{e^{ikr}}{r} e^{-ik\mathbf{u} \cdot \mathbf{r}} . \quad (42)$$

We now substitute G in the integral expression for the scattering wave function

$$\psi(\mathbf{r}) = e^{ikz} - \frac{1}{4\pi} \frac{e^{ikr}}{r} \int e^{-ik\mathbf{u} \cdot \mathbf{r}'} U(\mathbf{r}') \psi(\mathbf{r}') d^3 r' . \quad (43)$$

The latter is already not a function of the distance $r = OM$, but only of θ and ψ . Thus

$$f(\theta, \psi) = -\frac{1}{4\pi} \int e^{-ik\mathbf{u} \cdot \mathbf{r}'} U(\mathbf{r}') \psi(\mathbf{r}') d^3 r' . \quad (44)$$

We define now the incident wave vector \mathbf{k}_i as a vector of modulus k directed along the polar axis of the beam. Then $e^{ikz} = e^{i\mathbf{k}_i \cdot \mathbf{r}}$. Similarly, \mathbf{k}_d , of modulus k and of direction fixed by θ and φ , is called the shifted wave vector in the direction (θ, φ) : $\mathbf{k}_d = k\mathbf{u}$.

The *momentum transfer* in the direction (θ, φ) is introduced as the vectorial difference $\mathbf{K} = \mathbf{k}_d - \mathbf{k}_i$.

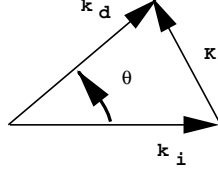


Fig. 7.3

Hence we can write the integral equation in the form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_i \cdot \mathbf{r}} + \int G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') \psi(\mathbf{r}') d^3 r' \quad (45)$$

One can try to solve this equation iteratively. Putting $\mathbf{r} \rightarrow \mathbf{r}'$; $\mathbf{r}' \rightarrow \mathbf{r}''$, we can write

$$\psi(\mathbf{r}') = e^{i\mathbf{k}_i \cdot \mathbf{r}'} + \int G(\mathbf{r}', \mathbf{r}'') U(\mathbf{r}'') \psi(\mathbf{r}'') d^3 r'' . \quad (46)$$

Substituting in 45, we get

$$\begin{aligned} \psi(\mathbf{r}) = & e^{i\mathbf{k}_i \cdot \mathbf{r}} + \int G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') e^{i\mathbf{k}_i \cdot \mathbf{r}'} d^3 r' + \\ & \int \int G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') G(\mathbf{r}', \mathbf{r}'') U(\mathbf{r}'') \psi(\mathbf{r}'') d^3 r'' d^3 r' . \end{aligned} \quad (47)$$

The first two terms in the right hand side are known and it is only the third one that includes the unknown function $\psi(\mathbf{r})$. We can repeat the procedure: substituting \mathbf{r} by \mathbf{r}'' , and \mathbf{r}' by \mathbf{r}''' , we get $\psi(\mathbf{r}''')$, that we can reintroduce in the eq. 47

$$\begin{aligned} \psi(\mathbf{r}) = & e^{i\mathbf{k}_i \cdot \mathbf{r}} + \int G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') e^{i\mathbf{k}_i \cdot \mathbf{r}'} + \\ & \int \int G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') G(\mathbf{r}', \mathbf{r}'') U(\mathbf{r}'') e^{i\mathbf{k}_i \cdot \mathbf{r}''} d^3 r'' d^3 r' + \\ & \int \int \int G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') G(\mathbf{r}', \mathbf{r}'') U(\mathbf{r}'') e^{i\mathbf{k}_i \cdot \mathbf{r}'''} G(\mathbf{r}'', \mathbf{r}''') U(\mathbf{r}''') \psi(\mathbf{r}''') . \end{aligned} \quad (48)$$

The first three terms are now known and the unknown function $\psi(\mathbf{r})$ has been sent to the fourth term. In this way, by successive iterations we can build the stationary dispersed wave function. Notice that each term of the series expansion has one more power in the potential with respect to the previous one. We can go on until we get a negligible expression in the right hand side, obtaining $\psi(\mathbf{r})$ as a function of only known quantities.

Substituting the expression of $\psi(\mathbf{r})$ in $f(\theta, \varphi)$, we get the expansion in Born series of the scattering amplitude. In first order in U , one should replace $\psi(\mathbf{r}')$ by $e^{i\mathbf{k}_i \cdot \mathbf{r}'}$ in the right hand side to get

$$f^{(B)}(\theta, \varphi) = \frac{-1}{4\pi} \int e^{i\mathbf{k}_i \cdot \mathbf{r}'} U(\mathbf{r}') e^{-i\mathbf{k}_d \cdot \mathbf{r}'} d^3 r' = \frac{-1}{4\pi} \int e^{-i(\mathbf{k}_d - \mathbf{k}_i) \cdot \mathbf{r}'} U(\mathbf{r}') d^3 r' = \frac{-1}{4\pi} \int e^{-i\mathbf{K} \cdot \mathbf{r}'} U(\mathbf{r}') d^3 r' \quad (49)$$

\mathbf{K} is the momentum transfer vector. Thus, the differential cross section is simply related to the potential, $V(\mathbf{r}) = \frac{\hbar^2}{2m} U(\mathbf{r})$. Since $\sigma(\theta, \varphi) = |f(\theta, \varphi)|^2$, the result is

$$\sigma^{(B)}(\theta, \varphi) = \frac{m^2}{4\pi^2 \hbar^4} \left| \int e^{-i\mathbf{K} \cdot \mathbf{r}} V(\mathbf{r}) d^3 r \right|^2 \quad (50)$$

The direction and modulus of \mathbf{K} depends on the modulus k of \mathbf{k}_i and \mathbf{k}_d as well as on the scattering direction (θ, φ) . For given θ and φ , it is a function of k , the energy of the incident beam. Analogously, for a given energy, $\sigma^{(B)}$ is a function of θ and φ . Born's approximation allows one to get information on the potential $V(\mathbf{r})$ from the dependence of the differential cross section on the scattering direction and the incident energy.

7N. Note - The following paper of Born was practically the first dealing with quantum scattering:

M. Born, "Quantenmechanik der Stossvorgänge" ["Quantum mechanics of scattering processes"], Zf. f. Physik **37**, 863-867 (1926)

7P. Problems

Problem 7.1

Calculus of complex variable for the scattering Green function

We recall that we already obtained the result

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^3} \int \frac{e^{iqR}}{k^2 - q^2} d^3 q, \text{ cu } R = |\mathbf{r} - \mathbf{r}'|. \text{ Since } d^3 q = q^2 \sin \theta dq d\theta d\phi,$$

we get after integrating in angular variables

$$G(\mathbf{r}, \mathbf{r}') = \frac{i}{4\pi^2 R} \int_{-\infty}^{\infty} \frac{(e^{-iqR} - e^{iqR})}{k^2 - q^2} q dq .$$

Putting $C = \frac{i}{4\pi^2 R}$, we separate the integral in two parts

$$C \left(\int_{-\infty}^{\infty} \frac{e^{-iqR}}{k^2 - q^2} q dq - \int_{-\infty}^{\infty} \frac{e^{iqR}}{k^2 - q^2} q dq \right) .$$

Let us make now $q \rightarrow -q$ in the first integral

$$\int_{-\infty}^{\infty} \frac{e^{-i(-q)R}}{k^2 - (-q)^2} (-q) d(-q) = \int_{\infty}^{-\infty} \frac{e^{iqR}}{k^2 - q^2} q dq = - \int_{-\infty}^{\infty} \frac{e^{iqR}}{k^2 - q^2} q dq ,$$

so that

$$G(\mathbf{r}, \mathbf{r}') = -2C \left(\int_{-\infty}^{\infty} \frac{q e^{iqR}}{k^2 - q^2} dq \right) .$$

Substituting C , leads to

$$G(\mathbf{r}, \mathbf{r}') = \frac{-i}{2\pi^2 R} \int_{-\infty}^{\infty} \frac{q e^{iqR}}{k^2 - q^2} dq$$

In this form, the integral can be calculated by means of the theorem of residues of its poles. Notice the presence of simple poles at $q = \pm k$.

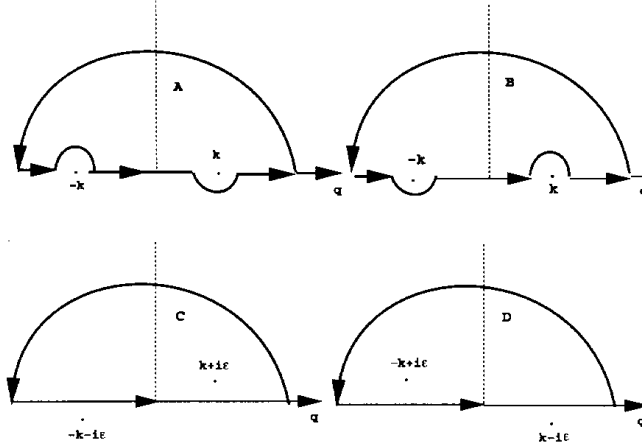


Fig. 7.4: Contour rules around the poles for G_+ and G_-

We use the contour of fig. 7.4 encircling the poles as shown, because in this way we get the physically correct effect from the theorem of residues

$$G(r) = -\frac{1}{4\pi} \frac{e^{ikr}}{r} \quad (\text{Im}k > 0) ,$$

$$G(r) = -\frac{1}{4\pi} \frac{e^{-ikr}}{r} \quad (\text{Im}k < 0) .$$

The solution of interest is the first one, because it provides divergent waves, whereas the latter solution holds for convergent waves (propagating towards the target). Moreover, the linear combination

$$\frac{1}{2} \lim_{\epsilon \rightarrow 0} [G_{k+i\epsilon} + G_{k-i\epsilon}] = -\frac{1}{4\pi} \frac{\cos kr}{r}$$

corresponds to stationary waves.

The formal calculation of the integral can be performed by taking $k^2 - q^2 \rightarrow k^2 + i\epsilon - q^2$, so that: $\int_{-\infty}^{\infty} \frac{q e^{iqR}}{k^2 - q^2} dq \rightarrow \int_{-\infty}^{\infty} \frac{q e^{iqR}}{(k^2 + i\epsilon) - q^2} dq$. This is possible for $R > 0$. This is why the contour for the calculation will be placed in the upper half plane. Thus, the poles of the integrand are located at $q = \pm \sqrt{k^2 + i\epsilon} \simeq \pm(k + \frac{i\epsilon}{2k})$. The procedure of taking the limit $\epsilon \rightarrow 0$ should

be applied *after* calculating the integral.

Problem 7.2

Asymptotic form of the radial function

As we have already seen in the chapter *Hydrogen atom* the radial part of the Schrödinger equation can be written

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)R_{nlm}(r) - \frac{2m}{\hbar^2}[V(r) + \frac{l(l+1)\hbar^2}{2mr^2}]R_{nlm}(r) + \frac{2mE}{\hbar^2}R_{nlm}(r) = 0 .$$

n, l, m are the spherical quantum numbers. For the sake of convenience of writing we shall discard them hereafter. R is the radial wave function (i.e., depends only on r). We assume that the potential goes to zero stronger than $1/r$, and that $\lim_{r \rightarrow 0} r^2 V(r) = 0$.

Using $u(r) = rR$, since $\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)\frac{u}{r} = \frac{1}{r}\frac{d^2}{dr^2}u$, we have

$$\frac{d^2}{dr^2}u + \frac{2m}{\hbar^2}[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}]u = 0 .$$

Notice that the potential displays a supplementary term

$$V(r) \rightarrow V(r) + \frac{l(l+1)\hbar^2}{2mr^2} ,$$

which corresponds to a repulsive centrifugal barrier. For a free particle $V(r) = 0$, and the equation becomes

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right]R + k^2R = 0 .$$

Introducing the variable $\rho = kr$, we get

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R + R = 0 .$$

The solutions are the so-called spherical Bessel functions. The regular solution is

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \left(\frac{\sin \rho}{\rho}\right) ,$$

while the irregular one

$$n_l(\rho) = -(-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \left(\frac{\cos \rho}{\rho}\right) .$$

For large ρ , the functions of interest are the spherical Hankel functions

$$h_l^{(1)}(\rho) = j_l(\rho) + in_l(\rho) \text{ si } h_l^{(2)}(\rho) = [h_l^{(1)}(\rho)]^* .$$

The behaviour for $\rho \gg l$ is of special interest

$$j_l(\rho) \simeq \frac{1}{\rho} \sin\left(\rho - \frac{l\pi}{2}\right) \quad (51)$$

$$n_l(\rho) \simeq -\frac{1}{\rho} \cos\left(\rho - \frac{l\pi}{2}\right) . \quad (52)$$

Then

$$h_l^{(1)} \simeq -\frac{i}{\rho} e^{i(\rho - l\pi/2)} .$$

The solution regular at the origin is $R_l(r) = j_l(kr)$.

The asymptotic form is (using eq. 51)

$$R_l(r) \simeq \frac{1}{2ikr} [e^{-ikr-l\pi/2} - e^{ikr-l\pi/2}] .$$

Problem 7.3

Born approximation for Yukawa potentials

Let us consider the potential of the form

$$V(\mathbf{r}) = V_0 \frac{e^{-\alpha r}}{r} , \quad (53)$$

where V_0 and α are real constants and α is positive. The potential is either attractive or repulsive depending on the sign of V_0 ; the larger $|V_0|$, the stronger the potential. We assume that $|V_0|$ is sufficiently small that Born's approximation holds. According to a previous formula, the scattering amplitude is given by

$$f^{(B)}(\theta, \varphi) = -\frac{1}{4\pi} \frac{2mV_0}{\hbar^2} \int e^{-i\mathbf{K}\cdot\mathbf{r}} \frac{e^{-\alpha r}}{r} d^3r .$$

Since this potential depends only on r , the angular integrals are trivial leading to the form

$$f^{(B)}(\theta, \varphi) = \frac{1}{4\pi} \frac{2mV_0}{\hbar^2} \frac{4\pi}{|\mathbf{K}|} \int_0^\infty \sin |\mathbf{K}|r \frac{e^{-\alpha r}}{r} r dr .$$

Thus, we obtain

$$f^{(B)}(\theta, \varphi) = -\frac{2mV_0}{\hbar^2} \frac{1}{\alpha^2 + |\mathbf{K}|^2} .$$

From the figure we can notice that $|\mathbf{K}| = 2k \sin \frac{\theta}{2}$. Therefore

$$\sigma^{(B)}(\theta) = \frac{4m^2V_0^2}{\hbar^4} \frac{1}{[\alpha^2 + 4k^2 \sin^2 \frac{\theta}{2}]^2} .$$

The total cross section is obtained by integrating

$$\sigma^{(B)} = \int \sigma^{(B)}(\theta) d\Omega = \frac{4m^2V_0^2}{\hbar^4} \frac{4\pi}{\alpha^2(\alpha^2 + 4k^2)} .$$

8. PARTIAL WAVES

Introduction

The partial waves method is quite general and applies to particles interacting in very small spatial regions with another one, which is usually known as scattering center because of its physical characteristics. (for example, because it can be considered as fixed). Beyond the interaction region, the interaction between the two particles is usually negligible. Under this circumstances, it is possible to describe the scattered particle by means of the Hamiltonian

$$H = H_0 + V , \quad (1)$$

where H_0 corresponds to the free particle Hamiltonian. Our problem is to solve the equation

$$(H_0 + V) | \psi \rangle = E | \psi \rangle . \quad (2)$$

Obviously, the spectrum will be continuous since we study the case of elastic scattering. The solution will be

$$| \psi \rangle = \frac{1}{E - H_0} V | \psi \rangle + | \phi \rangle . \quad (3)$$

It is easy to see that for $V = 0$ one can obtain the solution $| \phi \rangle$, i.e., the solution corresponding to the free particle. It is worth noting that in a certain sense the operator $\frac{1}{E - H_0}$ is anomalous, because it has a continuum of poles on the real axis at positions coinciding with the eigenvalues of H_0 . To get out of this trouble, it is common to produce a small shift in the imaginary direction ($\pm i\epsilon$) of the cut on the real axis

$$| \psi^\pm \rangle = \frac{1}{E - H_0 \pm i\epsilon} V | \psi^\pm \rangle + | \phi \rangle \quad (4)$$

This equation is known as the Lippmann-Schwinger equation. Finally, the shift of the poles is performed in the positive sense of the imaginary axis because in this case the causality principle holds (cf. Feynman). Let us consider the \mathbf{x} representation

$$\langle \mathbf{x} | \psi^\pm \rangle = \langle \mathbf{x} | \phi \rangle + \int d^3x' \left\langle \mathbf{x} \left| \frac{1}{E - H_0 \pm i\epsilon} \right| \mathbf{x}' \right\rangle \langle \mathbf{x}' | V | \psi^\pm \rangle . \quad (5)$$

The first term on the right hand side corresponds to a free particle, while the second one is interpreted as a spherical wave getting out from the

scattering center. The kernel of the previous integral can be considered as a Green function (also called propagator in quantum mechanics). It is a simple matter to calculate it

$$G_{\pm}(\mathbf{x}, \mathbf{x}') = \frac{\hbar^2}{2m} \left\langle \mathbf{x} \left| \frac{1}{E - H_0 \pm i\varepsilon} \right| \mathbf{x}' \right\rangle = -\frac{1}{4\pi} \frac{e^{\pm ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x} - \mathbf{x}'|}, \quad (6)$$

where $E = \hbar^2 k^2 / 2m$. Writing the wave function as a plane wave plus a divergent spherical one (up to a constant factor),

$$\langle \mathbf{x} | \psi^+ \rangle = e^{\mathbf{k} \cdot \mathbf{x}} + \frac{e^{ikr}}{r} f(\mathbf{k}, \mathbf{k}'). \quad (7)$$

the quantity $f(\mathbf{k}, \mathbf{k}')$ is known as the scattering amplitude and is explicitly

$$f(\mathbf{k}, \mathbf{k}') = -\frac{1}{4\pi} (2\pi)^3 \frac{2m}{\hbar^2} \langle \mathbf{k}' | V | \psi^+ \rangle. \quad (8)$$

Let us now define an operator T such that

$$T | \phi \rangle = V | \psi^+ \rangle \quad (9)$$

If we multiply the Lippmann-Schwinger equation by V and make use of the previous definition, we get

$$T | \phi \rangle = V | \phi \rangle + V \frac{1}{E - H_0 + i\varepsilon} T | \phi \rangle. \quad (10)$$

Iterating this equation (as in perturbation theory) we can get the Born approximation and its higher-order corrections.

Partial waves method

Let us now consider the case of a central potential. In this case, using the definition (9), it is found that the operator T commutes with \vec{L}^2 and \vec{L} ; it is said that T is a scalar operator. To simplify the calculations it is convenient to use spherical coordinates, because of the symmetry of the problem that turns the T operator diagonal. Let us see now a more explicit form of the scattering amplitude

$$f(\mathbf{k}, \mathbf{k}') = \text{const.} \sum_{lm'l'm'} \int dE \int dE' \langle \mathbf{k}' | E' l' m' \rangle \langle E' l' m' | T | Elm \rangle \langle Elm | \mathbf{k} \rangle, \quad (11)$$

where $\text{const.} = -\frac{1}{4\pi} \frac{2m}{\hbar^2} (2\pi)^3$. After some calculation, one gets

$$f(\mathbf{k}, \mathbf{k}') = -\frac{4\pi^2}{k} \sum_l \sum_m T_l(E) Y_l^m(\mathbf{k}') Y_l^{m*}(\mathbf{k}) . \quad (12)$$

Choosing the coordinate system such that the vector \mathbf{k} have the same direction with the z axis, one infers that only the spherical harmonics of $m = 0$ will contribute to the scattering amplitude. If we define by θ the angle between \mathbf{k} and \mathbf{k}' , we will get

$$Y_l^0(\mathbf{k}') = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta) . \quad (13)$$

Employing the following definition

$$f_l(k) \equiv -\frac{\pi T_l(E)}{k} , \quad (14)$$

eq. (12) can be written as follows

$$f(\mathbf{k}, \mathbf{k}') = f(\theta) = \sum_{l=0}^{\infty} (2l+1) f_l(k) P_l(\cos\theta) . \quad (15)$$

For $f_l(k)$ a simple interpretation can be provided, which is based on the expansion of a plane wave in spherical waves. Thus, we can write the function $\langle \mathbf{x} | \psi^+ \rangle$ for large values of r in the following form

$$\begin{aligned} \langle \mathbf{x} | \psi^+ \rangle &= \frac{1}{(2\pi)^{3/2}} \left[e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right] = \\ &= \frac{1}{(2\pi)^{3/2}} \left[\sum_l (2l+1) P_l(\cos\theta) \left(\frac{e^{ikr} - e^{i(kr-l\pi)}}{2ikr} \right) + \sum_l (2l+1) f_l(k) P_l(\cos\theta) \frac{e^{ikr}}{r} \right] \\ &= \frac{1}{(2\pi)^{3/2}} \sum_l (2l+1) \frac{P_l(\cos\theta)}{2ik} \left[[1 + 2ik f_l(k)] \frac{e^{ikr}}{r} - \frac{e^{i(kr-l\pi)}}{r} \right] . \quad (16) \end{aligned}$$

This expression can be interpreted as follows. The two exponential terms correspond to spherical waves: the first to a divergent wave, and the latter to a convergent one. Moreover, the scattering effect is conveniently displayed in the coefficient of the divergent wave, which is unity when there are no scattering centers.

Phase shifts

We consider now a surface enclosing the scattering center. Assuming that there is no creation and annihilation of particles, one has

$$\int \mathbf{j} \cdot d\mathbf{S} = 0 , \quad (17)$$

where the integration region is the aforementioned surface, and \mathbf{j} is the probability current density. Moreover, because of the conservation of the orbital momentum, the latter equation should hold for each partial wave. The theoretical formulation of the problem does not change if one assumes the wave packet as a flux of noninteracting particles propagating through a region of central potential for which the angular momentum of each particle is conserved, so that the ‘particle’ content of the wave packet really does not change. Thus, one may think even intuitively that only phase factor effects can be introduced under these circumstances. Thus, if one defines

$$S_l(k) \equiv 1 + 2ikf_l(k) \quad (18)$$

we should have

$$|S_l(k)| = 1 . \quad (19)$$

These results can be interpreted using the conservation of probabilities. They are natural and expected because we assumed that there is no creation and annihilation of particles. Therefore, the effects of the scattering center is reduced to adding a phase factor in the components of the divergent wave. Taking into account the unitarity of the phase factor, we can write it in the form

$$S_l = e^{2i\delta_l} , \quad (20)$$

where δ_l is a real function of k . Taking into account the definition (18), we can write

$$f_l = \frac{e^{2i\delta_l} - 1}{2ik} = \frac{e^{i\delta_l} \sin(\delta_l)}{k} = \frac{1}{k \cot(\delta_l) - ik} . \quad (21)$$

The total cross section has the following form

$$\begin{aligned} \sigma_{total} &= \int |f(\theta)|^2 d\Omega = \\ &= \frac{1}{k^2} \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos(\theta)) \sum_l \sum_{l'} (2l+1)(2l'+1) e^{i\delta_l} \sin(\delta_l) e^{i\delta_{l'}} \sin(\delta_{l'}) P_l P_{l'} \\ &= \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2(\delta_l) . \end{aligned} \quad (22)$$

Getting the phase shifts

Let us consider now a potential V that is zero for $r > R$, where the parameter R is known as the range of the potential. Thus, the region $r > R$ corresponds to a spherical unperturbed/free wave. On the other hand, the general form of the expansion of a plane wave in spherical ones is

$$\langle \mathbf{x} | \psi^+ \rangle = \frac{1}{(2\pi)^{3/2}} \sum_l i^l (2l+1) A_l(r) P_l(\cos \theta) \quad (r > R), \quad (23)$$

where the coefficient A_l is by definition

$$A_l = c_l^{(1)} h_l^{(1)}(kr) + c_l^{(2)} h_l^{(2)}(kr). \quad (24)$$

$h_l^{(1)}$ and $h_l^{(2)}$ are the spherical Hankel functions whose asymptotic forms are the following

$$h_l^{(1)} \sim \frac{e^{i(kr-l\pi/2)}}{ikr}$$

$$h_l^{(2)} \sim -\frac{e^{-i(kr-l\pi/2)}}{ikr}.$$

Inspecting the following asymptotic form of the expression (23)

$$\frac{1}{(2\pi)^{3/2}} \sum_l (2l+1) P_l \left[\frac{e^{ikr}}{2ikr} - \frac{e^{-i(kr-l\pi)}}{2ikr} \right], \quad (25)$$

one can see that

$$c_l^{(1)} = \frac{1}{2} e^{2i\delta_l} \quad c_l^{(2)} = \frac{1}{2}. \quad (26)$$

This allows to write the radial wave function for $r > R$ in the form

$$A_l = e^{2i\delta_l} [\cos \delta_l j_l(kr) - \sin \delta_l n_l(kr)]. \quad (27)$$

Using the latter equation, we can get the logarithmic derivative in $r = R$, i.e., at the boundary of the potential range

$$\beta_l \equiv \left(\frac{r}{A_l} \frac{dA_l}{dr} \right)_{r=R} = kR \left[\frac{j_l' \cos \delta_l - n_l'(kR) \sin \delta_l}{j_l \cos \delta_l - n_l(kR) \sin \delta_l} \right]. \quad (28)$$

j_l' is the derivative of j_l with respect to r evaluated at $r = R$. Another important result that can be obtained from the knowledge of the previous one is the phase shift

$$\tan \delta_l = \frac{kR j_l'(kR) - \beta_l j_l(kR)}{kR n_l'(kR) - \beta_l n_l(kR)}. \quad (29)$$

To get the complete solution of the problem in this case, it is necessary to make the calculations for $r < R$, i.e., within the range of the potential. For a central potential, the 3D Schrödinger equation reads

$$\frac{d^2 u_l}{dr^2} + \left(k^2 - \frac{2m}{\hbar^2} V - \frac{l(l+1)}{r^2} \right) u_l = 0 , \quad (30)$$

where $u_l = rA_l(r)$ is constrained by the boundary condition $u_l|_{r=0} = 0$. Thus, one can calculate the logarithmic derivative, which, taking into account the continuity of the log-derivative (equivalent to the continuity condition of the derivative at a discontinuity point) leads to

$$\beta_l|_{in} = \beta_l|_{out} . \quad (31)$$

An example: scattering on a hard sphere

Let us now consider an important illustrative case, that of the hard sphere potential

$$V = \begin{cases} \infty & r < R \\ 0 & r > R . \end{cases} \quad (32)$$

It is known that a particle cannot penetrate into a region where the potential is infinite. Therefore, the wave function should be zero at $r = R$. Since we deal with an impenetrable sphere we also have

$$A_l(r)|_{r=R} = 0 . \quad (33)$$

Thus, from eq. (27), we get

$$\tan \delta_l = \frac{j_l(kR)}{n_l(kR)} . \quad (34)$$

One can see that the phase shift calculation is an easy one for any l . In the $l = 0$ case (s wave scattering), we have

$$\delta_l = -kR$$

and from eq. (27)

$$A_{l=0}(r) \sim \frac{\sin kr}{kr} \cos \delta_0 + \frac{\cos kr}{kr} \sin \delta_0 = \frac{1}{kr} \sin(kr + \delta_0) . \quad (35)$$

We immediately see that there is an additional phase contribution with regard to the motion of the free particle. It is also clear that in more general cases the various waves will have different phase shifts leading to a transient distortion of the scattered wave packet. At small energies, i.e., $kR \ll 1$, the spherical Bessel functions (entering the formulas for the spherical Hankel functions) are the following

$$j_l(kr) \sim \frac{(kr)^l}{(2l+1)!!} \quad (36)$$

$$n_l(kr) \sim -\frac{(2l-1)!!}{(kr)^{l+1}}, \quad (37)$$

leading to

$$\tan \delta_l = \frac{-(kR)^{2l+1}}{(2l+1)[(2l-1)!!]^2}. \quad (38)$$

From this formula, one can see that a substantial contribution to the phase shift is given by the $l = 0$ waves. Moreover, since $\delta_0 = -kR$ the cross section is obtained as follows

$$\sigma_{total} = \int \frac{d\sigma}{d\Omega} d\Omega = 4\pi R^2. \quad (39)$$

One can see that the total scattering cross section is four times bigger than the classical one and coincides with the total area of the impenetrable sphere. For large values of the incident energy, one can work in the hypothesis that all values of l up to a maximum value $l_{max} \sim kR$ contribute to the total cross section

$$\sigma_{total} = \frac{4\pi}{k^2} \sum_{l=0}^{l \sim kR} (2l+1) \sin^2 \delta_l. \quad (40)$$

In this way, from eq. (34), we have

$$\sin^2 \delta_l = \frac{\tan^2 \delta_l}{1 + \tan^2 \delta_l} = \frac{[j_l(kR)]^2}{[j_l(kR)]^2 + [n_l(kR)]^2} \sim \sin^2 \left(kR - \frac{l\pi}{2} \right), \quad (41)$$

where the expressions

$$j_l(kr) \sim \frac{1}{kr} \sin \left(kr - \frac{l\pi}{2} \right)$$

$$n_l(kr) \sim -\frac{1}{kr} \cos \left(kr - \frac{l\pi}{2} \right).$$

have been used.

Inspection of δ_l shows a negative jump of $\frac{\pi}{2}$ whenever l is augmented by a unity. Thus, it is clear that $\sin^2\delta_l + \sin^2\delta_{l+1} = 1$ holds. Approximating $\sin^2\delta_l$ by its mean value $\frac{1}{2}$ over a period and using the sum of odd numbers, one gets

$$\sigma_{total} = \frac{4\pi}{k^2}(kR)^2\frac{1}{2} = 2\pi R^2 . \quad (42)$$

Once again the quantum-mechanical result, although quite similar to the corresponding classical result is nevertheless different. What might be the origin of the factor of two that makes the difference ? To get an explanation, we first separate eq. (15) in two parts

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{l=kR} (2l+1)e^{2i\delta_l} P_l \cos(\theta) + \frac{i}{2k} \sum_{l=0}^{l=kR} (2l+1)P_l \cos(\theta) = f_{\text{refl}} + f_{\text{shadow}} . \quad (43)$$

Calculation of $\int |f_{\text{refl}}|^2 d\Omega$ gives

$$\int |f_{\text{refl}}|^2 d\Omega = \frac{2\pi}{4k^2} \sum_{l=0}^{l_{max}} \int_{-1}^1 (2l+1)^2 [P_l \cos(\theta)]^2 d(\cos \theta) = \frac{\pi l_{max}^2}{k^2} = \pi R^2 . \quad (44)$$

Analysing now f_{shadow} at small angles, we get

$$f_{\text{shadow}} \sim \frac{i}{2k} \sum (2l+1)J_0(l\theta) \sim ik \int_0^R b J_0(kb\theta) db = \frac{iR J_1(kR\theta)}{\theta} . \quad (45)$$

This formula is rather well known in optics. It corresponds to the Fraunhofer diffraction. Employing the change of variable $z = kR\theta$ one can calculate the integral $\int |f_{\text{shadow}}|^2 d\Omega$

$$\int |f_{\text{shadow}}|^2 d\Omega \sim 2\pi R^2 \int_0^\infty \frac{[J_1(z)]^2}{z} dz \sim \pi R^2 . \quad (46)$$

Finally, neglecting the interference between f_{refl} and f_{shadow} (since the phase oscillates between $2\delta_{l+1} = 2\delta_l - \pi$), one gets the result (42). The label ‘shadow’ for one of the terms is easily explained if one thinks of the wavy behaviour of the scattered particle (from the physical viewpoint there is no difference between a wave packet and a particle in this case). Its origin can be traced back to the backward-scattered components of the wave packet leading to a phase shift with respect to the incident waves and destructive interference.

Coulomb scattering

In this section we briefly consider the Coulomb scattering in the quantum-mechanical approach. For this case, the Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_1 Z_2 e^2}{r}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad E > 0, \quad (47)$$

where m is the reduced mass of the system, $E > 0$ since we deal with the simple scattering case where no kind of bound states are allowed to form. The previous equation is equivalent to the following expression (for adequate values of the constants k and γ)

$$\left(\nabla^2 + k^2 + \frac{2\gamma k}{r}\right)\psi(\mathbf{r}) = 0. \quad (48)$$

If we do not consider the centrifugal barrier, i.e., we look only to the s waves, we really deal with a pure coulombian interaction, for which one can propose a solution of the following form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\chi(u), \quad (49)$$

where

$$u = ikr(1 - \cos\theta) = ik(r - z) = ikw,$$

$$\mathbf{k} \cdot \mathbf{r} = kz.$$

$\psi(\mathbf{r})$ is the complete solution of the Schrödinger equation with an asymptotic 'physical' behaviour to which a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ and a spherical wave are expected to contribute $r^{-1}e^{ikr}$ are expected to contribute. Defining new variables

$$z = z \quad w = r - z \quad \lambda = \phi,$$

and by employing of previous relationships, eq. (48) takes the form

$$\left[u\frac{d^2}{du^2} + (1-u)\frac{d}{du} - i\gamma\right]\chi(u) = 0. \quad (50)$$

To solve this equation, one should first study its asymptotic behaviour. Since we have already tackled this issue, we merely present the asymptotic normalized wave function that is the final result of all previous calculations

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \left(e^{i[\mathbf{k}\cdot\mathbf{r} - \gamma \ln(kr - \mathbf{k}\cdot\mathbf{r})]} + \frac{f_c(k, \theta) e^{i[kr + \gamma \ln 2kr]}}{r} \right). \quad (51)$$

As one can see, this wave function displays terms that turns it quite different from the form in eq. (7). This is due to the fact that the Coulomb potential is of infinite range. Performing the exact calculation for the Coulomb scattering amplitude is not an easy matter. Here we give only the final result for the ‘normalized’ wave function

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \left(e^{i[\mathbf{k}\cdot\mathbf{r}-\gamma\ln(kr-\mathbf{k}\cdot\mathbf{r})]} + \frac{g_1^*(\gamma)}{g_1(\gamma)} \frac{\gamma}{2k \sin(\theta/2)^2} \frac{e^{i[kr+\gamma\ln 2kr]}}{r} \right), \quad (52)$$

where $g_1(\gamma) = \frac{1}{\Gamma(1-i\gamma)}$.

In addition, we reduce the partial wave analysis to a clear cut presentation of the results, of which some have already been mentioned. First of all, we write the wave function $\psi(\mathbf{r})$ in (49) as follows

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \chi(u) = A e^{i\mathbf{k}\cdot\mathbf{r}} \int_C e^{ut} t^{i\gamma-1} (1-t)^{-i\gamma} dt, \quad (53)$$

where A is a ‘normalization’ constant, while all the integral part is the inverse Laplace transform of the direct transform of eq. (50). A convenient form of the latter equation is

$$\psi(\mathbf{r}) = A \int_C e^{i\mathbf{k}\cdot\mathbf{r}} (1-t) e^{ikrt} (1-t) d(t, \gamma) dt \quad (54)$$

where

$$d(t, \gamma) = t^{i\gamma-1} (1-t)^{-i\gamma-1}. \quad (55)$$

Within the partial wave analysis we proceed by writing

$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty} (2l+1) i^l P_l(\cos \theta) A_l(kr), \quad (56)$$

where

$$A_l(kr) = A \int_C e^{ikrt} j_l[kr(1-t)] (1-t) d(t, \gamma). \quad (57)$$

Applying the relationships between the spherical Bessel functions and the Hankel functions, we get

$$A_l(kr) = A_l^{(1)}(kr) + A_l^{(2)}(kr). \quad (58)$$

We shall not sketch here how these coefficients are obtained (this is quite messy). They are

$$A_l^{(1)}(kr) = 0 \quad (59)$$

$$A_l^{(2)}(kr) \sim -\frac{Ae^{\pi\gamma/2}}{2ikr} [2\pi i g_1(\gamma)] \left(e^{-i[kr-(l\pi/2)+\gamma \ln 2kr]} - e^{2i\eta_l(k)} e^{i[kr-(l\pi/2)+\gamma \ln 2kr]} \right) \quad (60)$$

where

$$e^{2i\eta_l(k)} = \frac{\Gamma(1+l-i\gamma)}{\Gamma(1+l+i\gamma)}. \quad (61)$$

Calculation of the Coulomb scattering amplitude

If we perform the Laplace transform of eq. (50), we get

$$\chi(u) = A \int_C e^{ut} t^{i\gamma-1} (1-t)^{-i\gamma} dt. \quad (62)$$

The contour C goes from $-\infty$ to ∞ on the real axis and closes through the upper half-plane. There are two poles in this case at $t = 0$ and $t = 1$. By the change of variable $s = ut$, we get

$$\chi(u) = A \int_{C_1} e^s s^{i\gamma-1} (u-s)^{-i\gamma} ds. \quad (63)$$

$\chi(u)$ should be regular in zero. Indeed, we get

$$\chi(0) = (-1)^{-i\gamma} A \int_{C_1} \frac{e^s}{s} ds = (-1)^{-i\gamma} A 2\pi i \quad (64)$$

Performing now the limit $u \rightarrow \infty$, let's do an infinitesimal shift to avoid the location of the poles on the contour. Moreover, by the change of variable $\frac{s}{u} = -\frac{(s_0 \pm i\varepsilon)}{i\kappa}$, we see that this expression goes to zero when $u \rightarrow \infty$. Thus, we can expand $(u-s)$ in power series of $\frac{s}{u}$ for the pole with $s = 0$. This expansion is not the right one in $s = 1$, because in this case $s = -s_0 + i(\kappa \pm \varepsilon)$. It comes out that $\frac{s}{u} = 1 - \frac{(s_0 \pm i\varepsilon)}{\kappa}$ tends to 1 when $\kappa \rightarrow \infty$. If instead we do the change of variable $s' = s - u$, we get rid of this difficulty

$$\chi(u) = A \int_{C_2} \left([e^s s^{i\gamma-1} (u-s)^{-i\gamma}] ds + [e^{s'+u} (-s')^{i\gamma} (u+s')^{i\gamma-1}] ds' \right). \quad (65)$$

Expanding the power series, it is easy to calculate the previous integrals, but one should take the limit $\frac{s}{u} \rightarrow 0$ in the result in order to get the correct asymptotic forms for the Coulomb scattering

$$\chi(u) \sim 2\pi i A \left[u^{-i\gamma} g_1(\gamma) - (-u)^{i\gamma-1} e^u g_2(\gamma) \right]$$

$$\begin{aligned}
2\pi g_1(\gamma) &= i \int_{C_2} e^s s^{i\gamma-1} ds \\
2\pi g_2(\gamma) &= i \int_{C_2} e^s s^{-i\gamma} ds .
\end{aligned} \tag{66}$$

After all this chain of variable changes, we get back to the original s one to obtain

$$\begin{aligned}
(u^*)^{i\gamma} &= (-i)^{i\gamma} [k(r-z)]^{i\gamma} = e^{\gamma\pi/2} e^{i\gamma \ln k(r-z)} \\
(u)^{-i\gamma} &= (i)^{-i\gamma} [k(r-z)]^{-i\gamma} = e^{\gamma\pi/2} e^{-i\gamma \ln k(r-z)} .
\end{aligned} \tag{67}$$

The calculation of χ , once effected, is equivalent with having $\psi_{\mathbf{k}}(\mathbf{r})$ starting from (49).

Eikonal approximation

We shall briefly expound on the eikonal approximation whose philosophy is the same to that used when one wants to pass from the wave optics to the geometrical optics. Therefore, it is the right approximation when the potential varies slowly over distances comparable to to the wavelength of the scattered wave packet, i.e., for the case $E \gg |V|$. Thus, this approximation may be considered as a quasiclassical one. First, we propose that the quasiclassical wave function has the known form

$$\psi \sim e^{iS(\mathbf{r})/\hbar} , \tag{68}$$

where S satisfies the Hamilton-Jacobi equation, having the solution

$$\frac{S}{\hbar} = \int_{-\infty}^z \left[k^2 - \frac{2m}{\hbar^2} V(\sqrt{b^2 + z'^2}) \right]^{1/2} dz' + \text{constant} . \tag{69}$$

The additive constant is chosen in such a way to fulfill

$$\frac{S}{\hbar} \rightarrow kz \quad \text{for} \quad V \rightarrow 0 . \tag{70}$$

The term multiplying the potential can be interpreted as a change of phase of of the wave packet, having the following explicit form

$$\Delta(b) \equiv \frac{-m}{2k\hbar^2} \int_{-\infty}^{\infty} V(\sqrt{b^2 + z^2}) dz . \tag{71}$$

Within the method of partial waves, the eikonal approximation has the following application. We know it is correct at high energies, where many

partial waves do contribute to the scattering. Thus, we can consider l as a continuous variable and by analogy to classical mechanics we let $l = bk$. Moreover, as we already mentioned $l_{max} = kR$, which plugged into eq. (15) leads to

$$f(\theta) = -ik \int b J_0(kb\theta) [e^{2i\Delta(b)} - 1] db . \quad (72)$$

8P. Problems

Problem 8.1

Obtain the phase shift and the differential cross section at small angles for a scattering centre of potential $U(r) = \frac{\alpha}{r^2}$. It should be taken into account that for low-angle scattering the main contribution is given by the partial waves of large l .

Solution:

Solving the equation

$$R_l'' + \left[k^2 - \frac{l(l+1)}{r^2} - \frac{2m\alpha}{\hbar^2 r^2} \right] = 0$$

with the boundary conditions $R_l(0) = 0$, $R_l(\infty) = N$, where N is a finite number, we get

$$R_l(r) = A\sqrt{r} I_\lambda(kr) ,$$

where $\lambda = \left[\left(l + \frac{1}{2} \right)^2 + \frac{2m\alpha}{\hbar^2} \right]^{1/2}$ and I is the first modified Bessel function.

To determine δ_l , one should use the asymptotic expression of I_λ :

$$I_\lambda(kr) \propto \left(\frac{2}{\pi kr} \right)^{1/2} \sin\left(kr - \frac{\lambda\pi}{2} + \frac{\pi}{4} \right) .$$

Therefore

$$\delta_l = -\frac{\pi}{2} \left(\lambda - l - \frac{1}{2} \right) = -\frac{\pi}{2} \left(\left[\left(l + \frac{1}{2} \right)^2 + \frac{2m\alpha}{\hbar^2} \right]^{1/2} - \left(l + \frac{1}{2} \right) \right) .$$

The condition of large l leads us to

$$\delta_l = -\frac{\pi m \alpha}{(2l+1)\hbar^2},$$

whence one can see that $|\delta_l| \ll 1$ for large l .

From the general expression of the scattering amplitude

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) (e^{2i\delta_l} - 1),$$

at small angles one gets $e^{2i\delta_l} \approx 1 + 2i\delta_l$, so that

$$\sum_{l=0}^{\infty} P_l(\cos \theta) = \frac{1}{2 \sin \frac{\theta}{2}}.$$

Thus

$$f(\theta) = -\frac{\pi \alpha m}{k\hbar^2} \frac{1}{2 \sin \frac{\theta}{2}}.$$

The final result is

$$\frac{d\sigma}{d\theta} = \frac{\pi^3 \alpha^2 m}{2\hbar^2 E} \text{ctg} \frac{\theta}{2}.$$