Module I

Nonrelativistic Quantum Mechanics

1

Basic Concepts of Quantum Mechanics

1.1 Probability interpretation of the wave function

In quantum mechanics the **state** of some particle moving in time and space is described by a (complex) **wave function** $\psi(\boldsymbol{r}, t)$ of the space coordinate $\boldsymbol{r}$ $(= \boldsymbol{i}x + \boldsymbol{j}y + \boldsymbol{k}z)$ and time coordinate t. The state of the particle is "described" by $\psi(\boldsymbol{r}, t)$ in the sense that knowledge of the precise form of this function enables us to make precise predictions of the probabilities of the various possible outcomes of any given type of physical measurement on the particle. In particular, in a **position** measurement the probability of finding the particle to be in an infinitesimal box of volume $\mathrm{d}x\mathrm{d}y\mathrm{d}z \equiv \mathrm{d}^3\boldsymbol{r}$ with centre at $\boldsymbol{r}$ at time t is

$$P(\boldsymbol{r}, t)\mathrm{d}x\mathrm{d}y\mathrm{d}z = \psi^*(\boldsymbol{r}, t)\psi(\boldsymbol{r}, t)\mathrm{d}x\mathrm{d}y\mathrm{d}z, \tag{1.1}$$

where $\psi^*(\boldsymbol{r}, t)$ is the complex conjugate of the function $\psi(\boldsymbol{r}, t)$. Equation (1.1) may be written alternatively as

$$P(\boldsymbol{r}, t)\mathrm{d}^3\boldsymbol{r} = |\psi(\boldsymbol{r}, t)|^2\,\mathrm{d}^3\boldsymbol{r}. \tag{1.2}$$

Clearly, since any probability must be a dimensionless number, and $\mathrm{d}^3\boldsymbol{r}$ has the dimensions of volume $[L]^3$, the quantity $P(\boldsymbol{r}, t)$ is a **probability density**, with dimensions $[L]^{-3}$.

The wave function $\psi(\boldsymbol{r}, t)$ is also known as the **probability amplitude**, and has (in three-dimensional space) dimensions $[L]^{-3/2}$.

Since the particle must be found somewhere in space, the continuous sum (i.e., integral) of the probabilities (1.2) over infinitesimal boxes filling all space must be equal to unity:

$$\int_{\text{all space}} |\psi|^2\,\mathrm{d}^3\boldsymbol{r} = 1. \tag{1.3}$$

A wave function ψ satisfying (1.3) is said to be **normalized**.

A Course in Theoretical Physics, First Edition. P. J. Shepherd.

1.2 States of definite energy and states of definite momentum

If a particle is in a state of **definite energy** E, the corresponding wave function $\psi(\boldsymbol{r}, t)$ can be separated as a product of a space-dependent factor $\phi(\boldsymbol{r})$ and a **time-dependent** factor that takes the form of a pure harmonic wave $\mathrm{e}^{-i\omega t}$ [i.e., there is only one Fourier component (one frequency) in the Fourier decomposition of the time dependence], where the frequency ω is given by $\omega = E/\hbar$ (the **Einstein relation** $E = \hbar\omega$), in which $\hbar$ ($= 1.055 \times 10^{-34}$ Js) is Planck's constant h divided by 2π.

Thus, the time dependence of the wave function of a particle (or, indeed, a system of many particles) with definite energy E is **always** of the form $\mathrm{e}^{-iEt/\hbar}$.

If a particle is in a state of **definite momentum** $\boldsymbol{p} = \boldsymbol{i}p_x + \boldsymbol{j}p_y + \boldsymbol{k}p_z$ (so that the energy is also well defined and the above-mentioned factorization occurs), the **space-dependent** part $\phi(\boldsymbol{r})$ of the corresponding wave function $\psi(\boldsymbol{r}, t)$ is a harmonic plane wave $\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ [i.e., there is only one Fourier component (one wave vector $\boldsymbol{k}$) in its Fourier decomposition], where the wave vector $\boldsymbol{k} = \boldsymbol{i}k_x + \boldsymbol{j}k_y + \boldsymbol{k}k_z$ is related to the momentum $\boldsymbol{p}$ by $\boldsymbol{k} = \boldsymbol{p}/\hbar$, i.e., $k_x = p_x/\hbar$, and so on. [This is the well known **de Broglie relation** $\boldsymbol{p} = \hbar\boldsymbol{k}$, which, for the magnitudes, gives

$$p \equiv |\boldsymbol{p}| = \hbar\,|\boldsymbol{k}| \equiv \hbar k = \frac{h}{2\pi}\cdot\frac{2\pi}{\lambda} = \frac{h}{\lambda},$$

where λ is the wavelength associated with wave number k.]

Thus, the space dependence of the wave function of a particle with definite momentum $\boldsymbol{p}$ is the **plane wave**

$$\phi_{\boldsymbol{p}}(\boldsymbol{r}) = \mathrm{e}^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}. \tag{1.4}$$

[To see the reason for the designation "plane wave", we choose the z axis to lie along the direction of the momentum $\boldsymbol{p}$. Then (1.4) takes the form $\mathrm{e}^{ipz/\hbar}$, which clearly has the same phase (and so takes the same value) over any surface $z = \text{const}$ (a plane).]

Successive planes on which the function (1.4) has the same phase are separated by a distance equal to the wavelength λ and are called **wave fronts**.

To understand the motion of wave fronts, consider a particle of definite energy E and definite momentum $\boldsymbol{p}$ (along the z axis). Then the corresponding wave function is

$$\psi_{E,\boldsymbol{p}}(t) \propto \mathrm{e}^{i(pz-Et)/\hbar},$$

and the equation of motion of a wave front, that is, of a plane $z = z_{\mathrm{P}}$ with given phase of the wave function, is found by equating the phase of $\psi_{E,\boldsymbol{p}}(t)$ to a constant:

$$pz_{\mathrm{P}} - Et = \text{const},$$

that is,

$$z_{\mathrm{P}} = z_{\mathrm{P}}(t) = \frac{E}{p}t + \text{const} \equiv v_{\mathrm{P}}t + \text{const},$$

Thus, a wave front (surface of constant phase) moves with **phase velocity** $v_{\mathrm{P}} = E/p$ (> 0) along the positive z axis, that is, in the direction of the momentum $\boldsymbol{p}$.

1.3 Observables and operators

With every physically measurable quantity ("**observable**") A we can associate an operator $\hat{A}$, such that, if a particle is in a state with a well defined value a of A [we denote the wave function corresponding to this state by $\psi_a(\boldsymbol{r}, t)$], then

$$\hat{A}\psi_a(\boldsymbol{r}, t) = a\psi_a(\boldsymbol{r}, t). \tag{1.5}$$

Thus, the action of the operator $\hat{A}$ on the function $\psi_a(\boldsymbol{r}, t)$ is to reproduce precisely the same function of $\boldsymbol{r}$ and t but scaled by a constant factor a equal to the well defined value of A in this state. We say that $\psi_a(\boldsymbol{r}, t)$ is an **eigenfunction** of the operator $\hat{A}$, and a is the corresponding **eigenvalue** of the operator $\hat{A}$.

1.4 Examples of operators

As follows from section 1.2, the state of a particle with definite energy E and definite momentum $\boldsymbol{p}$ is described by a wave function of the form

$$\psi_{E,\boldsymbol{p}}(\boldsymbol{r}, t) \propto \mathrm{e}^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} = \mathrm{e}^{i(\boldsymbol{p}\cdot\boldsymbol{r}-Et)/\hbar}.$$

Accordingly [see (1.5)], there must exist an **energy operator** $\hat{E}$ and a **momentum operator** $\hat{\boldsymbol{p}}$ such that

$$\hat{E}\mathrm{e}^{i(\boldsymbol{p}\cdot\boldsymbol{r}-Et)/\hbar} = E\mathrm{e}^{i(\boldsymbol{p}\cdot\boldsymbol{r}-Et)/\hbar}$$

and

$$\hat{\boldsymbol{p}}\mathrm{e}^{i(\boldsymbol{p}\cdot\boldsymbol{r}-Et)/\hbar} = \boldsymbol{p}\mathrm{e}^{i(\boldsymbol{p}\cdot\boldsymbol{r}-Et)/\hbar}.$$

The differential operators

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \tag{1.6}$$

and

$$\hat{\boldsymbol{p}} = -i\hbar\left(\boldsymbol{i}\frac{\partial}{\partial x} + \boldsymbol{j}\frac{\partial}{\partial y} + \boldsymbol{k}\frac{\partial}{\partial z}\right) \equiv -i\hbar\boldsymbol{\nabla} \tag{1.7}$$

clearly have the required properties (if we bear in mind that $\boldsymbol{p}\cdot\boldsymbol{r} = p_x x + p_y y + p_z z$).

Just as we have found the energy and momentum operators by considering wave functions corresponding to definite energy and definite momentum, we can find the **position operator** by considering a wave function corresponding to definite position. We restrict ourselves, for the moment, to motion confined to one dimension. Then a particle with (at some given time) a definite position $x = x_1$ will be described by a wave function with the following spatial dependence (at that time):

$$\phi_{x_1}(x) = \delta(x - x_1),$$

where $\delta(x - x_1)$ is the **Dirac delta-function**, equal to zero when $x \neq x_1$ and with the properties

$$\int f(x)\delta(x - x_1)\mathrm{d}x = f(x_1) \quad \text{and} \quad \int \delta(x - x_1)\mathrm{d}x = 1,$$

(provided that the range of integration includes the point $x = x_1$). We need an operator $\hat{x}$ with the following effect:

$$\hat{x}\phi_{x_1}(x) = x_1\phi_{x_1}(x),$$

that is,

$$\hat{x}\delta(x - x_1) = x_1\delta(x - x_1). \tag{1.8}$$

The purely multiplicative operator

$$\hat{x} = x$$

has the required property, since (1.8) becomes

$$x\delta(x - x_1) = x_1\delta(x - x_1),$$

which is clearly true both for $x \neq x_1$ and for $x = x_1$. Similarly, we have $\hat{y} = y$ and $\hat{z} = z$, and so the operator of the three-dimensional position vector $\boldsymbol{r}$ is $\hat{\boldsymbol{r}} = \boldsymbol{r}$.

The operator corresponding to a general observable $A(\boldsymbol{r}, \boldsymbol{p})$ is obtained by the prescription

$$A \rightarrow \hat{A} = A(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}) \tag{1.9}$$

with

$$\hat{\boldsymbol{r}} = \boldsymbol{r} \quad \text{and} \quad \hat{\boldsymbol{p}} = -i\hbar\boldsymbol{\nabla}. \tag{1.10}$$

For example, the angular momentum, about the coordinate origin, of a particle at a vector distance $\boldsymbol{r}$ from the origin and with momentum $\boldsymbol{p}$ is given classically by the vector product $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$, and the corresponding operator $\hat{\boldsymbol{L}}$ is given by:

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = -i\hbar\boldsymbol{r} \times \boldsymbol{\nabla}. \tag{1.11}$$

1.5 The time-dependent Schrödinger equation

The total energy E of a particle at a given point $\boldsymbol{r}$ at time t is given by the sum of the kinetic energy $T(\boldsymbol{r}, t)$ and potential energy $V(\boldsymbol{r}, t)$:

$$\begin{aligned} E &= E(\boldsymbol{r}, t) = T(\boldsymbol{r}, t) + V(\boldsymbol{r}, t) \\ &= \frac{\boldsymbol{p} \cdot \boldsymbol{p}}{2m} + V(\boldsymbol{r}, t) \equiv \frac{p^2}{2m} + V(\boldsymbol{r}, t), \end{aligned} \tag{1.12}$$

where $\boldsymbol{p} = \boldsymbol{p}(\boldsymbol{r}, t)$ is the momentum of the particle (of mass m) at the point $\boldsymbol{r}$ at time t.

We make the operator replacements (section 1.4):

$$\begin{aligned} E &\to \hat{E} = i\hbar\frac{\partial}{\partial t}, \\ \boldsymbol{p} &\to \hat{\boldsymbol{p}} = -i\hbar\boldsymbol{\nabla} \qquad (\text{so that } p^2 \equiv \boldsymbol{p}\cdot\boldsymbol{p} \to -\hbar^2\boldsymbol{\nabla}\cdot\boldsymbol{\nabla} \equiv -\hbar^2\nabla^2), \\ V(\boldsymbol{r},t) &\to \hat{V} = V(\hat{\boldsymbol{r}},t) = V(\boldsymbol{r},t). \end{aligned} \tag{1.13}$$

Since the relation $E = T + V$ is a physical requirement, a physically acceptable wave function $\psi(\boldsymbol{r},t)$ must satisfy the equation $\hat{E}\psi = \hat{T}\psi + \hat{V}\psi$, that is,

$$i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r},t) + V(\boldsymbol{r},t)\psi(\boldsymbol{r},t). \tag{1.14}$$

This is the **time-dependent Schrödinger equation**, and is (for the nonrelativistic case and in three dimensions) a **completely general** differential equation (first order in time and second order in space) for the evolution of the wave function $\psi(\boldsymbol{r},t)$ of a particle whose energy may or may not be well defined, moving in a potential that may or may not be varying in time.

1.6 Stationary states and the time-independent Schrödinger equation

We now specialize to the case when the particle is in a state with definite energy E. For this case (section 1.2) the wave function is always of the form

$$\psi(\boldsymbol{r},t) = \phi(\boldsymbol{r})\mathrm{e}^{-iEt/\hbar}, \tag{1.15}$$

where $\phi(\boldsymbol{r})$ specifies the space-dependent part of the function. Because, from (1.15), $|\psi(\boldsymbol{r},t)|^2 = |\phi(\boldsymbol{r})|^2$, which is independent of the time t, such a state is called a **stationary state**. When (1.15) is substituted into the time-dependent Schrödinger equation (1.14) the left-hand side becomes $E\psi(\boldsymbol{r},t)$, and so, after cancellation of the factor $\mathrm{e}^{-iEt/\hbar}$, we obtain

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\boldsymbol{r}) + V(\boldsymbol{r})\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r}), \tag{1.16}$$

where we have also replaced $V(\boldsymbol{r}, t)$ by $V(\boldsymbol{r})$, since for a particle to be in a state of well-defined energy E it is a necessary (though not sufficient) condition that the potential-energy function be time independent. [This is clearly seen from the fact that equation (1.16) with different potentials $V_t(\boldsymbol{r}) \equiv V(\boldsymbol{r},t)$ at different times t will have different solutions $\phi_t(\boldsymbol{r})$ with different energy eigenvalues E_t, contradicting the assumption of a definite energy E.] The equation (1.16) is the **time-independent Schrödinger equation**, and is an eigenvalue equation [see (1.5)] of the form

$$\hat{H}\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r}) \tag{1.17}$$

with

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}) \tag{1.18}$$

(the hamiltonian operator, or **hamiltonian**).

1.7 Eigenvalue spectra and the results of measurements

The set of all possible eigenvalues a of an operator $\hat{A}$ is called the **spectrum** of the operator $\hat{A}$. **A measurement of** A **always yields a value belonging to this spectrum**.

Two cases are possible:

(a) The wave function $\psi(\boldsymbol{r}, t)$ describing the state of the particle is an eigenfunction $\psi_i(\boldsymbol{r}, t)$ of $\hat{A}$, that is,

$$\hat{A}\psi_i(\boldsymbol{r}, t) = a_i \psi_i(\boldsymbol{r}, t). \tag{1.19}$$

Then the result of measuring A will certainly be a_i.

(b) The wave function $\psi(\boldsymbol{r}, t)$ describing the state of the particle is not an eigenfunction of $\hat{A}$; that is, the action of $\hat{A}$ on $\psi(\boldsymbol{r}, t)$ gives a function that is not simply a scaled version of $\psi(\boldsymbol{r}, t)$. But since the eigenfunctions $\psi_i(\boldsymbol{r}, t)$ of $\hat{A}$ form a complete set, in the sense that any normalized function can be expanded in terms of them, we may write $\psi(\boldsymbol{r}, t)$ as such an expansion:

$$\psi(\boldsymbol{r}, t) = \sum_i c_i \psi_i(\boldsymbol{r}, t). \tag{1.20}$$

Then a measurement of A can yield any eigenvalue a_i for which the corresponding eigenfunction appears in the sum (1.20) with nonzero weight c_i. For example, a measurement of A yields the result a_j with probability $|c_j|^2$.

1.8 Hermitian operators

The operators corresponding to all physical observables are **hermitian**.

Definition. An operator $\hat{A}$ is said to be hermitian if, for any pair of normalizable wave functions $\psi(\boldsymbol{r}, t)$ and $\chi(\boldsymbol{r}, t)$, the relation

$$\int \chi^* \hat{A}\psi \, \mathrm{d}^3\boldsymbol{r} = \int (\hat{A}\chi)^* \psi \, \mathrm{d}^3\boldsymbol{r} \tag{1.21}$$

always holds.

The eigenvalues of hermitian operators are real. This is proved as follows. Choose χ and ψ to be the same eigenfunction ψ_i of the operator $\hat{A}$, with corresponding eigenvalue a_i; that is, choose

$$\chi = \psi = \psi_i \qquad (\hat{A}\psi_i = a_i \psi_i).$$

Then (1.21) becomes

$$a_i \int \psi_i^* \psi_i \, \mathrm{d}^3\boldsymbol{r} = a_i^* \int \psi_i^* \psi_i \, \mathrm{d}^3\boldsymbol{r},$$

that is, $a_i = a_i^*$, or, in other words, the eigenvalue a_i (and hence any eigenvalue of $\hat{A}$) is real.

Now choose χ and ψ to be two different eigenfunctions of $\hat{A}$: let χ be ψ_i with eigenvalue a_i, and let ψ be ψ_j with eigenvalue a_j. Then (1.21) becomes

$$\int \psi_i^* \hat{A} \psi_j \mathrm{d}^3 \boldsymbol{r} = \int (\hat{A}\psi_i)^* \psi_j \mathrm{d}^3 \boldsymbol{r},$$

whence

$$a_j \int \psi_i^* \psi_j \mathrm{d}^3 \boldsymbol{r} = a_i^* \int \psi_i^* \psi_j \mathrm{d}^3 \boldsymbol{r}.$$

But $a_i^* = a_i$ and, since $a_j \neq a_i$, we have:

$$\int \psi_i^* \psi_j \mathrm{d}^3 \boldsymbol{r} = 0. \tag{1.22}$$

This result states that eigenfunctions of a hermitian operator that correspond to different eigenvalues of that operator are **orthogonal**.

We now use the idea of orthogonality to prove an inequality

$$\left| \int \phi^* \chi \mathrm{d}^3 \boldsymbol{r} \right|^2 \leq \left(\int \phi^* \phi \mathrm{d}^3 \boldsymbol{r} \right) \left(\int \chi^* \chi \mathrm{d}^3 \boldsymbol{r} \right) \tag{1.23}$$

that will be used in section 1.11 to prove the **general uncertainty relation**. The case when the functions ϕ and χ are the same function clearly corresponds to the equality in (1.23). The inequality (1.23), if true, will be true for any normalization of ϕ and χ, since when we multiply ϕ and χ by arbitrary factors these factors cancel in the inequality (1.23). Therefore, for convenience in examining the left-hand side of (1.23), we choose unit normalization for ϕ and χ. But if in the left-hand side $|\int \phi^* \chi \mathrm{d}^3 \boldsymbol{r}|^2$ the function χ contains not only a part proportional to ϕ but also a part proportional to a normalized function ρ **orthogonal** to ϕ, so that $\chi = a\phi + b\rho$, with $|a|^2 + |b|^2 = 1$ (note that then, in particular, $|a| \leq 1$), we have:

$$\left| \int \phi^* \chi \mathrm{d}^3 \boldsymbol{r} \right| = \left| \int \phi^* (a\phi + b\rho) \mathrm{d}^3 \boldsymbol{r} \right| = |a| \int \phi^* \phi \mathrm{d}^3 \boldsymbol{r} \leq \int \phi^* \phi \mathrm{d}^3 \boldsymbol{r}. \tag{1.24}$$

Similarly, expressing ϕ in this case as $\phi = c\chi + d\eta$, with the function η orthogonal to χ and with both χ and η normalized to unity (so that $|c|^2 + |d|^2 = 1$ and, in particular, $|c| \leq 1$), we have

$$\left| \int \phi^* \chi \mathrm{d}^3 \boldsymbol{r} \right| = \left| \int \chi^* \phi \mathrm{d}^3 \boldsymbol{r} \right| = \left| \int \chi^* (c\chi + d\eta) \mathrm{d}^3 \boldsymbol{r} \right| = |c| \int \chi^* \chi \mathrm{d}^3 \boldsymbol{r} \leq \int \chi^* \chi \mathrm{d}^3 \boldsymbol{r}, \tag{1.25}$$

so that, taking the product of (1.24) and (1.25), we obtain (1.23).

1.9 Expectation values of observables

The **expectation value** of an observable A in a particle state described by a wave function $\psi(\boldsymbol{r}, t)$ is defined as the average result of N ($\rightarrow \infty$) measurements of A, all carried out on a particle in the same state $\psi(\boldsymbol{r}, t)$. The prescription for calculating the expectation value when the (normalized) function $\psi(\boldsymbol{r}, t)$ is known is

$$\langle A\rangle_{\psi(\boldsymbol{r},t)} \equiv \int \psi^*(\boldsymbol{r}, t)\hat{A}\psi(\boldsymbol{r}, t)\mathrm{d}^3\boldsymbol{r}. \tag{1.26}$$

To show that this prescription is equivalent to the definition of the expectation value as an average, we substitute the expansion (1.20) into (1.26) and use the fact that the eigenfunctions $\psi_i(\boldsymbol{r}, t)$ of $\hat{A}$ are normalized and mutually orthogonal (an **orthonormal** set). (We showed in section 1.8 that eigenfunctions belonging to different eigenvalues of a hermitian operator are always mutually orthogonal. Also, although eigenfunctions belonging to the same eigenvalue need not be mutually orthogonal, it is always possible to form linear combinations of them that are.) The result is

$$\langle A\rangle_{\psi(\boldsymbol{r},t)} = \sum_i |c_i|^2\, a_i. \tag{1.27}$$

This relation asserts (in precise accord with its definition as an average) that the expectation value of A in the state $\psi(\boldsymbol{r}, t)$ is the sum of all possible outcome a_i, each weighted by the probability $|c_i|^2$ that in this state a measurement of A will yield the result a_i.

1.10 Commuting observables and simultaneous observability

If the operators corresponding to two observables A and B have a common, complete set of eigenfunctions ψ_{ij} (i labels the corresponding eigenvalues a_i of $\hat{A}$, and j labels the corresponding eigenvalues b_j of $\hat{B}$), we say that A and B can be **simultaneously well defined**, or, equivalently, that they are simultaneously observable.

The **commutator** $[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$ of any pair of simultaneously well-definable observables A and B is identically zero, in the sense that its action on an arbitrary normalizable function ψ gives zero. To show this, we use the fact that any such function ψ can be written as a linear combination of the common eigenfunctions ψ_{ij} of $\hat{A}$ and $\hat{B}$, so that

$$[\hat{A}, \hat{B}]\psi = [\hat{A}, \hat{B}]\sum_{i,j} c_{ij}\psi_{ij} = \sum_{i,j} c_{ij}[\hat{A}, \hat{B}]\psi_{ij} = 0, \tag{1.28}$$

which follows from the fact that

$$\begin{aligned}[\hat{A}, \hat{B}]\psi_{ij} &\equiv \hat{A}\hat{B}\psi_{ij} - \hat{B}\hat{A}\psi_{ij} = \hat{A}b_j\psi_{ij} - \hat{B}a_i\psi_{ij}\\ &= b_j\hat{A}\psi_{ij} - a_i\hat{B}\psi_{ij} = b_j a_i\psi_{ij} - a_i b_j\psi_{ij} = 0.\end{aligned}$$

The converse is clearly also true, in that if two operators $\hat{A}$ and $\hat{B}$ commute, that is, $[\hat{A}, \hat{B}] = 0$, they can be simultaneously well defined.

1.11 Noncommuting observables and the uncertainty principle

If $[\hat{A}, \hat{B}] \neq 0$, the observables A and B cannot be simultaneously well defined. We define the **uncertainty** in A in the state ψ by

$$(\Delta A)_\psi = \sqrt{\left\langle \left(\hat{A} - \langle \hat{A} \rangle_\psi \right)^2 \right\rangle_\psi} \tag{1.29}$$

(which is clearly the standard deviation of A, i.e., the root mean square deviation of A from the mean of A, where the "mean" here is the expectation value in the state ψ). Then, as is proved below, the product of the uncertainties in two observables A and B is given by the inequality (**general uncertainty relation**)

$$(\Delta A)_\psi (\Delta B)_\psi \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle_\psi \right|. \tag{1.30}$$

Proof: With the definition (1.29) in mind, we set $\phi \equiv (\hat{A} - \langle \hat{A} \rangle_\psi)\psi$ and $\chi \equiv (\hat{B} - \langle \hat{B} \rangle_\psi)\psi$, so that

$$\begin{aligned} \int \phi^* \phi \mathrm{d}^3 \boldsymbol{r} &= \int \left[\left(\hat{A} - \langle \hat{A} \rangle_\psi \right) \psi \right]^* \left(\hat{A} - \langle \hat{A} \rangle_\psi \right) \psi \mathrm{d}^3 \boldsymbol{r} \\ &= \int \psi^* \left(\hat{A} - \langle \hat{A} \rangle_\psi \right) \left(\hat{A} - \langle \hat{A} \rangle_\psi \right) \psi \mathrm{d}^3 \boldsymbol{r} = (\Delta A)_\psi{}^2, \end{aligned}$$

where we have used the fact that $\hat{A}$ is a hermitian operator [see (1.21)]. Similarly, $\int \chi^* \chi \mathrm{d}^3 \boldsymbol{r} = (\Delta B)_\psi{}^2$. Then the inequality (1.23) becomes:

$$\begin{aligned} (\Delta A)_\psi{}^2 (\Delta B)_\psi{}^2 &= \left(\int \phi^* \phi \mathrm{d}^3 \boldsymbol{r} \right) \left(\int \chi^* \chi \mathrm{d}^3 \boldsymbol{r} \right) \geq \left| \int \phi^* \chi \mathrm{d}^3 \boldsymbol{r} \right|^2 = \left| \mathrm{Re} \left(\int \phi^* \chi \mathrm{d}^3 \boldsymbol{r} \right) \right|^2 + \left| \mathrm{Im} \left(\int \phi^* \chi \mathrm{d}^3 \boldsymbol{r} \right) \right|^2 \\ &\geq \left| \mathrm{Im} \left(\int \phi^* \chi \mathrm{d}^3 \boldsymbol{r} \right) \right|^2 = \left| \frac{\int \phi^* \chi \mathrm{d}^3 \boldsymbol{r} - \int \chi^* \phi \mathrm{d}^3 \boldsymbol{r}}{2i} \right|^2 \\ &= \frac{1}{4} \left| \int \left(\left(\hat{A} - \langle \hat{A} \rangle_\psi \right) \psi \right)^* \left(\hat{B} - \langle \hat{B} \rangle_\psi \right) \psi \mathrm{d}^3 \boldsymbol{r} - \int \left(\left(\hat{B} - \langle \hat{B} \rangle_\psi \right) \psi \right)^* \left(\hat{A} - \langle \hat{A} \rangle_\psi \right) \psi \mathrm{d}^3 \boldsymbol{r} \right|^2 \\ &= \frac{1}{4} \left| \int \psi^* \left(\hat{A} - \langle \hat{A} \rangle_\psi \right) \left(\hat{B} - \langle \hat{B} \rangle_\psi \right) \psi \mathrm{d}^3 \boldsymbol{r} - \int \psi^* \left(\hat{B} - \langle \hat{B} \rangle_\psi \right) \left(\hat{A} - \langle \hat{A} \rangle_\psi \right) \psi \mathrm{d}^3 \boldsymbol{r} \right|^2, \end{aligned}$$

where we have again used the fact that that $\hat{A}$ and $\hat{B}$ are hermitian operators. Thus, we have

$$\begin{aligned} (\Delta A)_\psi{}^2 (\Delta B)_\psi{}^2 &\geq \frac{1}{4} \left| \langle \hat{A}\hat{B} \rangle_\psi - 2 \langle \hat{A} \rangle_\psi \langle \hat{B} \rangle_\psi + \langle \hat{A} \rangle_\psi \langle \hat{B} \rangle_\psi - \left(\langle \hat{B}\hat{A} \rangle_\psi - 2 \langle \hat{B} \rangle_\psi \langle \hat{A} \rangle_\psi + \langle \hat{B} \rangle_\psi \langle \hat{A} \rangle_\psi \right) \right|^2 \\ &= \frac{1}{4} \left| \langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle_\psi \right|^2 \equiv \frac{1}{4} \left| \langle [\hat{A}, \hat{B}] \rangle_\psi \right|^2, \end{aligned}$$

from which (1.30 follows). For example, when $\hat{A} = \hat{x} = x$ and $\hat{B} = \hat{p}_x = -i\hbar \partial / \partial x$, we have $[\hat{x}, \hat{p}_x]\psi = -i\hbar \left(x \frac{\partial \psi}{\partial x} - \frac{\partial}{\partial x}(x\psi) \right) = i\hbar\psi$. From this we see that $[\hat{x}, \hat{p}_x] = i\hbar$, and so (1.30) yields $(\Delta x)_\psi (\Delta p_x)_\psi \geq \frac{\hbar}{2}$, which asserts that for a particle in one-dimensional motion no state ψ exists for which the product of the uncertainties in the position and momentum is smaller than $\hbar/2$. In fact, the equality $(\Delta x)_\psi(\Delta p_x)_\psi = \frac{\hbar}{2}$ (corresponding to the smallest possible product of the position and momentum uncertainties) is found in the case of a one-dimensional harmonic oscillator in its ground state, as can be seen by substituting the gaussian space-dependent part $\phi(x) \propto \exp(-\alpha x^2)$ of the latter [see (3.36)] into the expressions for $(\Delta x)_\psi$ and $(\Delta p_x)_\psi$.

1.12 Time dependence of expectation values

Using the expression (1.26) for the expectation value of an observable A, and also the time-dependent Schrödinger equation (1.14) in the form

$$i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = \hat{H}\psi(\boldsymbol{r},t) \tag{1.31}$$

(together with the complex conjugate of this equation), we can immediately obtain an expression for the rate of change of the expectation value with time:

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle_\psi = \left\langle[\hat{A},\hat{H}]\right\rangle_\psi + i\hbar\left\langle\partial\hat{A}/\partial t\right\rangle_\psi, \tag{1.32}$$

which is known as **Ehrenfest's theorem**.

1.13 The probability-current density

We now use the time-dependent Schrödinger equation (1.14) to find the time rate of change of the probability density $P(\boldsymbol{r},t) = \psi^*(\boldsymbol{r},t)\psi(\boldsymbol{r},t)$. We find

$$\frac{\partial P(\boldsymbol{r},t)}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t) = 0 \tag{1.33}$$

(the **continuity equation** for the probability density). Here,

$$\boldsymbol{j} = -\frac{i\hbar}{2m}\left(\psi^*\boldsymbol{\nabla}\psi - (\boldsymbol{\nabla}\psi^*)\psi\right) \tag{1.34}$$

is the **probability-current density**.

1.14 The general form of wave functions

In this section, for simplicity, we consider the case of **one-dimensional** motion of a particle of mass m and potential energy $V(x)$.

The space part $\phi_E(x)$ of the wave function of a stationary state with energy E satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\phi_E}{\mathrm{d}x^2} + V(x)\phi_E = E\phi_E, \tag{1.35}$$

that is

$$\frac{1}{\phi_E}\frac{\mathrm{d}^2\phi_E}{\mathrm{d}x^2} = \frac{2m}{\hbar^2}[V(x) - E].$$

Case (a): Consider points x at which $E > V(x)$, that is, points at which the kinetic energy $T(x)$ is positive, corresponding to a classically allowed situation. At such points,

$$\frac{1}{\phi_E}\frac{\mathrm{d}^2\phi_E}{\mathrm{d}x^2} < 0,$$

that is, $\phi_E(x)$ is **concave** to the x axis.

Case (b): At points x at which $E < V(x)$, that is, points at which the kinetic energy $T(x)$ is negative, corresponding to a classically forbidden situation, we have:

$$\frac{1}{\phi_E}\frac{\mathrm{d}^2\phi_E}{\mathrm{d}x^2} > 0,$$

that is, $\phi_E(x)$ is **convex** to the x axis.

These features of $\phi_E(x)$ are made clear in figure 1.1, in which, as a convention, we plot schematically the real part (or it could be the imaginary part) of $\phi_E(x)$ at the level of E.

The kinetic energy (and hence the momentum $p = \hbar k$) is greatest at the deepest part of the well (the centre, in this case); that is, k is largest, and hence the "local wavelength" $\lambda = 2\pi/k$ is shortest, near the centre of the well.

Similarly, since higher values of E correspond to higher values of the kinetic energy T (and hence of the momentum p) at all points, the wave functions of the higher-energy states have more oscillations (and hence more nodes).

Suppose now that the potential energy V is piecewise-constant in space, for example, as in the case of the "potential barrier" shown in figure 1.2.

In regions in which V is constant and smaller than E (**classically allowed regions**, such as the regions to the left and to the right of the barrier in figure 1.2), the space-dependent part of the wave function always has the **oscillatory** form

$$\phi_E(x) = A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx}, \tag{1.36}$$

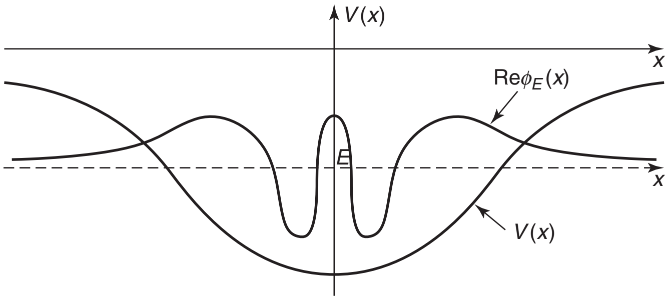


Figure 1.1 *Real or imaginary part (schematic) of the space part $\phi_E(x)$ of the wave function of a particle of definite energy E moving in a potential V(x).*

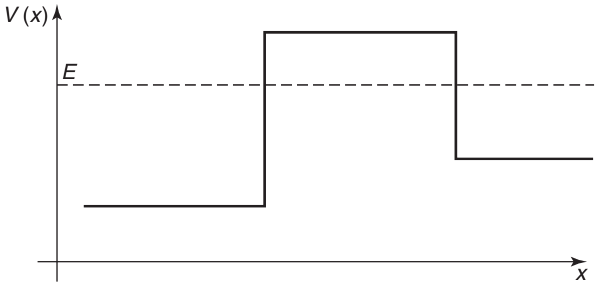


Figure 1.2 *A "potential barrier" V(x). The dashed line denotes the level of the total energy E of the particle.*

where k is found from the relation

$$E - V = T = \frac{\hbar^2 k^2}{2m},$$

in which V is the constant potential energy in the given region. Thus, the wave number k in (1.36) is given by

$$k = \left[\frac{2m}{\hbar^2}(E - V)\right]^{1/2}.$$

In regions in which V is constant and greater than E (**classically forbidden regions**, such as the region of the barrier in figure 1.2), the space-dependent part of the wave function has the general form of an **exponentially increasing** and an **exponentially decreasing** term:

$$\phi_E(x) = C\mathrm{e}^{\gamma x} + D\mathrm{e}^{-\gamma x}, \tag{1.37}$$

with

$$\frac{\hbar^2 \gamma^2}{2m} = V - E,$$

where V is the constant potential energy in the given region. Thus, γ in (1.37) is given by

$$\gamma = \left[\frac{2m}{\hbar^2}(V - E)\right]^{1/2}.$$

To find the constants of the type A, B in the forms (1.36) or of the type C, D in the forms (1.37) in all the regions of constant V, we impose the following requirements on the wave function $\phi_E(x)$:

(i) The function $\phi_E(x)$ is continuous.
(ii) The first derivative $\mathrm{d}\phi_E(x)/\mathrm{d}x$ is continuous [except at singularities or infinite discontinuities of $V(x)$].
(iii) The function $\phi_E(x)$ is normalized.

These conditions are, in fact, **general physical requirements** on the space part of the wave function of a particle with a definite energy E. Moreover, it turns out that, in the general case, they cannot be met for **arbitrary** values of E, and the time-independent Schrödinger equation has solutions that satisfy these requirements only if the energy E is specified to have a value belonging to a specified spectrum. In certain regions of energy this spectrum may be discrete, and so the above requirements lead naturally to **energy quantization**.

1.15 Angular momentum

The vector angular-momentum operator $\hat{\boldsymbol{L}}$ (1.11) has the following cartesian components:

$$\begin{aligned}
\hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right),\\
\hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right),\\
\hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial\varphi},
\end{aligned}$$

and, therefore,

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{1.38}$$

As will be proved in chapter 2, the eigenvalue spectrum of $\hat{L}^2$ is

$$0,\ 2\hbar^2,\ 6\hbar^2,\ 12\hbar^2,\ 20\hbar^2, \ldots,$$

that is,

$$l(l+1)\hbar^2, \text{ with } \quad l = 0, 1, 2, 3, 4, \ldots,$$

and the eigenvalue spectrum of $\hat{L}_z$ is

$$0, \pm\hbar, \pm 2\hbar, \pm 3\hbar, \ldots, \pm l\hbar,$$

that is,

$$m\hbar, \text{ with } \quad m = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l.$$

It is easily shown that $[\hat{L}^2, \hat{L}_z] = 0$, and so (see section 1.10) the operators $\hat{L}^2$ and $\hat{L}_z$ have a set of common eigenfunctions, labelled by the quantum numbers l and m [the **spherical harmonics** $Y_{lm}(\theta, \varphi)$]:

$$\begin{aligned}
\hat{L}^2 Y_{lm}(\theta,\varphi) &= l(l+1)\hbar^2 Y_{lm}(\theta,\varphi),\\
\hat{L}_z Y_{lm}(\theta,\varphi) &= m\hbar Y_{lm}(\theta,\varphi).
\end{aligned} \tag{1.39}$$

The spherical harmonics are given by the expression

$$Y_{lm}(\theta, \varphi) = N_{lm} P_l^m(\cos\theta) \mathrm{e}^{im\varphi}, \tag{1.40}$$

where the $P_l^m(\cos\theta)$ are the **associated Legendre functions**, defined by

$$P_l^m(w) = \left(1 - w^2\right)^{|m|/2} \frac{\mathrm{d}^{|m|} P_l(w)}{\mathrm{d}w^{|m|}} \tag{1.41}$$

[$P_l(w)$ is a **Legendre polynomial** – see below], and the normalization constants N_{lm} are given by

$$N_{lm} = \varepsilon \left[\frac{2l+1}{4\pi} \cdot \frac{(l-|m|)!}{(l+|m|)!} \right]^{\frac{1}{2}}, \text{ with } \varepsilon = \begin{cases} (-1)^m & (m > 0) \\ 1 & (m \leq 0) \end{cases}$$

The $P_l(w)$ ($l = 0, 1, 2, \ldots$) are polynomials of order l (power series in w containing a finite number of powers of w, the highest being w^l), called **Legendre polynomials**, and are polynomial solutions of Legendre's equation

$$\frac{\mathrm{d}}{\mathrm{d}w}\left[(1-w^2)\frac{\mathrm{d}}{\mathrm{d}w}P_l(w)\right] + l(l+1)P_l(w) = 0.$$

The $P_l(w)$ are defined on the interval $|w| \leq 1$ and normalized by the requirement that

$$\int_{-1}^{1} P_l(w) P_{l'}(w) \mathrm{d}x = \frac{2}{2l+1}\delta_{ll'}.$$

The first few Legendre polynomials $P_l(w)$ are

$$P_0(w) = 1,\ P_1(w) = w,\ P_2(w) = \frac{1}{2}\left(3w^2 - 1\right),\ P_3(w) = \frac{1}{2}\left(5w^3 - 3w\right), \cdots$$

The polynomials $P_l(w)$ have the parity of l, that is, they are even functions of w if the integer l is even, and odd functions of w if l is odd.

Since

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar L_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y, \tag{1.42}$$

that is, since the components of $\hat{\boldsymbol{L}}$ do not commute with one another, only one of the components of $\boldsymbol{L}$ can be well defined.

1.16 Particle in a three-dimensional spherically symmetric potential

For motion in a three-dimensional spherically symmetric potential $V(\boldsymbol{r}) = V(r)$ the time-independent Schrödinger equation for stationary states of energy E is [see (1.16)]

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\boldsymbol{r}) + V(\boldsymbol{r})\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r}). \tag{1.43}$$

In spherical polar coordinates this becomes

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\phi(\boldsymbol{r}) + V(r)\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r}).$$

We now multiply this equation by $-2mr^2/\hbar^2$, try the substitution

$$\phi(\boldsymbol{r}) = \phi(r, \theta, \varphi) = R(r)Y(\theta, \varphi),$$

and divide the resulting equation by $\phi = RY$. The result is

$$\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{2mr^2}{\hbar^2}(E - V(r)) = -\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right]. \tag{1.44}$$

(Note that the first term on the left involves a total, not a partial, derivative with respect to r, since R depends only on r.) Since the left-hand side is a function of r, and the right-hand side is a function of θ and φ, and yet the two sides are equal, they must be equal to the same constant Λ. The right-hand side then becomes

$$-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] = \Lambda Y. \tag{1.45}$$

Comparison with (1.38) shows that this can be written as

$$\frac{\hat{L}^2}{\hbar^2}Y = \Lambda Y, \quad \text{or} \quad \hat{L}^2 Y = \Lambda\hbar^2 Y.$$

This is none other than the first eigenvalue equation in (1.39), and so we can make the identifications

$$\Lambda = l(l+1),$$
$$Y(\theta, \varphi) = Y_{lm}(\theta, \varphi).$$

With this Λ the radial equation (obtained by setting the left-hand side of (1.44) equal to Λ) is, after division by r^2,

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \left[\frac{2m}{\hbar^2}(E - V(r)) - \frac{l(l+1)}{r^2}\right]R = 0. \tag{1.46}$$

1.17 The hydrogen-like atom

In the case of a hydrogen-like atom (i.e., one-electron atom), with nuclear charge Ze (Z is the number of protons and e is the modulus of the electron charge $-e$) and nuclear mass m_{nuc}, equation (1.46) describes the **relative motion** of the electron–nucleus system if we identify r with the electron–nucleus distance $r = |\boldsymbol{r}_{\text{elec}} - \boldsymbol{r}_{\text{nuc}}|$, replace m by the **reduced mass** μ of the electron–nucleus system:

$$m = \mu = \frac{m_{\text{elec}} m_{\text{nuc}}}{m_{\text{elec}} + m_{\text{nuc}}},$$

and set $V(r)$ equal to the Coulomb potential energy of the electron–nucleus system:

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}. \tag{1.47}$$

The radial equation then has negative-energy (**bound-state**) solutions that satisfy the physical requirements of continuity, continuity of gradient (except at the singularity $r = 0$ of the Coulomb potential), and normalizability **only** if E belongs to the spectrum of values

$$E = E_n = -\frac{1}{2n^2} \cdot \frac{Ze^2}{4\pi\varepsilon_0 a_0(Z)}, \tag{1.48}$$

where the **principal quantum number** $n = 1, 2, 3, \ldots$, and

$$a_0(Z) = \frac{4\pi\varepsilon_0 \hbar^2}{\mu Z e^2} = \frac{a_0(1)}{Z} \equiv \frac{a_0}{Z} \tag{1.49}$$

is the **Bohr radius** in the case when the nucleus has charge Ze.

The corresponding radial solutions are:

$$R_{nl}(r) = \mathrm{e}^{-\frac{1}{2}\alpha r}(\alpha r)^l L_{n+l}^{2l+1}(\alpha r),$$

with $\alpha = \left(\frac{8\mu|E_n|}{\hbar^2}\right)^{1/2}$ (i.e., α depends on the quantum number n), and $L_{n+l}^{2l+1}(\alpha r)$ is a polynomial (**Laguerre polynomial**) of degree $n' = n - l - 1$, that is, with $n - l - 1$ nodes.

For example,

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} \cdot 2\mathrm{e}^{-r/a_0(Z)}, \tag{1.50}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) \mathrm{e}^{-r/2a_0(Z)}, \tag{1.51}$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{r}{\sqrt{3}a_0(Z)} \mathrm{e}^{-r/2a_0(Z)}. \tag{1.52}$$

These radial functions are depicted schematically in figure 1.3.

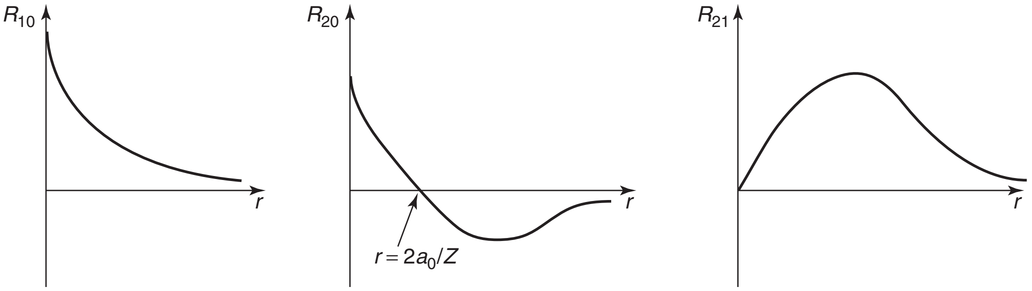


Figure 1.3 *The radial functions $R_{10}(r)$, $R_{20}(r)$ and $R_{21}(r)$.*

The full solutions have the form

$$\phi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi).$$

Consider the effect on these of **inversion**, that is, of replacing $\boldsymbol{r}$ by $-\boldsymbol{r}$, which means replacing (r,θ,φ) by $(r,\pi-\theta,\varphi+\pi)$. Under inversion,

$$\mathrm{e}^{im\varphi} \to \mathrm{e}^{im(\varphi+\pi)} = \begin{cases} \mathrm{e}^{im\varphi} \text{ if } m \text{ is even,} \\ -\mathrm{e}^{im\varphi} \text{ if } m \text{ is odd,} \end{cases}$$

that is, the factor $\mathrm{e}^{im\varphi}$ is even under inversion if m is even, and odd under inversion if m is odd. We say that $\mathrm{e}^{im\varphi}$ has the **parity** of m.

Similarly, since $P_l(\cos\theta)$ has the parity of l under inversion, and

$$P_l^m(w) = \left(1-w^2\right)^{\frac{1}{2}|m|} \frac{\mathrm{d}^{|m|}P_l(w)}{\mathrm{d}w^{|m|}},$$

it follows that $P_l^m(\cos\theta)$ has the parity of $l-|m|$ under inversion.

Therefore, the spherical harmonic

$$Y_{lm}(\theta,\varphi) = N_{lm}P_l^m(\cos\theta)\mathrm{e}^{im\varphi}$$

has the parity of l.

Thus, wave functions with even l are even under inversion, and wave functions with odd l are odd under inversion.

For example, the functions $\phi_{nlm} = \phi_{100}$, ϕ_{200} and ϕ_{300} are all even under inversion, and hence, as can be seen from the graphs in figure 1.3, have a cusp (a discontinuous gradient) at $r = 0$.

For example,

$$\frac{\partial}{\partial x}\frac{\partial\phi_{100}}{\partial x}\bigg|_{r=0} = -\infty. \tag{1.53}$$

This discontinuity of gradient is perfectly permissible in the case of the Coulomb potential, since the potential energy (1.47) is singular at $r = 0$ (it tends to $-\infty$ at $r = 0$), so that, for a given fixed total energy E, the kinetic energy tends to $+\infty$ at $r = 0$. Since, as can be seen from (1.12) and (1.13), the operator representing minus the kinetic energy contains second-derivative operators with respect to x, y and z, the relation (1.53) has a natural interpretation.

Functions with $l = 0, 1, 2, 3, 4, \ldots$ are called $s, p, d, f, g, \ldots$ functions, respectively. Since for $l = 0$ we must have $m = 0$ always, all s functions contain the factor

$$Y_{00} = 1/\sqrt{4\pi},$$

and so are independent of θ and φ, that is, are spherically symmetric functions.

For any given value of the principal quantum number n (except $n = 1$) there are three p functions ($l = 1$, $m = 1, 0, -1$). For these the radial part is $R_{n1}(r)$ and the three possible spherical harmonics are

$$\begin{aligned} Y_{10}(\theta, \varphi) &= \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta, \\ Y_{1,\pm1}(\theta, \varphi) &= \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \mathrm{e}^{\pm i\varphi}. \end{aligned}$$

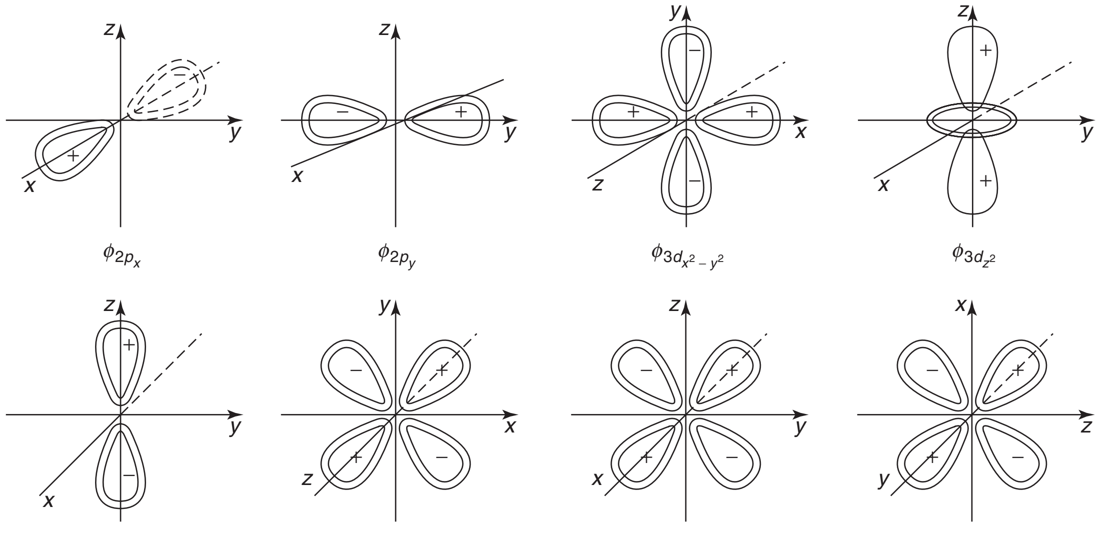
Any linear combination of the three functions ϕ_{n1m} ($m = 1, 0, -1$) will also be a solution of the Schrödinger equation for the hydrogen-like atom. In particular, consider the combinations

$$\begin{aligned} \phi_{n10} &= R_{n1}Y_{10} \propto R_{n1}\cos\theta, \\ \frac{1}{2}(\phi_{n11} + \phi_{n1,-1}) &= \frac{R_{n1}}{2}(Y_{11} + Y_{1,-1}) \propto R_{n1}\sin\theta\cos\varphi, \\ \frac{1}{2i}(\phi_{n11} - \phi_{n1,-1}) &= \frac{R_{n1}}{2i}(Y_{11} - Y_{1,-1}) \propto R_{n1}\sin\theta\sin\varphi. \end{aligned} \tag{1.54}$$

Since $\cos\theta = z/r$, $\sin\theta\cos\varphi = x/r$ and $\sin\theta\sin\varphi = y/r$, the three functions (1.54) are simply z, x and y, respectively, multiplied by a spherically symmetric function. Since spherically symmetric functions are invariant under coordinate rotations and reflections, the three functions (1.54) transform under coordinate rotations and reflections like z, x and y, respectively, and so are designated $\phi_{np_z}(\boldsymbol{r})$, $\phi_{np_x}(\boldsymbol{r})$ and $\phi_{np_y}(\boldsymbol{r})$. For example, we can depict the function $\phi_{2p_z}(\boldsymbol{r})$ by drawing surfaces of constant $\left|\phi_{2p_z}(\boldsymbol{r})\right|$, as in one of the diagrams in figure 1.4. The nodal plane $z = 0$ is one such surface and the proportionality to z is indicated by the opposite signs of the function in the half-spaces $z > 0$ and $z < 0$.

Similarly, from the five $l = 2$ spherical harmonics (corresponding to d functions) we can construct five linear combinations that transform, under coordinate rotations and reflections, like xy, yz, zx, $x^2 - y^2$, and $3z^2 - r^2$. For the example of $n = 3$ (the $3d$ functions) these are also depicted, with the corresponding designation of the respective functions, in figure 1.4.

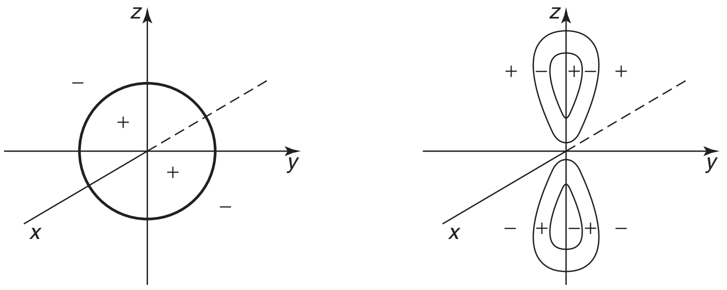
For the $2p$ functions and for the $3d$ functions the number of nodes of the radial part is zero ($n - l - 1 = 0$ in both cases). Examples for which the radial part of the wave function has one node (the function $\phi_{2s}(\boldsymbol{r})$, for which $n - l - 1 = 1$) or two nodes (the function $\phi_{4p_z}(\boldsymbol{r})$, for which $n - l - 1 = 2$) are illustrated in figure 1.5 .



ϕ_{2p_x} ϕ_{2p_y} $\phi_{3d_{x^2-y^2}}$ $\phi_{3d_{z^2}}$

ϕ_{2p_z} $\phi_{3d_{xy}}$ $\phi_{3d_{yz}}$ $\phi_{3d_{zx}}$

Figure 1.4 *Surfaces of constant modulus of the three 2p and five 3d functions.*



(a) (b)

Figure 1.5 *Nodal surfaces and relative signs of (a) the function* $\phi_{2s}(\boldsymbol{r})$ *and (b) the function* $\phi_{4p_z}(\boldsymbol{r})$.