

9. The Mathematical Framework of Quantum Theory

As we saw in the previous chapter, classical physics is unable to offer a satisfactory explanation of the structure of even the simplest atom, that of hydrogen. This was first achieved by quantum theory. We shall therefore go into the theory in more depth, beginning where Chap. 7 left off. We shall be particularly, but not exclusively, concerned with bound states, of which the simplest example is

9.1 The Particle in a Box

In order to become more familiar with the formalism of quantum theory, which will then lead to quantitative predictions, we first consider the one-dimensional motion of an enclosed particle. “Enclosed” means that it can only move in a “box” of length a . The probability of finding the particle outside the box is zero (Fig. 9.1). We shall now attempt to construct the appropriate wavefunction. We require that

$$\begin{aligned}\psi &= 0 & \text{for } x < 0, \\ \psi &= 0 & \text{for } x > a,\end{aligned}\tag{9.1}$$

because the particle cannot be outside the box. We further postulate that the wavefunction $\psi(x)$ inside the box is continuous with the function outside, i.e. that

$$\psi(0) = 0, \quad \psi(a) = 0.\tag{9.2}$$

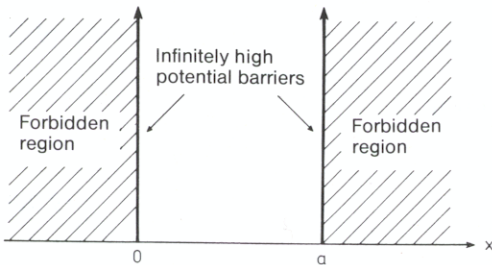


Fig. 9.1. Potential barriers for a particle in a box

We are seeking wavefunctions which describe a particle in this box and simultaneously guarantee that the particle always has a certain definite energy. We recall the de Broglie waves

$$A \exp [i(kx - \omega t)].\tag{9.3}$$

According to the basic laws of quantum theory, the wavenumber k and the frequency ω are related to the particle's energy and momentum by the relations

$$E = \hbar \omega \quad (9.4)$$

and

$$p = \hbar k. \quad (9.5)$$

From the experiments described above, we know that we can use the relationship from classical physics,

$$E = \frac{p^2}{2m_0}. \quad (9.6)$$

If we express p in terms of k , and solve for k , we obtain two possible values for k ,

$$k_{1,2} = \pm \frac{1}{\hbar} \sqrt{2m_0 E}, \quad (9.7)$$

for the given value of total energy E .

In addition to the wavefunction (9.3), the wavefunction

$$A \exp(-ikx - i\omega t) \quad (9.8)$$

yields the same energy. This will help us out of a difficulty. As one can see by substituting $x = 0$ and $x = a$ in (9.3), the wavefunction (9.3) does not satisfy the boundary conditions (9.2). One way out is the following: since electron waves display diffraction and interference, we may infer that we can superpose waves in quantum mechanics, as we did in fact with wave packets in Sect. 7.1. We therefore generate a new wavefunction by superposing (9.3) and (9.8):

$$\psi(x, t) = (C_1 e^{ikx} + C_2 e^{-ikx}) e^{-i\omega t}, \quad (9.9)$$

where the constants C_1 and C_2 are still unknown.

To abbreviate, we write (9.9) in the form

$$\psi(x, t) = \phi(x) e^{-i\omega t} \quad (9.9a)$$

where

$$\phi(x) = C_1 e^{ikx} + C_2 e^{-ikx}. \quad (9.9b)$$

In order to determine the constants C_1 and C_2 , we substitute (9.9) in the first equation (9.2) and obtain

$$\phi(0) = 0: \quad C_1 + C_2 = 0. \quad (9.10)$$

Thus C_2 can be expressed in terms of C_1 . (9.9) then takes the form

$$\phi(x) = C_1(e^{ikx} - e^{-ikx}) = 2iC_1 \sin kx; \quad (9.11)$$

here we have made use of the definition of the sine function. To fulfil the second condition of (9.2), we substitute (9.11) in (9.2) and obtain:

$$\text{because } \phi(a) = 0; \quad \text{the condition } \sin ka = 0. \quad (9.12)$$

Since the sine can only be zero if its argument is a whole multiple of π , we can only satisfy (9.12) by the choice of

$$k = \frac{n\pi}{a}, \quad n = 1, 2, 3, 4, \dots \quad (9.13)$$

This result means that the only waves which will fit into the box have a half-wavelength equal to a whole fraction of the length of the box, a (Fig. 9.2). If we substitute (9.13) in the expression for kinetic energy (9.6), we obtain

$$E = \frac{\hbar^2}{2m_0} \left(\frac{n\pi}{a} \right)^2 \quad (9.14)$$

for the energy of the particle, with the condition that $n \geq 1$ must be an integer. The parameter n cannot be equal to zero, because otherwise the wavefunction would be identically equal to zero. In other words, there would be no particle.

The result (9.14) is typical for quantum theory. The energies are no longer continuous as in classical physics, but are quantised. In order to determine C_1 in (9.11), which is still open, we remember that the wavefunction must be normalised. We thus have the condition $\int \psi^* \psi dx = 1$ to fulfil. If we substitute (9.11) in this, we first obtain

$$\int_0^a |\phi(x)|^2 dx = |C_1|^2 \int_0^a (2 - e^{i\frac{2\pi n}{a}x} - e^{-i\frac{2\pi n}{a}x}) dx. \quad (9.15)$$

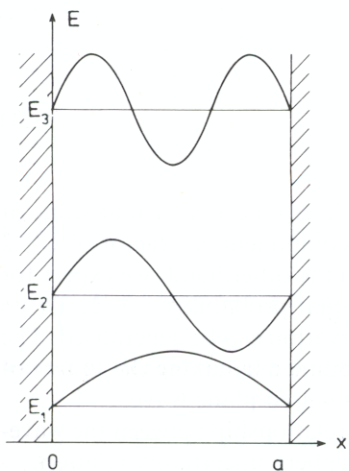


Fig. 9.2. Potential barriers, energies and wavefunctions of the particle in the box. *Two different parameters are plotted in the same figure.* 1) The energies E_1, E_2, E_3 of the first 3 states are plotted along the E (= energy) axis. (There is an infinite series of higher energies above these.) 2) The x axis is drawn to the right of each of the E values, and the wavefunction appropriate to each energy is shown on it. One should notice that the number of times the wavefunction crosses the x axis inside the box increases by 1 for each higher energy state

This integral is easy to evaluate and yields

$$\int_0^a |\phi(x)|^2 dx = |C_1|^2 \cdot 2a. \quad (9.16)$$

Because the integral (9.15) has to be equal to 1 to fulfil the normalisation condition, the normalisation constant C_1 has the form

$$C_1 = \frac{1}{\sqrt{2a}}. \quad (9.17)$$

It should be remembered that C_1 can only be determined up to the constant phase factor $\exp(i\alpha)$. As we shall see later, this type of phase factor has no physical meaning, because it disappears during the calculation of expectation values (see below). Our final result thus has the form

$$\phi(x) = \frac{1}{\sqrt{2a}} \exp(ixn\pi/a) - \frac{1}{\sqrt{2a}} \exp(-ixn\pi/a), \quad (9.18)$$

or in another notation,

$$\phi(x) = \sqrt{\frac{2}{a}} \cdot i \sin(x \cdot n\pi/a). \quad (9.19)$$

As we have seen, the wavefunction (9.18) is associated with a *definite energy*. Does this also hold for the momentum? This is clearly not the case, because it describes both a wave with $k = n\pi/a$ and a wave with $k = -n\pi/a$. If we should measure the momentum, we would thus find values $p = \hbar k$ and $p = -\hbar k$ with equal frequencies. In order to derive the probability of occurrence of a given momentum from the wavefunction, let us first consider the wavefunction

$$\frac{1}{\sqrt{a}} \exp(ixn\pi/a) \quad (9.20)$$

which is obviously normalised in the region from 0 to a :

$$\int_0^a \left| \frac{1}{\sqrt{a}} \exp\left(i \frac{n\pi}{a} x\right) \right|^2 dx = \frac{1}{a} \int_0^a dx = 1. \quad (9.21)$$

When we measure the momentum, it means that we determine a particular value of k , i.e., we select one of the components of (9.18). This component is a factor of $1/\sqrt{2}$ smaller than the corresponding component of (9.20). On the other hand, we expect for symmetry reasons that both components occur with equal probability = 1/2. To go from $1/\sqrt{2}$ to 1/2, of course, we square $1/\sqrt{2}$. This observation can be generalised: The probability of measuring a given momentum k can be obtained by taking the square of the absolute value of the coefficient in front of the normalised plane wave.

We leave it to the reader as an exercise to explain the relationship between the wavefunction (9.18) and the momentum (9.5) using the Heisenberg uncertainty relation.

9.2 The Schrödinger Equation

As we saw in the preceding example, there are for a given problem, in this case the particle in a box, infinitely many solutions, each with a corresponding energy level (9.14). In this case it was relatively easy to find these solutions, which is decidedly not the case for other quantum mechanical problems. In such cases it is often useful first to look for an equation which determines ψ . In the case of the electron which is not subjected to any forces, we find it as follows: we ask if there is an equation for ψ such that its solutions automatically fulfil the relation

$$\hbar \omega = \frac{\hbar^2 k^2}{2m_0}. \quad (9.22)$$

Since the parameters k and ω are found in the de Broglie wave $\exp(ikx - i\omega t)$, we can formulate the question thus: what must be done to obtain $\hbar^2 k^2/2m_0$ from $\exp(ikx)$ and $\hbar \omega$ from $\exp(-i\omega t)$, so that the relation

$$\frac{\hbar^2 k^2}{2m_0} = \hbar \omega \quad (9.23)$$

will be fulfilled? If we differentiate $\exp(ikx)$ twice with respect to x and multiply by $-\hbar^2/2m_0$, we obtain the left side of (9.23) as a factor. Correspondingly, the right side of (9.23) is obtained if we differentiate $\exp(-i\omega t)$ with respect to time and multiply by $i\hbar$. In this way we obtain the basic Schrödinger equation for the force-free particle:

$$-\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} \psi = i\hbar \dot{\psi}. \quad (9.24)$$

It must be said, however, that it is generally not possible to derive the basic equations of physics from still more fundamental principles. Instead, one must try to comprehend the physics by heuristic thought processes, to arrive at an equation, and then to compare the possible solutions with experimentally testable facts. In this way it has been found that the Schrödinger equation is completely valid in *nonrelativistic* quantum mechanics. We generalise (9.24) to three dimensions by writing the kinetic energy in the form

$$E = \frac{1}{2m_0} (p_x^2 + p_y^2 + p_z^2). \quad (9.25)$$

It seems reasonable to generalise the wavefunction to

$$\exp(ik_x x + ik_y y + ik_z z) \exp(-i\omega t). \quad (9.26)$$

Instead of (9.23) we have the relation

$$\frac{1}{2m_0} \hbar^2 (k_x^2 + k_y^2 + k_z^2) = \hbar \omega. \quad (9.27)$$

The left side of (9.27) is obtained from (9.26) by taking the second derivatives of (9.26) with respect to the position coordinates x , y and z , adding these and multiplying the result by $-\hbar^2/2m_0$. The right side of (9.27) results by differentiation of (9.26) with respect to time and multiplication by $i\hbar$. We thus obtain the equation

$$-\frac{\hbar^2}{2m_0} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = i\hbar \frac{\partial}{\partial t} \psi. \quad (9.28)$$

The left side can be abbreviated by introducing the Laplace operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad (9.29)$$

which yields the usual form of the Schrödinger equation for the force-free particle in three dimensions,

$$-\frac{\hbar^2}{2m_0} \nabla^2 \psi = i\hbar \frac{\partial}{\partial t} \psi. \quad (9.30)$$

Now we are naturally not so interested in the force-free motion of the particle as in its motion in a force field. However, (9.30) gives us a hold on the subject. We see that the left side was derived from the expression $p^2/2m_0$ for the kinetic energy by replacing it by a differentiation rule $-(\hbar^2/2m_0) \nabla^2$. This rule acts on ψ and is called the kinetic energy operator. In the presence of a potential field, the total energy according to classical mechanics is the sum of the kinetic and the potential energy:

$$\frac{1}{2m_0} p^2 + V(\mathbf{r}) = E. \quad (9.31)$$

We can arrive heuristically at the *total energy operator* of the quantum treatment by simply adding V to the kinetic energy operator. We thus obtain the *time-dependent Schrödinger equation in the presence of a potential field*:

$$\left(-\frac{\hbar^2}{2m_0} \nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t). \quad (9.32)$$

The expression

$$\mathcal{H} = -\frac{\hbar^2}{2m_0} \nabla^2 + V(\mathbf{r}) \quad (9.33)$$

is called the *Hamiltonian* (operator).

The beginner may not be used to working with operators. One can quickly become accustomed to them, if one remembers that they are only convenient abbreviations. One must also remember that such operators are always to be applied to functions.

If the potential field on the left side of (9.32) does not depend on time, we can proceed from the time-dependent to the time-independent Schrödinger equation. In

doing so, just as in (9.9a), we separate a time factor $\exp(-i\omega t)$ from $\psi(\mathbf{r}, t)$. In quantum mechanics it is customary to write E/\hbar instead of ω , so that we write

$$\psi(\mathbf{r}, t) = e^{-iEt/\hbar} \phi(\mathbf{r}). \quad (9.34)$$

Since the time differentiation only applies to ψ on the right side of (9.32), we need here only to differentiate the exponential function with respect to time, which yields the factor E . If we then divide both sides of the corresponding equation by the exponential function, we obtain as the result the *time-independent Schrödinger equation*

$$\left(-\frac{\hbar^2}{2m_0} \nabla^2 + V(\mathbf{r}) \right) \phi(\mathbf{r}) = E \phi(\mathbf{r}). \quad (9.35)$$

As we saw in the preceding example, the wavefunction must ordinarily be subject to boundary conditions (9.2). If these are not specified, we apply the so-called natural boundary conditions, which require that ψ vanishes at infinity, so that the wavefunction can be normalised, i.e.

$$\int |\psi|^2 dV = 1. \quad (9.36)$$

Before we proceed to the solution of the Schrödinger equation, we shall again take up the question of observations, measured values and operators.

9.3 The Conceptual Basis of Quantum Theory

9.3.1 Observations, Values of Measurements and Operators

Determination and Probability of Position

In the preceding sections, we saw that the explanation of microcosmic processes required new ways of thinking which are fundamentally different from the ideas of classical physics. In classical mechanics, the motion of a body, such as the fall of a stone or the flight of a rocket, can be precisely predicted by the laws of motion. According to these laws, the position and momentum of a body can be determined to as great a precision as is desired.

The wavefunction is the new concept which is central to quantum physics. As the solution of the time-dependent Schrödinger equation, it describes the time evolution of physical processes in the microcosm. In this section we shall explore the physical implications of the wavefunction, or in other words, which experimental results the theoretical physicist can predict for the experimental physicist. The (conceptually) simplest experiment would be to determine the position of a particle. As we already know, the wave function ψ can only make a probabilistic prediction. The expression

$$|\psi(x, y, z)|^2 dx dy dz \quad (9.37)$$

gives the probability that the particle will be found in a volume element $dx dy dz$ about the point x, y, z . We now ask whether the wavefunction can also predict the results of observations of momentum.

9.3.2 Momentum Measurement and Momentum Probability

Let us first consider as an example the wavefunction of the particle in a box (Sect. 9.1),

$$\phi(x) = \frac{1}{\sqrt{2}} \underbrace{\frac{1}{\sqrt{a}} \exp(ikx)}_{u_1(x)} - \frac{1}{\sqrt{2}} \underbrace{\frac{1}{\sqrt{a}} \exp(-ikx)}_{u_2(x)}. \quad (9.38)$$

The two underlined wavefunctions each satisfy the normalisation conditions (9.36). According to the basic rules of quantum mechanics, the momentum associated with the wavefunction $u_1(x)$ is given by $\hbar k$, while the momentum of the second wavefunction $u_2(x)$ is $\hbar(-k) = -\hbar k$.

Both of these momenta are thus represented by the wavefunction (9.38). If we determine the momentum of the particle in the box described by the wavefunction (9.38), we expect to observe either $+\hbar k$ or $-\hbar k$. However, we cannot predict which of the two momenta we will observe. If we imagine that the particle flies back and forth in the box, it is intuitively clear that we will observe the momenta $\hbar k$ and $-\hbar k$ with a probability of $1/2$ each. As we saw in Sect. 9.1, the squares of the absolute values of the coefficients C_1 and C_2 give the probability of finding the corresponding momentum. We generalise this insight to the determination of the probability distribution of the momenta of a generalised wave packet. Here the particle is no longer confined in a box. This type of wave packet has the general form

$$\psi(x) = \int_{-\infty}^{+\infty} a_k e^{ikx} dk. \quad (9.39)$$

In order to connect the coefficients a_k with a probabilistic interpretation, we must be sure that the wavefunctions $\exp(ikx)$ are normalised in infinite space. This is somewhat difficult, and will not be demonstrated here (see Appendix A). We shall simply state the result. If we introduce the momentum variable p in the place of the integration variable k , and at the same time use the correct normalisation of the wavefunction in one dimension, we obtain

$$\psi(x) = \int_{-\infty}^{+\infty} \underbrace{c(p) \frac{1}{\sqrt{2\pi\hbar}}}_{\text{normalised}} e^{ipx/\hbar} dp. \quad (9.40)$$

The underlined wavefunction is normalised. As a generalisation of our considerations above, we see $|c(p)|^2 dp$ as the probability of observing momentum p in the interval $p, \dots, p + dp$. This result can be immediately expanded to three dimensions: if we represent a wavefunction $\psi(x, y, z)$ as a superposition of normalised plane waves,

$$\psi(x, y, z) = \iiint_{-\infty}^{+\infty} c(p_x, p_y, p_z) (2\pi\hbar)^{-3/2} \exp(ip \cdot r/\hbar) d^3p, \quad \text{with} \quad (9.41)$$

$p \cdot r = p_x x + p_y y + p_z z$, then

$$|c(p_x, p_y, p_z)|^2 dp_x dp_y dp_z$$

is the probability that the components of the observed momentum of the particle p will lie in the intervals $p_x \dots p_x + dp_x$, $p_y \dots p_y + dp_y$, $p_z \dots p_z + dp_z$.

9.3.3 Average Values and Expectation Values

To explain these concepts, we think again about the example of the dice. The individual possible “observed values” are the numbers of spots, $1, 2, \dots, 6$. For a single throw we cannot predict which of these numbers we will obtain. We can only make predictions if we throw many times and keep track of the frequency F_n with which we obtain the number n ($n = 1, 2, \dots, 6$). The average number \bar{n} is then given by

$$\bar{n} = \frac{\sum_{n=1}^6 nF_n}{\sum_{n=1}^6 F_n}. \quad (9.42)$$

This average value can be predicted statistically (in the limiting case of an infinite number of throws) through the use of the concept of probability. This is the ratio of the number of times the desired result is obtained divided by the total number of attempts. The probability of obtaining n spots (“desired result” is n) is denoted by P_n . Since each number of spots is equally probable, $P_1 = P_2 \dots = P_6$. Further, since $\sum_{n=1}^6 P_n = 1$ must hold, we use the equality of the individual probabilities to obtain immediately

$$P_n = 1/6, \quad n = 1, 2, \dots, 6. \quad (9.43)$$

(We exclude loaded dice.) According to probability theory, \bar{n} may be expressed in terms of P_n as follows:

$$\bar{n} = \sum_{n=1}^6 n \cdot P_n = 1 \cdot \frac{1}{6} + 2 \cdot \frac{1}{6} + \dots + 6 \cdot \frac{1}{6}. \quad (9.44)$$

These relatively simple concepts may be applied directly to the definition of the mean value of position and of momentum in quantum mechanics. In general, we can make no definite predictions as to which position or which momentum will be measured; we can only give probabilities. If we repeat the measurement of position or of momentum many times and calculate the mean value, the latter may be defined exactly as for the dice. The theoretician can, as we saw in the dice game, predict this mean value for the experimentalist. This mean value is therefore called the *expectation value*; it is defined as follows: *Expectation value = Sum over the individual values measured, times the probability that that value would be found.*

Let us apply this definition to some examples.

a) Mean Value of the Position (one-dimensional example), Fig. 9.3

A single measurement yields the result that the particle is to be found in the interval $x \dots x + dx$. The corresponding probability is $|\psi(x)|^2 dx$. Since the position x is con-

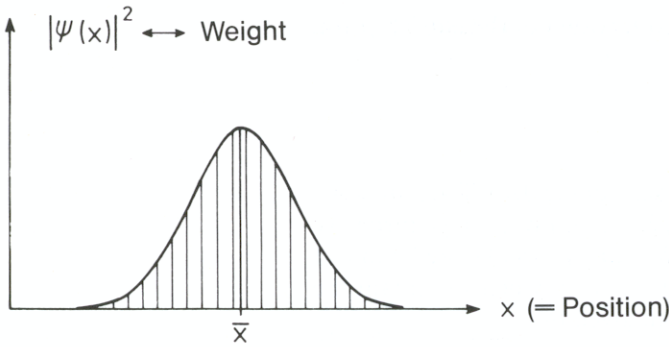


Fig. 9.3. Explanation of the mean value of the position. The location of a vertical line indicates the value of a measurement of the position coordinate x and the length of the line is proportional to the frequency with which that value is found (probability density). If we interpret the latter as a weight, the calculation of \bar{x} corresponds to the calculation of the centre of gravity \bar{x} of an object

tinuously variable, while the number of spots on the die was discrete, we use an integral instead of the sum (9.44). The mean value of the position is thus defined as

$$\bar{x} = \int_{-\infty}^{+\infty} x |\psi(x)|^2 dx. \quad (9.45)$$

In the calculation of (9.45) and in the following, the normalisation of the wavefunction was assumed, i.e.

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 1. \quad (9.46)$$

Correspondingly, we can take the n th power of x , x^n , and then generalise the definition (9.45) to obtain the mean value of the n th power:

$$\bar{x}^n = \int_{-\infty}^{+\infty} x^n |\psi(x)|^2 dx. \quad (9.47)$$

If we replace the function x^n quite generally by the potential energy function $V(x)$, we obtain the definition of the mean value of the potential energy,

$$\bar{V} = \int_{-\infty}^{+\infty} V(x) |\psi(x)|^2 dx. \quad (9.48)$$

b) *Mean Value of the Momentum* (one-dimensional example), Fig. 9.4.

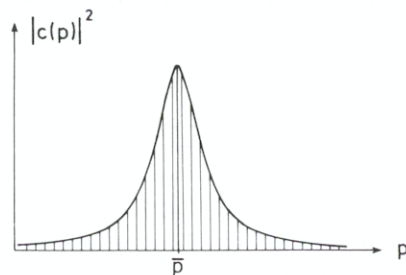


Fig. 9.4. Explanation of the mean value of the momentum. See caption of Fig. 9.3

In this case, we first take the wavefunction to be given by a superposition of plane waves:

$$\psi(x) = \int_{-\infty}^{+\infty} c(p) \frac{1}{\sqrt{h}} e^{ipx/h} dp. \quad (9.49)$$

If we now measure the momentum, the probability of finding its value in the interval $p \dots p + dp$ is given by $|c(p)|^2 dp$. In complete analogy to the mean value of the position, we find the definition of the mean value of the momentum to be

$$\bar{p} = \int_{-\infty}^{+\infty} p |c(p)|^2 dp, \quad (9.50)$$

or for the n th power

$$\overline{p^n} = \int_{-\infty}^{+\infty} p^n |c(p)|^2 dp. \quad (9.51)$$

As we shall see later, wavefunctions are normally expressed as functions of position, in the form $\psi(x)$. It is therefore difficult to calculate the expansion (9.49) in detail in order to determine the mean of the momentum, because the coefficients $c(p)$ would first have to be calculated. We shall now show that there is a very simple computational rule which allows us to calculate the mean value of the momentum without following the indirect route via (9.49).

We assert that the mean value of the momentum is given by the basic formula

$$\bar{p} = \int_{-\infty}^{+\infty} \psi^*(x) \left(\frac{\hbar}{i} \frac{d}{dx} \right) \psi(x) dx. \quad (9.52)$$

The notation $(\hbar/i)(d/dx)\psi(x)$ may seem unfamiliar to the reader; it is a common form in quantum mechanics. It means that we are to differentiate $\psi(x)$ by x , that is, we calculate

$$\frac{\hbar}{i} \frac{d\psi}{dx}. \quad (9.53)$$

This notation (9.52) is also referred to as applying the “momentum operator” $(\hbar/i)(d/dx)$ to the wavefunction $\psi(x)$. The proof that (9.52) is the same as (9.50) is relatively simple, but requires some basic mathematical knowledge. We begin by substituting (9.49) in (9.52). After differentiation with respect to x and exchanging the order of integration with respect to x and p , we obtain

$$\bar{p} = \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dp' p' c^*(p) c(p') \underbrace{\frac{1}{h} \int_{-\infty}^{+\infty} \exp(-ipx/h) \exp(ip'x/h) dx}_{\delta(p-p')}. \quad (9.54)$$

The underlined part, however, is merely the Dirac δ function, $\delta(p-p')$ (Appendix A). The definition of the δ function eliminates the integration over p' , and leads to $p' = p$, so that p' is replaced by p . We then obtain directly

$$\bar{p} = \int_{-\infty}^{+\infty} dp p |c(p)|^2. \quad (9.55)$$

If we go through the calculation again in detail, we recognise that we have replaced the factor p in (9.50) by the differential operator $(\hbar/i)d/dx$. In order to arrive at (9.51), we would have had to apply this operator n times to the wavefunction $\psi(x)$.

c) Average Values of Energy

Our results to this point enable us to calculate average energy values. The kinetic energy of a particle is $p^2/2m_0$. The probability of observing the momentum p in the interval $p \dots p + dp$ is given by $|c(p)|^2 dp$.

Thus the average kinetic energy is given by

$$\bar{E}_{\text{kin}} = \int_{-\infty}^{+\infty} |c(p)|^2 \frac{p^2}{2m_0} dp. \quad (9.56)$$

If we use the computational rule discussed above, we immediately obtain

$$\bar{E}_{\text{kin}} = \iiint_{-\infty}^{\infty} \psi^* \left(-\frac{\hbar^2}{2m_0} \nabla^2 \psi \right) dx dy dz, \quad (9.57)$$

where we have used the abbreviation

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (9.58)$$

and generalised the result to three dimensions. Equation (9.48) can be extended in the same way, which yields the expectation value for the potential energy:

$$\bar{E}_{\text{pot}} = \iiint_{-\infty}^{\infty} \psi^* V(\mathbf{r}) \psi dx dy dz. \quad (9.59)$$

Since the total energy is equal to the sum of the kinetic and the potential energy, the expectation value for the total energy is, finally,

$$\bar{E}_{\text{tot}} = \iiint_{-\infty}^{\infty} \psi^* \left[-\frac{\hbar^2}{2m_0} \nabla^2 + V(\mathbf{r}) \right] \psi dx dy dz. \quad (9.60)$$

9.3.4 Operators and Expectation Values

With the help of the above results, we can now discuss the conceptual framework and the computational rules of quantum theory. In classical physics, we have certain mechanical parameters, like the position $x(t)$, momentum $p(t)$, energy, etc. In quantum theory, these classical parameters are assigned certain expectation values [compare (9.45, 52, 60)]. These quantum mechanical expectation values can be obtained from classical physics by means of a very simple translation process according to the follow-

ing “recipe”: The classical parameters are assigned operators, which are nothing but multiplication or differentiation rules, which act on the wavefunctions following them. The position operator x is assigned to $x(t)$, which simply says that one multiplies the wavefunction $\psi(x)$ by x . It may seem strange at first that a time-independent operator x can be assigned to a time-dependent parameter $x(t)$. As we shall see below, however, the time-dependence is reintroduced in the process of finding the average, if the wavefunction itself is time-dependent. The momentum is assigned the operator $-i\hbar(d/dx)$ which differentiates the wavefunction. After carrying out the appropriate operator multiplication or differentiation, one multiplies the result by ψ^* and integrates over all space to obtain the quantum mechanical expectation value.

Using these rules, we can define still other operators which we have not yet considered. One important parameter is the angular momentum l , which has the components l_x , l_y and l_z . In classical physics, l_z , for example, is defined as $xp_y - yp_x$. In quantum theory we obtain the corresponding operator by replacing p_x and p_y by $(\hbar/i)\partial/\partial x$ and $(\hbar/i)\partial/\partial y$, respectively. The z component of the angular momentum operator is thus

$$\hat{l}_z = \frac{\hbar}{i} x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} . \quad (9.61)$$

In order to prevent confusion between the classical angular momentum and the angular momentum operator, we use here and in the following text the symbol $\hat{}$ (read “hat”) over the angular momentum operator.

The following table summarises what has been said above.

Classical variable	Operator	Quantum theoretical Expectation value
Position $x(t)$	x	$\bar{x} = \int \psi^*(x, t) x \psi(x, t) dx$
Momentum $p(t)$	$\frac{\hbar}{i} \frac{d}{dx}$ (Jordan's rule)	$\bar{p} = \int \psi^*(x, t) \frac{\hbar}{i} \frac{d}{dx} \psi(x, t) dx$
Energy $E = \mathcal{H}(x(t), p(t))$	$-\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + V(x)$	$\bar{E} = \int \psi^*(x, t) \left[-\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + V(x) \right] \psi(x, t) dx$
Angular momentum $l = [r \times p]$	$\left[r \times \frac{\hbar}{i} \nabla \right]$	$\bar{l} = \int \psi^* \left[r \times \frac{\hbar}{i} \nabla \right] \psi dx dy dz$

In the preceding discussion, we have given no consideration to the wavefunction ψ , which has, so to speak, fallen from heaven. We must still consider the principles by which we can determine the wavefunction, in case it is not determined by the Schrödinger equation.

9.3.5 Equations for Determining the Wavefunction

We have already presented equations which were explicitly or implicitly applicable to the determination of ψ . As the simplest example, let us take the plane wave $\psi \sim \exp(ikx)$. As we already know, this wave determines the propagation of a particle

with momentum $\hbar k$. Can we regard this plane wave as a solution of an equation which relates directly to momentum? This is in fact the case, because if we differentiate the plane wave with respect to x and multiply by \hbar/i , we obtain the relation

$$\frac{\hbar}{i} \frac{d}{dx} e^{ikx} = \hbar k e^{ikx} \equiv p e^{ikx}. \quad (9.62)$$

The plane wave thus satisfies an equation of the following form: The momentum operator $(\hbar/i)d/dx$ applied to the plane wave yields $p \equiv \hbar k$ times the plane wave.

As a second example, let us consider the time-independent Schrödinger equation. The application of the Hamiltonian operator to the wavefunction gives an energy \bar{E} times the wavefunction. A glance at the above table shows that the Hamiltonian is precisely that quantum mechanical operator associated with the classical energy expression $E_{\text{kin}} + E_{\text{pot}}$.

When we extract what is common to these examples, we see that these functions are so-called *eigenfunctions* which satisfy the following equation:

$$\text{Operator} \cdot \text{Eigenfunction} = \text{Eigenvalue} \cdot \text{Eigenfunction}.$$

If we denote the operator by Ω , the eigenfunction by ϕ and the eigenvalue by ω , this relationship is

$$\Omega \phi = \omega \phi. \quad (9.63)$$

The eigenvalue indicated here and in Sect. 9.3.6 following should not be confused with a frequency. It can have quite different physical meanings, e.g. momentum. In the example (9.62), we had

$$\Omega = \frac{\hbar}{i} \frac{d}{dx}, \quad \phi = e^{ikx}, \quad \omega = \hbar k.$$

We must now make use of a few basic facts of the mathematical treatment of such eigenvalue equations without being able to derive them here. As can be shown mathematically, eigenfunctions and eigenvalues are determined by (9.63), if appropriate boundary conditions for the wavefunction (eigenfunction) are given. One example for a set of boundary conditions is the particle in a box. If no explicit boundary conditions are given, we must require that the wavefunction be normalisable, which implies that the wavefunction must go to zero rapidly enough as infinity is approached.

When the operator Ω in (9.63) and the boundary conditions are given, there is a particular sequence of eigenvalues, e.g. discrete energy values as in the particle in the box, etc. The calculation of these eigenvalues and the associated eigenfunctions is thus the task of mathematicians or theoretical physicists. In order to make them agree with experimental observations, one makes use of the basic postulate of the quantum theory: *the eigenvalues are identical with the observed values*. This basic postulate has enormous significance, and we can accept it, because it has been repeatedly confirmed in innumerable experiments. If we measure the energy of the electron in a hydrogen atom, for example, this must agree with the quantum mechanically calculated eigenvalues E_n . If there is a discrepancy, one does not impute this to a failure of quantum

theory, but rather looks for interactions which have not yet been taken into account. In this way, an excellent agreement has so far been attained.

As we can see from our example (9.62), the Schrödinger equation is only one of many possible ways to determine the wavefunction. We are always concerned here with the physical problem. Thus whenever we use the Schrödinger equation, we would always assume that we have access to observations which measure the energy exactly. When we have then measured the energy, we have identified the associated eigenfunctions as solutions of the Schrödinger equation. We might also wish to measure the momentum. Since the wavefunction is known and, as one can easily demonstrate by Fourier analysis, this function contains several momentum eigenfunctions, we are no longer able to predict exactly the momentum of the particle, but can only calculate the expectation value. The simplest example for this is again the particle in the box.

9.3.6 Simultaneous Observability and Commutation Relations

As we saw above, there is a very close relationship between wavefunctions and eigenvalues on the one hand and individual observations on the other. If a wavefunction is an eigenfunction for a particular operator – that is, if it satisfies an equation like (9.63) – then we know that the eigenvalue will be found by measurement. If we repeat this measurement, we shall find exactly the same eigenvalue. It follows from this that:

If ψ_λ is an eigenfunction of a specific operator Ω , the eigenvalue ω_λ agrees with the expectation value $\bar{\Omega}$. In fact, if we know the operator Ω and the associated eigenvalue ω_λ , then

$$\Omega \psi_\lambda = \omega_\lambda \psi_\lambda; \quad \bar{\Omega} = \int \psi_\lambda^* \Omega \psi_\lambda dx = \int \psi_\lambda^* \omega_\lambda \psi_\lambda dx = \omega_\lambda \int \psi_\lambda^* \psi_\lambda dx = \omega_\lambda.$$

What happens, though, when we want to determine another parameter with the second measurement? One example for this was examined in more detail in Sect. 7.3, where we wanted to measure first the momentum and then the position of the particle. In that case, the measurement of position destroyed the results of the previous momentum determination. On the other hand, we can measure first the momentum and then the kinetic energy of a particle. In the first measurement, we obtain a certain value p . We have then “prepared” the particle into a particular state which is an eigenfunction of the momentum operator; the wavefunction after the measurement is thus (aside from a normalisation factor) given by $\exp(ipx/\hbar)$. If we now measure the kinetic energy, this measurement corresponds to the mathematical operation of applying the kinetic energy operator, $-(\hbar^2/2m_0)d^2/dx^2$. In the process, the “prepared” plane wave yields the eigenvalue $E = p^2/2m_0$, and the plane wave remains as wavefunction. In this case, the second measurement does *not* destroy the result of the first measurement. There exist, apparently, measurements which do not disturb each other, or, in other words, which can be simultaneously carried out with arbitrary accuracy.

We will now derive a necessary criterion for simultaneous measurability. For this purpose, we consider the operators $\Omega^{(1)}$ and $\Omega^{(2)}$, which could, for example, be operators for the momentum and the kinetic energy. We now require that the wavefunction ψ be simultaneously an eigenfunction of both characteristic equations

$$\Omega^{(1)} \psi = \omega^{(1)} \psi \tag{9.64}$$

and

$$\Omega^{(2)} \psi = \omega^{(2)} \psi. \tag{9.65}$$

If we apply operator $\Omega^{(2)}$ to the left side of the first equation and operator $\Omega^{(1)}$ to the second equation, then subtract one equation from the other, rearrange, and finally apply (9.64) and (9.65) again, we obtain

$$(\Omega^{(1)}\Omega^{(2)} - \Omega^{(2)}\Omega^{(1)})\psi = (\omega^{(1)}\omega^{(2)} - \omega^{(2)}\omega^{(1)})\psi = 0. \quad (9.66)$$

The simultaneous measurability of *all* wavefunctions which simultaneously fulfil (9.64) and (9.65), not merely special cases, should be guaranteed. Therefore the ψ in (9.66) is omitted in quantum theory, and one writes

$$\Omega^{(1)}\Omega^{(2)} - \Omega^{(2)}\Omega^{(1)} = 0. \quad (9.67)$$

This, however, should be understood to be an abbreviation. When one sees such an equation, one should always remember that any desired wavefunction ψ stands to the right of the operators, i.e., (9.66) applies. It can be mathematically shown that the converse of the above is also true: if two operators $\Omega^{(1)}$ and $\Omega^{(2)}$ fulfil the commutation relation (9.67), then eigenfunctions of $\Omega^{(1)}$ can always be determined to be eigenfunctions of $\Omega^{(2)}$ as well; they fulfil (9.64) and (9.65). If there is only a single eigenfunction belonging to the eigenvalue $\omega^{(1)}$ of $\Omega^{(1)}$, this is itself an eigenfunction of $\Omega^{(2)}$. However, if there are several eigenfunctions of $\Omega^{(1)}$ associated with $\omega^{(1)}$, then it will always be possible to find linear combinations of these which are also eigenfunctions of $\Omega^{(2)}$.

Let us consider a few examples. If we choose as $\Omega^{(1)}$ the momentum operator $(\hbar/i)d/dx$, and the kinetic energy operator $(-\hbar^2/2m_0)d^2/dx^2$ as $\Omega^{(2)}$, these operators commute. The result of differentiating a wavefunction twice and then once with respect to x is naturally the same as that of differentiating first once and then twice with respect to x :

$$\left(-\frac{\hbar^2}{2m_0}\right) \cdot \frac{\hbar}{i} \left(\frac{d}{dx} \cdot \frac{d^2}{dx^2} - \frac{d^2}{dx^2} \cdot \frac{d}{dx}\right) = 0. \quad (9.68)$$

It can be shown in the same way that the x components of the momentum and the y components of the position mutually commute.

Let us take as a second example the x component of the momentum and the coordinate x itself. Thus $\Omega^{(1)} = (\hbar/i)d/dx$ and $\Omega^{(2)} = x$:

$$(\Omega^{(1)}\Omega^{(2)} - \Omega^{(2)}\Omega^{(1)})\psi = \left(\frac{\hbar}{i} \frac{d}{dx} x - x \frac{\hbar}{i} \frac{d}{dx}\right)\psi. \quad (9.69)$$

We now evaluate this expression. First we remove the parentheses:

$$= \frac{\hbar}{i} \frac{d}{dx} x\psi - x \frac{\hbar}{i} \frac{d\psi}{dx}. \quad (9.70)$$

d/dx means, of course, that everything to the right of the operator is to be differentiated, and

$$\frac{d}{dx}(x\psi) = \frac{dx}{dx}\psi + x\frac{d\psi}{dx}. \quad (9.71)$$

If we substitute this in (9.70), we obtain

$$\frac{\hbar}{i}\psi. \quad (9.72)$$

If we again write out the right side of (9.69), we obtain the relation

$$\left(\frac{\hbar}{i}\frac{d}{dx}x - x\frac{\hbar}{i}\frac{d}{dx}\right)\psi = \frac{\hbar}{i}\psi. \quad (9.73)$$

Since this relationship holds for any function ψ , one can also write in abbreviated form

$$\frac{\hbar}{i}\frac{d}{dx}x - x\frac{\hbar}{i}\frac{d}{dx} = \frac{\hbar}{i}. \quad (9.74)$$

This is the famous Heisenberg commutation relation between the momentum operator and the position operator. It says that the momentum and the position operators do not commute, which means that the position and momentum cannot be simultaneously determined to any desired degree of precision (see Sect. 7.3).

The following formulation is often used to express the commutation relation between the two operators $\Omega^{(1)}$ and $\Omega^{(2)}$:

$$[\Omega^{(1)}, \Omega^{(2)}] \equiv \Omega^{(1)}\Omega^{(2)} - \Omega^{(2)}\Omega^{(1)}. \quad (9.75)$$

In this form, the Heisenberg commutation relation is

$$\left[\frac{\hbar}{i}\frac{d}{dx}, x\right] = \frac{\hbar}{i}. \quad (9.76)$$

We leave it to the reader to derive the following relations:

$$\left[\frac{\hbar}{i}\frac{d}{dx}, V\right] = \frac{\hbar}{i}\frac{dV}{dx}.$$

For the components of the angular momentum [compare the definition in (9.61)].

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z, \quad (9.77)$$

$$[\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x, \quad (9.78)$$

$$[\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y, \quad (9.79)$$

$$[\hat{l}^2, \hat{l}_j] = 0, \quad j = x, y, z. \quad (9.80)$$

These equations say that the components of the angular momentum are not simultaneously measurable, although one component and the square of the angular momentum can be simultaneously measured.

9.4 The Quantum Mechanical Oscillator

Aside from the particle in the box, the harmonic oscillator is one of the simplest examples of quantum theory. Although this example does not apply to the motion of an electron in an atom, because a different force law applies there, the harmonic oscillator has innumerable applications in all areas of quantum physics. We shall return to it repeatedly. In classical physics, the equation of motion of the harmonic oscillator is given by $m_0\ddot{x} = -kx$ (Fig. 9.5). The associated kinetic energy is $(m_0/2)\dot{x}^2$ and the potential energy $(k/2)x^2$. To convert this to quantum mechanics, we express the velocity \dot{x} in terms of the momentum: $m_0\dot{x} = p$. We also make use of the classical relation between oscillation frequency ω , mass and force constant, $\omega^2 = k/m_0$. In this way we obtain the following expression for the total energy (or mathematically expressed, for the Hamiltonian function):

$$\mathcal{H} = \frac{p^2}{2m_0} + \frac{m_0}{2} \omega^2 x^2. \quad (9.81)$$

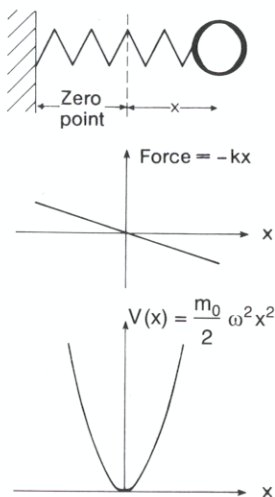


Fig. 9.5. The harmonic oscillator. *Above*, as an example, a point mass on a spring. *Middle*, force as a function of the displacement x . *Below*, potential energy as function of the displacement x

The corresponding Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + \frac{m_0}{2} \omega^2 x^2 \right) \psi(x) = E \psi(x). \quad (9.82)$$

As one can easily convince oneself, the energy E can only have positive values. We ensure this by multiplying both sides of (9.82) by $\psi^*(x)$ and integrating from $x = -\infty$ to $x = +\infty$. The integral on the right side of (9.82), $\int_{-\infty}^{+\infty} \psi^* \psi dx$, is positive, because

$\psi^* \psi = |\psi|^2 \geq 0$. The same applies to the term containing x^2 , $\int_{-\infty}^{+\infty} (m_0/2) \omega^2 x^2 |\psi|^2 dx$ on the left side of (9.82). The remaining term, $\int_{-\infty}^{+\infty} [-(\hbar^2/2m_0) \psi^* \cdot d^2\psi/dx^2] dx$, is rearranged by partial integration to yield

$$-\frac{\hbar^2}{2m_0} \psi^* \frac{d\psi}{dx} \Big|_{x=-\infty}^{x=+\infty} + \frac{\hbar^2}{2m_0} \int_{-\infty}^{+\infty} \frac{d\psi}{dx} \cdot \frac{d\psi^*}{dx} dx. \quad (9.82a)$$

If we substitute the limits of integration in the first term, it disappears, since we require that $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$. (Otherwise the normalisation integral $\int_{-\infty}^{+\infty} |\psi|^2 dx = 1$ would not exist!) The integral in (9.82a) is positive, and thus, so is the entire expression corresponding to the left side of (9.82). It now immediately follows that $E \geq 0$.

Since the Schrödinger equation includes several constants, we first carry out a transformation to a new, dimensionless coordinate ξ and a new energy, by setting

$$x = \sqrt{\frac{\hbar}{m_0 \omega}} \xi; \quad \varepsilon = \frac{E}{\hbar \omega}, \quad (9.83)$$

$$\psi(x) = \phi(\xi). \quad (9.84)$$

Then (9.82) becomes

$$\tilde{\mathcal{H}} \phi \equiv \frac{1}{2} \left(-\frac{d^2}{d\xi^2} + \xi^2 \right) \phi(\xi) = \varepsilon \phi(\xi). \quad (9.85)$$

If the differentiation operator $d/d\xi$ were an ordinary number, we could use the rule $-a^2 + b^2 = (-a+b)(a+b)$. Although this is naturally not possible with operators, we shall use it as an heuristic aid and write, so to speak, experimentally,

$$\underbrace{\frac{1}{\sqrt{2}} \left(-\frac{d}{d\xi} + \xi \right)}_{b^+} \underbrace{\frac{1}{\sqrt{2}} \left(\frac{d}{d\xi} + \xi \right)}_b \phi(\xi). \quad (9.86)$$

The order of the differentiation steps must be strictly observed here, that is, operators on the right must be applied before operators to the left of them. Let us now “multiply” out the parentheses, strictly observing the order of operations:

$$\frac{1}{2} \left(-\frac{d^2}{d\xi^2} + \xi^2 \right) \phi(\xi) + \frac{1}{2} \left(-\frac{d}{d\xi} \xi + \xi \frac{d}{d\xi} \right) \phi(\xi). \quad (9.87)$$

This is the left side of (9.85), with an extra term. Just as we did with the Heisenberg commutation relation (9.69), we can apply the differentiation in the extra term to the wavefunction, and we obtain $-\phi(\xi)/2$ for the second expression in (9.87). Equation

(9.86) thus differs from the middle expression in (9.85) only by the term $-\phi/2$. If we observe this and introduce, as shown in (9.86), the abbreviations b and b^+ , the original Schrödinger equation (9.82) can be given in the form

$$b^+ b \phi \equiv (\tilde{\mathcal{H}} - \frac{1}{2}) \phi = (\varepsilon - \frac{1}{2}) \phi. \quad (9.88)$$

In the following it is important to remember that b and b^+ are only certain abbreviations for operators, which are defined in (9.86). If we also substitute $\varepsilon - \frac{1}{2} = n$ and provide the wavefunction ϕ and this n with an index λ , the justification for which will be given below, we finally obtain the Schrödinger equation in the form

$$b^+ b \phi_\lambda = n_\lambda \phi_\lambda. \quad (9.89)$$

The operators b and b^+ satisfy the commutation relation

$$bb^+ - b^+b = 1. \quad (9.90)$$

We shall leave the proof of (9.90) to the reader as an exercise. One needs only to substitute the definition of b^+ and b and then proceed as above with the Heisenberg commutation rule.

Let us first consider (9.89) generally and multiply it from the left by the operator b , i.e., we apply the operator b to the left and right sides of (9.89). We then obtain

$$bb^+ b \phi_\lambda = n_\lambda b \phi_\lambda. \quad (9.91)$$

According to the commutation relation (9.90), we can substitute $1 + b^+b$ for bb^+ . When we do this with the first two factors on the left side of (9.91), we obtain

$$b^+ b(b \phi_\lambda) + b \phi_\lambda = n_\lambda b \phi_\lambda, \quad (9.92)$$

or, if we combine the terms containing $b \phi_\lambda$ on the right,

$$b^+ b(b \phi_\lambda) = (n_\lambda - 1)(b \phi_\lambda). \quad (9.93)$$

As we see, application of b to the wavefunction ϕ_λ produces a new wavefunction $\phi = (b \phi_\lambda)$ which satisfies (9.89), although its eigenvalue is 1 less: $n_\lambda \rightarrow n_\lambda - 1$. The operator b thus reduces the number n by 1. We refer to it as an *annihilation operator*. Since, as we observed earlier, the energy E must be positive, n must have a lower limit. There must therefore be a lowest number n_0 and a corresponding wavefunction ϕ_0 for (9.89). If we were to repeat this formalism on the lowest eigenstate with $\lambda = 0$, we would introduce a contradiction. We would have found a wavefunction with a still smaller eigenvalue, contrary to the assumption that ϕ_0 is already the lowest eigenstate. The contradiction is only resolved if $b \phi_0$ is identically equal to zero. Then (9.89) is fulfilled trivially for each value of n ; zero is, however, not a genuine eigenvalue. For the lowest state, we then have the condition

$$b \phi_0 = 0. \quad (9.94)$$

If we replace b with the operator which it symbolises (9.86), then (9.24) is equivalent to

$$\left(\frac{d}{d\xi} + \xi\right)\phi_0 = 0. \quad (9.95)$$

This first-order differential equation can also be written in the form

$$\frac{d\phi_0}{\phi_0} = -\xi d\xi, \quad (9.96)$$

from which we obtain on integration

$$\ln \phi_0 = -\frac{1}{2}\xi^2 + C', \quad (9.97)$$

or, taking the antilogarithm,

$$\phi_0 = C \exp\left(-\frac{1}{2}\xi^2\right). \quad (9.98)$$

The constant C must be determined by the normalisation condition.

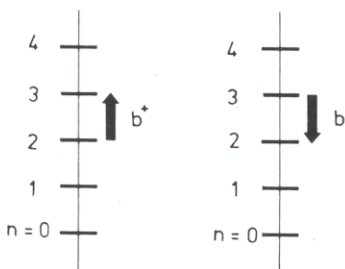


Fig. 9.6. Illustration of the effect of the creation and annihilation operators. *Left:* Application of b^+ means climbing up the “ladder” of states $n = 0, 1, \dots$ by one rung. *Right:* Application of b corresponds to climbing down by one rung

We will now investigate what happens if we apply not the annihilation operator b but rather the operator b^+ on both sides of (9.89). By analogy to the steps (9.91–93), we obtain using (9.90) the relation

$$b^+ b(b^+ \phi_\lambda) = (n_\lambda + 1)(b^+ \phi_\lambda), \quad (9.99)$$

i.e. by application of b^+ to ϕ_λ , we increase the eigenvalue by one unit. Therefore, b^+ is called a *creation operator* (Fig. 9.6). If we choose the ground state ϕ_0 for ϕ_λ , we obtain a proportionality

$$\phi_1 \propto b^+ \phi_0,$$

and a second application of b^+ gives

$$\phi_2 \propto b^+ \phi_1 \propto (b^+)^2 \phi_0, \quad \text{etc.}$$

Here we have used a proportionality sign and not an equals sign, since we do not yet know whether the functions $b^+ \phi_0$, $(b^+)^2 \phi_0$, etc. are normalised. In general, we obtain

$$\phi_\lambda = C_\lambda (b^+)^{\lambda} \phi_0, \quad (9.100)$$

where the constant factor C_λ serves as normalisation factor.

Since n always increases by an integer on application of b^+ , but the lowest eigenvalue is zero ($n_0 = 0$), we may identify the index λ with n . Including the normalisation factor (which we will not derive here), $C_n = 1/\sqrt{n!}$, we find the normalised wavefunctions:

$$\phi_n = \frac{1}{\sqrt{n!}} (b^+)^n \phi_0. \quad (9.101)$$

Relation (9.101) still looks terribly abstract. We shall therefore show by means of several examples how the explicit wavefunctions may be derived; for this purpose, we shall leave the normalisation factor out of consideration. For $n = 0$ we have already obtained $\phi_0 \propto \exp(-\xi^2/2)$. Using (9.88, 83), we find for the lowest energy value $E_0 = \hbar\omega/2$, the same zero-point energy which we have already discussed in Sect. 7.5. For $n = 1$ we obtain

$$\phi_1 \propto b^+ \phi_0,$$

or, using the explicit expressions for b^+ and ϕ_0 ,

$$\phi_1 \propto \left(-\frac{d}{d\xi} + \xi \right) \exp\left(-\frac{1}{2}\xi^2\right).$$

After carrying out the differentiation we have

$$\phi_1 \propto \xi \exp\left(-\frac{1}{2}\xi^2\right).$$

The corresponding energy is

$$E = (3/2)\hbar\omega.$$

For $n = 2$ we obtain

$$\phi_2 \propto b^+ \phi_1 \propto \left(-\frac{d}{d\xi} + \xi \right) \cdot \xi \exp\left(-\frac{1}{2}\xi^2\right),$$

or, after differentiating,

$$\phi_2 \propto (2\xi^2 - 1) \exp\left(-\frac{1}{2}\xi^2\right).$$

For the energy we find

$$E = (5/2)\hbar\omega.$$

If we continue this procedure, we obtain polynomials through multiplication by ξ or differentiation with respect to ξ . In general, for the n th wavefunction we obtain an expression of the type

$$\phi_n = e^{-1/2\xi^2} H_n(\xi), \tag{9.102}$$

where H_n is a polynomial which is known in the mathematical literature as a Hermite polynomial. The corresponding energy is given by

$$E_n = (n + \frac{1}{2}) h \omega, \quad n = 0, 1, 2 \dots \tag{9.103}$$

(Fig. 9.7). For completeness, we shall give the formula for finding the Hermite polynomials. It states

$$H_n(\xi) = \frac{(-1)^n}{\sqrt{2^n}} e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n} \frac{1}{\sqrt{n! \sqrt{\pi}}}. \tag{9.104}$$

If we return from the coordinate ξ to the original coordinate x , the correctly normalised eigenfunctions of the Schrödinger equation of the harmonic oscillator are given by

$$\psi_n(x) = \sqrt{\frac{4}{m_0 \omega h}} \exp(-\frac{1}{2} x^2 m_0 \omega / h) \cdot H_n(x \sqrt{m_0 \omega / h}). \tag{9.105}$$

In Fig. 9.8, we have plotted the potential $V(x)$. Furthermore, the energy levels $(n + 1/2) h \omega$ are given along the ordinate, as are, finally, the wavefunctions themselves. The first four wavefunctions in the energy scale are shown in more detail in Figs. 9.9a, b. Although we will for the most part use the configuration representation $\psi(x)$ for the wavefunctions in this book, the creation and annihilation operators b^+ and b are indispensable in many areas of modern quantum theory.

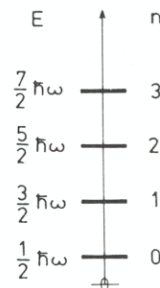


Fig. 9.7. The energy levels of the harmonic oscillator

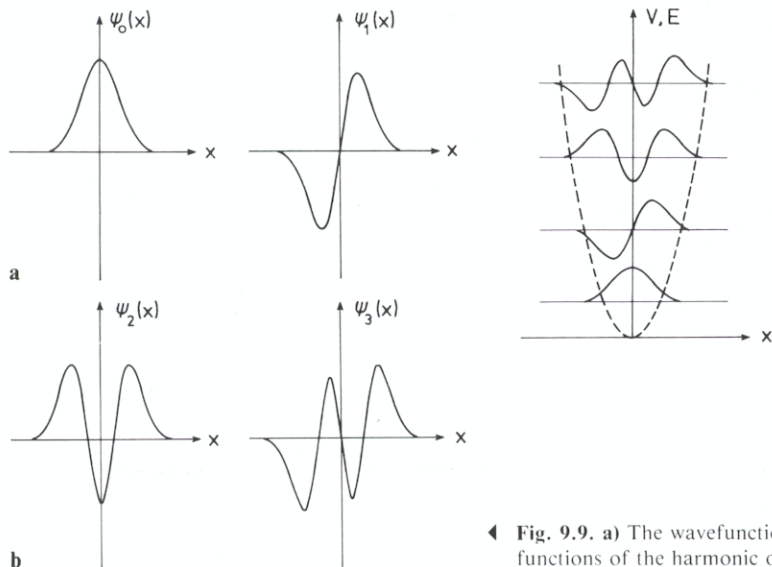


Fig. 9.8. A representation of the quantum mechanical harmonic oscillator which is often found in books. This figure contains three drawings in one: 1) The ordinate means total energy E . The horizontal lines (above the x axis) give the quantised energy levels. 2) The ordinate gives the potential $V(x)$. The dashed curve shows the shape of the potential curve as a function of position x . 3) Each of the horizontal lines serves as an x axis, on which the shape of the wavefunction of the corresponding energy is plotted

Fig. 9.9. a) The wavefunctions of the harmonic oscillator for $n = 0, 1$. b) The wavefunctions of the harmonic oscillator for $n = 2, 3$

Problems

9.1 By substituting the wave packet with $\omega = \hbar k^2/(2m_0)$ from Problem 7.1 into the Schrödinger equation, convince yourself that it is a solution for a particle which experiences no forces.

9.2 Let the wavefunctions ϕ_1 and ϕ_2 be solutions of the Schrödinger equation (9.35) with the eigenenergies E_1 and E_2 . Show that

$$\psi(r, t) = c_1 \exp(-iE_1 t/\hbar) \phi_1(r) + c_2 \exp(-iE_2 t/\hbar) \phi_2(r)$$

is a solution of the Schrödinger equation (9.32). What conditions must c_1 and c_2 satisfy, in order to normalise $\psi(r, t)$? Generalise this exercise to the wavepacket

$$\psi(r, t) = \sum_j c_j \exp(-iE_j t/\hbar) \phi_j(r).$$

Hint:

$$\int \phi_j^*(r) \phi_k(r) dV = \delta_{jk} \begin{cases} = 0 & \text{for } j \neq k \\ = 1 & \text{for } j = k. \end{cases}$$

9.3 The potential $V(r)$ is represented in one dimension by $-\beta\delta(x)$, where $\delta(x)$ is the Dirac δ function (see the Mathematical Appendix). Solve the Schrödinger equation for bound states, i.e. for $E < 0$.

Hint: Solve the Schrödinger equation for $x < 0$ and $x > 0$, in other words where $\delta(x) = 0$.

Where $x = 0$, the solutions found for ψ_- and ψ_+ must join in a continuous fashion.

Also, derive a second boundary condition (“jump condition”) for ψ'_- and ψ'_+ by integrating the Schrödinger equation over $-\varepsilon < x < \varepsilon$, $\varepsilon \rightarrow 0$. Write the wavefunction so that it can be normalised, and find the normalisation constants and the energy.

9.4 Find the bound states of a particle in a one-dimensional box, for which the potential is

$$\begin{aligned} V(x) &= 0 & \text{for } x < -L \\ V(x) &= -V_0 < 0 & \text{for } -L \leq x \leq L \\ V(x) &= 0 & \text{for } x > L. \end{aligned}$$

Hint: Solve the Schrödinger equation in the three subregions. Require $\psi(x) \rightarrow 0$ for $x \rightarrow \pm\infty$; $\psi(x)$ and $\psi'(x)$ are continuous at $x = \pm L$. Display the eigenvalue spectrum for $E < 0$, and discuss its dependence on L and V_0 .

9.5 Calculate the “scattering states”, in which $E \geq 0$, for a particle moving in the δ potential of Problem 9.3.

Hint: Use the trial solution $\psi(x) = \exp(ikx) + a \exp(-ikx)$ for $x \leq 0$ and $\psi = b \exp(ikx)$ for $x \geq 0$, and determine a and b . What is the physical interpretation of this

trial solution in the field of wave optics? It does not need to be normalised. How do a and b change when the sign of β is changed, i.e., when the potential is repulsive?

9.6 Let an otherwise free particle collide with an infinitely high potential barrier. What is its wavefunction (without normalisation)?

9.7 For the one-dimensional wave packet of Problem 7.1, calculate the expectation values of the position x , momentum p , kinetic energy, and x^2 . Why is the expectation value of x^2 more informative than that of x ?

9.8 Express the energy expectation value for the wave packet of a free particle in Problem 7.1 in terms of the energy eigenvalues of the kinetic energy operator.

9.9 Prove the commutation relations (9.77–80) for angular momentum.

Hint: Use the quantum mechanical definition of the angular momentum operator and the commutation relations between position and momentum in three dimensions.

9.10 Demonstrate the commutation relations between \hat{l}_x and x , and between \hat{l}_x and the central potential $V(r)$ which depends only on $r = |r|$.

9.11 The two functions ψ_1 and ψ_2 are to vanish at infinity.

Show that

$$\int_{-\infty}^{+\infty} \psi_1^* x \psi_2 dx = \left(\int_{-\infty}^{+\infty} \psi_2^* x \psi_1 dx \right)^*$$

$$\int_{-\infty}^{+\infty} \psi_1^* \frac{\hbar}{i} \frac{d}{dx} \psi_2 dx = \left(\int_{-\infty}^{+\infty} \psi_2^* \frac{\hbar}{i} \frac{d}{dx} \psi_1 dx \right)^*$$

$$\int_{-\infty}^{+\infty} \psi_1^* \mathcal{H} \psi_2 dx = \left(\int_{-\infty}^{+\infty} \psi_2^* \mathcal{H} \psi_1 dx \right)^* .$$

The properties of the operators x , $p = \frac{\hbar}{i} \frac{d}{dx}$, $\mathcal{H} = \frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + V(x)$, which are to be proved here, indicate that these operators are Hermitian.

Hint: Carry out partial integrations over d/dx and d^2/dx^2 .

9.12 Prove the Ehrenfest theorem

$$m_0 \frac{d}{dt} x = p, \quad \frac{d}{dt} p = - \left(\frac{dV}{dx} \right)$$

for the one-dimensional quantum mechanical motion of a particle.

Hint: Use the definition of the operators x , p and dV/dx , and the fact that ψ (and ψ^*) satisfy a Schrödinger equation with the potential $V(x)$. Make use also of the result of Problem 9.11.

What is the expression for this theorem in three dimensions?

9.13 Calculate the wavefunctions and energy values of a particle which is subjected to a force $F = -kx + k_0$, ($k = m_0\omega^2$).

Hint: Set up $V(x)$ and derive the new Schrödinger equation from the “old” one for the harmonic oscillator by means of a coordinate transformation.

9.14 Prove the commutation relation (9.90)

$$bb^+ - b^+b = 1$$

for the operators b and b^+ of the harmonic oscillator.

Hint: Use the definitions of b^+ and b (9.86) and the commutation relation between x and $\frac{\hbar}{i} \frac{d}{dx}$ (9.74).

9.15 Construct the wavepacket

$$\psi = \psi_0 \exp\left(-i \frac{\omega}{2} t\right) + \psi_1 \exp\left(-i \frac{3\omega}{2} t\right)$$

from the first two states of the harmonic oscillator and examine the change in $|\psi|^2$ with time by means of a graphical representation.

9.16 Let the Schrödinger equation of the harmonic oscillator be

$$b^+ b \phi_n = n \phi_n \quad (n = 0, 1, 2, \dots),$$

where $b^+ = (1/\sqrt{2}) \left(-\frac{d}{d\xi} + \xi\right)$, $b = (1/\sqrt{2}) \left(\frac{d}{d\xi} + \xi\right)$, $\phi = \phi(\xi)$. For b, b^+ , the commutation relation $[b, b^+] = 1$ holds.

Prove the following relations. The integrals extend from $-\infty$ to $+\infty$.

a) $\int [b^+ \phi(\xi)]^* \psi(\xi) d\xi = \int \phi^*(\xi) b \psi(\xi) d\xi$

$$\int [b \phi(\xi)]^* \psi(\xi) d\xi = \int \phi(\xi)^* b^+ \psi(\xi) d\xi$$

b) $\int (b^+ \phi_n)^* (b^+ \phi_n) d\xi = (n+1) \int \phi_n^* \phi_n d\xi$

c) If ϕ_n is normalised, then $\phi_{n+1} = 1/\sqrt{n+1} b^+ \phi_n$ is also normalised.

d) The normalised functions ϕ_n can be expressed as

$$\phi_n = 1/\sqrt{n!} (b^+)^n \phi_0, \quad b \phi_0 = 0.$$

e) $b^+ \phi_n = \sqrt{n+1} \phi_{n+1}$, $b \phi_n = \sqrt{n} \phi_{n-1}$.

f) $b(b^+)^n - (b^+)^n b = n(b^+)^{n-1}$, $b^+(b)^n - (b)^n b^+ = -n(b)^{n-1} = -\frac{\partial b^n}{\partial b}$.

Hints: a) Use the explicit expressions for b^+ and b in terms of ξ , $\frac{d}{d\xi}$ and partial integration.

b) Use a), the exchange relation and the Schrödinger equation.

c) Follows from a).

d) Mathematical induction method.

e) Follows from d) and the commutation relations.

f) Solve by the induction method (write $b(b^+)^n - (b^+)^n b$ as $b(b^+)^{n-1} - (b^+)^{n-1} b^+ b$).

9.17 Calculate the expectation value of the momentum, the kinetic energy and the potential energy for the n th excited state of the harmonic oscillator.

Hint: According to (9.83 and 84), change from x to ξ , transform ξ and $d/d\xi$ into b^+ and b , and use

$$\int \phi_n^*(\xi) \phi_m(\xi) d\xi = \delta_{mn} = \begin{cases} 0 & \text{for } m \neq n \\ 1 & \text{for } m = n, \end{cases}$$

$n, m = 0, 1, 2, \dots$

9.18 Prove for the wavefunctions of the harmonic oscillator, $\phi_n(\xi)$:

$$\int \phi_m^*(\xi) \phi_n(\xi) d\xi = \delta_{mn}.$$

Hint: Use the fact that

$$\phi_n = \frac{1}{\sqrt{n!}} (b^+)^n \phi_0,$$

$$b \phi_0 = 0,$$

and the result a) of Problem 9.16. Proceed by induction.

9.19 *The bra and ket notation*

The English physicist Dirac introduced a very concise notation, especially for expectation values and wavefunctions, which we shall demonstrate here for the case of the harmonic oscillator.

Instead of ϕ_n , one writes $|n\rangle$. The integral $\int \phi_n^*(\xi) \phi_n(\xi) d\xi$ is presented as $\langle n|n\rangle$, and the expectation value $\int \phi_n^*(\xi) b \phi_n(\xi) d\xi$ as $\langle n|b|n\rangle$. Since $\langle \rangle$ is a “bracket”, $\langle n|$ is called “bra”, and $|n\rangle$ is called “ket”. Using the results of Problems 9.16 and 9.18, show that

$$\text{a) } b^+ |n\rangle = \sqrt{n+1} |n+1\rangle$$

$$b |n\rangle = \sqrt{n} |n-1\rangle$$

$$\text{b) } \langle n | m \rangle = \delta_{n,m}$$

$$\text{c) } \langle n | b | n \rangle = 0$$

$$\langle n | b^+ | n \rangle = 0$$

$$\text{d) Calculate } \langle n | (b^+ + b)^2 | n \rangle \text{ and } \langle n | (b^+ - b)^2 | n \rangle.$$

What is the physical significance of these expectation values?

10. Quantum Mechanics of the Hydrogen Atom

10.1 Motion in a Central Field

In this chapter, we shall solve the Schrödinger equation of the hydrogen atom. For our calculations, we will not initially restrict ourselves to the Coulomb potential of the electron in the field of the nucleus of charge Z , $V(r) = -Ze^2/(4\pi\epsilon_0 r)$, but rather will use a general potential $V(r)$, which is symmetric with respect to a centre. As the reader may know from the study of classical mechanics, the angular momentum of a particle in a spherically symmetric potential field is conserved; this fact is expressed, for example, in Kepler's law of areas for the motion of the planets in the solar system. In other words, we know that in classical physics, the angular momentum of a motion in a central potential is a constant as a function of time. This tempts us to ask whether in quantum mechanics the angular momentum is simultaneously measurable with the energy. As a criterion for simultaneous measurability, we know that the angular momentum operators must commute with the Hamiltonian. As we have already noted, the components l_x , l_y , and l_z of the angular momentum l are not simultaneously measurable; on the other hand, l_z and l^2 , for example, *are* simultaneously measurable. A long but straightforward calculation reveals that these two operators also commute with the Hamiltonian for a central-potential problem. Since the details of this calculation do not provide any new physical insights, we shall not repeat it here.

In quantum mechanics as well as in classical mechanics, we may thus measure the total energy, the z component of the angular momentum, and the square of the angular momentum simultaneously to any desired accuracy. In the following, we shall therefore seek the simultaneous eigenfunctions of \hat{l}^2 , \hat{l}_z , and \mathcal{H} . We remind the reader that we denote the angular momentum *operators* by a $\hat{\ } (hat)$, in order to distinguish them from the classical quantities l . Since we are here dealing with a spherically symmetric problem it is reasonable not to use Cartesian coordinates, but to change to another coordinate system which better reflects the symmetry of the problem. This is naturally the spherical polar coordinate system. If we choose a particular point x, y, z in Cartesian coordinates, we shall describe its position by means of the following coordinates (Fig. 10.1):

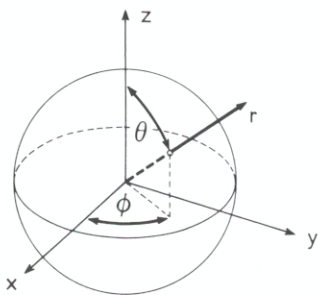


Fig. 10.1. Illustration of spherical polar coordinates

- 1) its distance from the origin, r ,
- 2) the angle θ between the z axis and the vector \mathbf{r} ,
- 3) the angle ϕ between the x axis and the projection of \mathbf{r} on the x - y plane.

Recalculating the Laplace operator $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ in terms of spherical polar coordinates is a lengthy mathematical procedure, which however contributes nothing to the understanding of quantum mechanics. We shall therefore simply write down the kinetic energy operator in polar coordinates; it is

$$-\frac{\hbar^2}{2m_0}\nabla^2 = -\frac{\hbar^2}{2m_0}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{2m_0r^2}\hat{l}^2, \quad (10.1)$$

with

$$\hat{l}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \quad (10.2)$$

We note that the operator \hat{l}^2 is nothing other than the square of the angular momentum operator, and contains only derivatives with respect to angles. Since the potential of our problem depends only on the radius coordinate r , it is reasonable to separate the radial and angular functions in a trial wavefunction as follows:

$$\psi(r, \theta, \phi) = R(r)F(\theta, \phi), \quad (10.3)$$

i.e., we write the wavefunction as the product of a function which depends only on r with a second function which depends only on the angles θ and ϕ . If we insert (10.3) into the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_0}\nabla^2 + V(r)\right]\psi = E\psi, \quad (10.4)$$

we obtain

$$\mathcal{H}\psi = F(\theta, \phi)\left[-\frac{\hbar^2}{2m_0}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + V(r)\right]R(r) + \frac{R(r)}{2m_0r^2}\hat{l}^2F(\theta, \phi) = ERF. \quad (10.5)$$

We now make use of our recognition of the fact that the wavefunction (10.3) can be chosen to be an eigenfunction of \hat{l}^2 and of \hat{l}_z as well as of \mathcal{H} . We write the corresponding eigenvalues in the (arbitrary) form $\hbar^2\omega$ and $\hbar m$. These new, additional equations are then¹

$$\hat{l}^2F(\theta, \phi) = \hbar^2\omega F(\theta, \phi) \quad \text{and} \quad (10.6)$$

$$\hat{l}_zF(\theta, \phi) = \hbar mF(\theta, \phi). \quad (10.7)$$

Note that m in (10.7) is the “magnetic quantum number” and must not be confused with the mass.

¹ In literature one often uses Y instead of F .

By assuming that (10.6) is already solved, we can express the term $R(r)/(2m_0r^2)\hat{l}^2F(\theta, \phi)$ in (10.5) in a simple form through the eigenvalue $\hbar^2\omega$. We then have eliminated all derivatives with respect to θ or ϕ on the left side of (10.5), and we may divide both sides of (10.5) by $F(\theta, \phi)$. We thus obtain an equation for the radial part $R(r)$ alone:

$$\left[-\frac{\hbar^2}{2m_0} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V(r) + \frac{\hbar^2\omega}{2m_0r^2} \right] R(r) = ER(r). \quad (10.8)$$

We have reduced the task of solving the three-dimensional Schrödinger equation (10.4), to that of solving the (as we shall see) simpler equations (10.6, 7 and 8).

Since the quantity $\hbar^2\omega$ in (10.8) is still an unknown parameter, which occurs as an eigenvalue in (10.6), our first problem is to determine this eigenvalue. We thus begin with the task of solving (10.6) and (10.7).

10.2 Angular Momentum Eigenfunctions

The first part of this section is somewhat more abstract. For the reader who would like to see the results first we give them here in compact form:

The eigenvalues of the square of the angular momentum \hat{l}^2 are

$$\hbar^2l(l+1), \quad (10.9)$$

where l is an integer,

$$l = 0, 1, 2, \dots$$

According to (10.7), the eigenvalues of the z component of the angular momentum are

$$\hbar m.$$

The integer m is called the magnetic quantum number, and takes on the values

$$-l \leq m \leq l.$$

The wavefunctions $F(\theta, \phi)$ naturally depend on the quantum numbers l and m and have the form

$$F_{l,m}(\theta, \phi) = e^{im\phi} P_l^m(\cos\theta). \quad (10.10)$$

These functions are drawn in Fig. 10.2. $P_l^{(0)}$ is called a Legendre polynomial, and P_l^m with $m \neq 0$ is called an associated Legendre function. The entire function (10.10) is called a spherical harmonic function.

We first address ourselves to the task of finding the eigenfunctions F as the solutions to (10.6, 7). We write (10.6) again, giving the components of \hat{l} explicitly:

$$(\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2)F_{l,m} = \hbar^2\omega_l F_{l,m}. \quad (10.11)$$

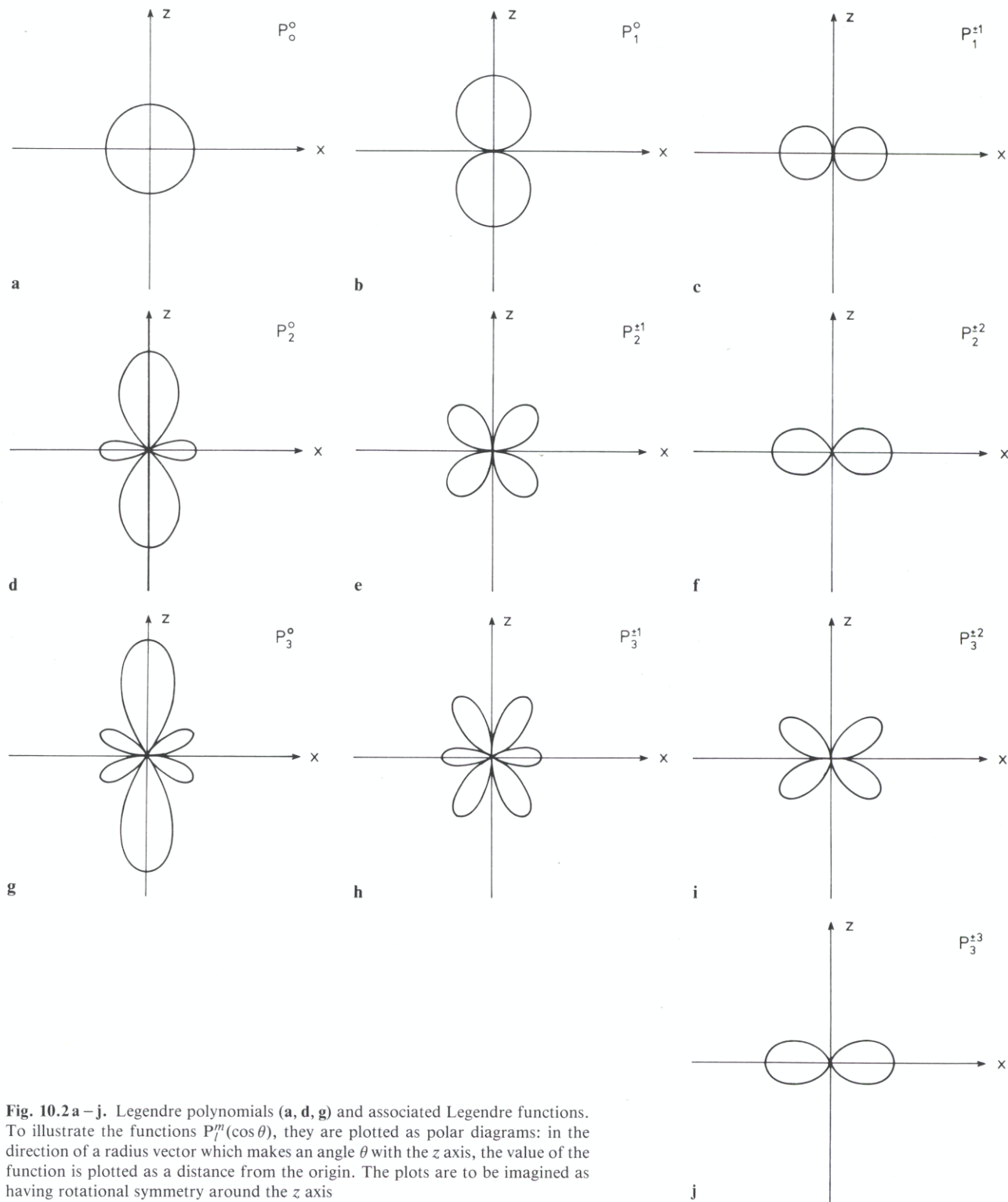


Fig. 10.2 a-j. Legendre polynomials (a, d, g) and associated Legendre functions. To illustrate the functions $P_l^m(\cos \theta)$, they are plotted as polar diagrams: in the direction of a radius vector which makes an angle θ with the z axis, the value of the function is plotted as a distance from the origin. The plots are to be imagined as having rotational symmetry around the z axis

Furthermore, we derive a new equation from (10.7) by applying the operator \hat{l}_z to both sides and then using (10.7) once more. This yields

$$\hat{l}_z^2 F_{l,m} = \hbar^2 m^2 F_{l,m}. \quad (10.12)$$

If we subtract (10.12) from (10.11), we obtain

$$(\hat{l}_x^2 + \hat{l}_y^2) F_{l,m} = \hbar^2 (\omega_l - m^2) F_{l,m}. \quad (10.13)$$

If we multiply both sides of this equation from the left by $F_{l,m}^*$ and integrate over the coordinates θ and ϕ , we can show, in a way similar to that used with the harmonic oscillator, that

$$\omega_l - m^2 \geq 0. \quad (10.13a)$$

In analogy to the harmonic oscillator, it seems reasonable to write $\hat{l}_x^2 + \hat{l}_y^2$ as the product of two factors $\hat{l}_+ = \hat{l}_x + i\hat{l}_y$ and $\hat{l}_- = \hat{l}_x - i\hat{l}_y$. We might suspect that these new linear combinations, like the operators b^+ and b with the harmonic oscillator, are a kind of creation and annihilation operators. As already stated in (9.77–80), the following commutation relations hold between the angular momentum operators:

$$\begin{aligned} [\hat{l}^2, \hat{l}_j] &= 0, \quad j = x, y, z, \\ [\hat{l}_x, \hat{l}_y] &= i\hbar \hat{l}_z, \\ [\hat{l}_y, \hat{l}_z] &= i\hbar \hat{l}_x, \\ [\hat{l}_z, \hat{l}_x] &= i\hbar \hat{l}_y. \end{aligned} \quad (10.14)$$

Further commutation relations can be derived from these by simple algebraic transformations:

$$[\hat{l}^2, \hat{l}_\pm] = 0, \quad (10.15)^2$$

$$[\hat{l}_z, \hat{l}_\pm] = \pm \hbar \hat{l}_\pm, \quad (10.16)$$

$$[\hat{l}_\pm, \hat{l}_z] = \mp \hbar \hat{l}_\pm. \quad (10.17)$$

In order to demonstrate that \hat{l}_+ is a kind of creation operator and \hat{l}_- a corresponding annihilation operator, we consider

$$\hat{l}_\pm F_{l,m}. \quad (10.18)$$

To find an equation for this quantity, we apply \hat{l}_\pm to the left of each side of (10.6) and then obtain, due to the commutativity with \hat{l}^2 , the equation

$$\hat{l}^2 (\hat{l}_\pm F_{l,m}) = \hbar^2 \omega_l (\hat{l}_\pm F_{l,m}). \quad (10.19)$$

This means that if $F_{l,m}$ is an eigenfunction of (10.6), so is the function (10.18). We now apply \hat{l}_\pm to the left of both sides of (10.7) and then, because of the commutation relation (10.17), we obtain after rearranging

$$\hat{l}_z (\hat{l}_\pm F_{l,m}) = \hbar (m \pm 1) (\hat{l}_\pm F_{l,m}). \quad (10.20)$$

² \hat{l}_\pm means that (10.15) holds for both \hat{l}_+ and \hat{l}_- . (10.16) and (10.17) are to be understood in the same way. In each case, the two upper signs belong together, as do the two lower signs.

\hat{l}_{\pm} thus increases (or decreases) the eigenvalue m by 1. Leaving off the normalisation factor, we can therefore write

$$\hat{l}_{\pm} F_{l,m} = F_{l,m\pm 1} \cdot (\text{Numerical normalisation factor}). \quad (10.21)$$

Equation (10.13 a), which requires that m^2 cannot be larger than ω_b , applies here. Therefore the series of new eigenfunctions $\hat{l}_{\pm} F_{l,m}$ must terminate at a maximum $m = m_{\max}$ and at a negative, minimum $m = m_{\min}$. Thus, just as in the case of the harmonic oscillator, we must require that

$$\hat{l}_{+} F_{l,m_{\max}} = 0 \quad (10.22)$$

and

$$\hat{l}_{-} F_{l,m_{\min}} = 0. \quad (10.23)$$

If we apply \hat{l}_{-} to the left of (10.22), and make use of the relations

$$\hat{l}_{\mp} \hat{l}_{\pm} = \hat{l}_x^2 + \hat{l}_y^2 \mp \hat{l}_z \hbar = \hat{l}^2 - \hat{l}_z (\hat{l}_z \pm \hbar) \quad (10.24)$$

and the fact that $F_{l,m}$ is an eigenfunction of \hat{l}^2 and \hat{l}_z , we obtain the basic equation

$$\hat{l}_{-} \hat{l}_{+} F_{l,m_{\max}} = \hbar^2 (\omega_l - m_{\max}^2 - m_{\max}) F_{l,m_{\max}} = 0. \quad (10.25)$$

In analogous fashion, by applying \hat{l}_{+} to (10.23), we obtain

$$\hat{l}_{+} \hat{l}_{-} F_{l,m_{\min}} = \hbar^2 (\omega_l - m_{\min}^2 + m_{\min}) F_{l,m_{\min}} = 0. \quad (10.26)$$

Since the eigenfunctions $F_{l,m}$ are not zero, the factors by which they are multiplied must vanish. It must therefore hold that

$$m_{\max}(m_{\max} + 1) = m_{\min}(m_{\min} - 1) = \omega_l. \quad (10.27)$$

This can be rearranged to

$$(m_{\max} + m_{\min})(m_{\max} - m_{\min} + 1) = 0. \quad (10.28)$$

Since $m_{\max} \geq m_{\min}$, it follows that the second factor in (10.28) must be different from zero, and therefore that the first factor is equal to zero. From this,

$$m_{\max} = -m_{\min}. \quad (10.29)$$

As we have seen, each application of \hat{l}_{+} to $F_{l,m}$ increases the eigenvalue m by 1. Therefore the difference $m_{\max} - m_{\min}$ must be an integer. It follows from (10.29) that

$$m_{\max} = \frac{\text{integer}}{2} \geq 0. \quad (10.30)$$

So far we have only made use of the fact that $F_{l,m}$ satisfies the Eqs. (10.6) and (10.7), and that the commutation relations (10.14) apply. As we shall see later, we must require for the *orbital* motion of the electron that all values of m , and thus in particular m_{\max} , must be integers. Interestingly, the electron and also a few other elementary particles have their own angular momentum, which is independent of the orbital angular momentum, for which $m_{\max} = \frac{1}{2}$. This independent angular momentum is called “spin”. We shall return to it in Sect. 14.2.1.

If we set $m_{\max} = l$, there are $2l + 1$ integers m between $+l$ and $-l$ which satisfy the condition

$$-l \leq m \leq l. \quad (10.31)$$

From (10.27) we know that the parameter ω_l , which appears in (10.6), is

$$\omega_l = l(l+1). \quad (10.32)$$

The eigenvalue of the operator “angular momentum squared” is thus

$$m_{\max}(m_{\max} + 1)\hbar^2 = l(l+1)\hbar^2. \quad (10.33)$$

With these results, we can give the original equations (10.6) and (10.7) with their exact eigenvalues

$$\hat{l}^2 F_{l,m} = \hbar^2 l(l+1) F_{l,m}, \quad (10.34)$$

$$\hat{l}_z F_{l,m} = \hbar m F_{l,m}. \quad (10.35)$$

The application of \hat{l}_+ to $F_{l,m}$ leads to a new function $F_{l,m+1}$ for which the normalisation factor N remains undetermined:

$$F_{l,m+1} = N \hat{l}_+ F_{l,m}. \quad (10.36)$$

It can be shown that

$$N = \frac{1}{\hbar} \frac{1}{\sqrt{(l-m)(l+m+1)}}. \quad (10.37)$$

We again proceed in analogy to the harmonic oscillator. There we constructed the eigenfunctions in space, in that we applied the operators b and b^+ successively to the ground state. Here we do exactly the same. First, one can express the angular momentum operators, which were given in Cartesian coordinates according to (9.61), in polar coordinates. As can be shown mathematically, the result is

$$\hat{l}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}, \quad (10.38)$$

$$\hat{l}_x = -\frac{\hbar}{i} \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right), \quad (10.39)$$

$$\hat{l}_y = \frac{\hbar}{i} \left(\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right). \quad (10.40)$$

Using (10.35) and (10.38), we represent $F_{l,m}$ as the following product:

$$F_{l,m} = e^{im\phi} f_{l,m}(\theta), \quad (10.41)$$

where we write the second factor on the right in the form

$$P_l^m(\cos \theta) \quad (10.42)$$

for later use. If we increase ϕ by 2π , we must naturally obtain a single-valued function $F_{l,m}$. This can only be guaranteed if m is an integer. Therefore the odd multiples of $1/2$ which would satisfy (10.30) are excluded.

We now calculate $F_{l,m}$ for $m = -l$ from the condition (10.23). If we substitute (10.39) and (10.40) into this equation, we obtain in simple fashion

$$(\hat{l}_x - i\hat{l}_y)F_{l,-l} = -\hbar e^{-i\phi} e^{-il\phi} \left[\frac{\partial}{\partial \theta} - l \cot \theta \right] f_{l,-l}(\theta) = 0. \quad (10.43)$$

The exponential functions can be removed from the second equation to give

$$\frac{\partial f_{l,-l}(\theta)}{\partial \theta} = l \cot \theta f_{l,-l}(\theta). \quad (10.44)$$

The solution of this differential equation is

$$f_{l,-l}(\theta) = C(\sin \theta)^l, \quad (10.45)$$

as the reader can be convinced by substitution. Here C must be determined by the normalisation. The condition

$$\int_0^{2\pi} \int_0^\pi |F|^2 \sin \theta d\theta d\phi = 1 \quad (10.46)$$

yields the coefficient C after carrying out the integration:

$$C = \frac{1}{\sqrt{4\pi}} \frac{\sqrt{(2l+1)!}}{l! 2^l}.$$

If we now apply \hat{l}_+ to $F_{l,m}$ consecutively in the form

$$\hat{l}_+ F_{l,m} = \hbar e^{i\phi} \left[\frac{\partial}{\partial \theta} - m \cot \theta \right] F_{l,m}, \quad (10.47)$$

we can construct all the angular momentum eigenfunctions.

In the following, we give the expressions obtained thus for $l = 0, 1$, and 2 . The functions $F_{l,m}$ are normalised according to (10.46). They are given both as functions of the angular coordinates θ and ϕ and as functions of the Cartesian coordinates x, y, z (with $r = \sqrt{x^2 + y^2 + z^2}$); they are denoted in the standard notation by $Y_{l,m}(\theta, \phi)$.

$$l = 0$$

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \quad (10.48)$$

$$\begin{aligned}
 l = 1 \\
 Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \cos \theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \\
 Y_{1,\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} = \mp \sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r}
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} Y_{1,0} \\ Y_{1,\pm 1} \end{aligned}} \right\} \quad (10.49)$$

$$\begin{aligned}
 l = 2 \\
 Y_{2,0} &= \sqrt{\frac{5}{4\pi}} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) = \frac{1}{2} \sqrt{\frac{5}{4\pi}} \frac{2z^2 - x^2 - y^2}{r^2} \\
 Y_{2,\pm 1} &= \mp \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{\pm i\phi} = \mp \frac{1}{2} \sqrt{\frac{15}{2\pi}} \frac{(x \pm iy)z}{r^2} \\
 Y_{2,\pm 2} &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{\pm 2i\phi} = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \left(\frac{x \pm iy}{r} \right)^2.
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} Y_{2,0} \\ Y_{2,\pm 1} \\ Y_{2,\pm 2} \end{aligned}} \right\} \quad (10.50)$$

10.3 The Radial Wavefunctions in a Central Field *

Before we turn to the problem of hydrogen, let us consider the general case of an electron in a centrally symmetrical potential field $V(r)$, of which we assume only that it vanishes at infinity. The starting point is then (10.8), which we repeat here:

$$\left[-\frac{\hbar^2}{2m_0} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2m_0 r^2} + V(r) \right] R(r) = ER(r). \quad (10.51)$$

Let us rewrite the underlined differential expression:

$$\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \quad (10.52)$$

and multiply the equation by $-2m_0/\hbar^2$ to obtain

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left[A - \tilde{V}(r) - \frac{l(l+1)}{r^2} \right] R = 0, \quad (10.53)$$

where we have used the abbreviations

$$A = \frac{2m_0}{\hbar^2} E = \begin{cases} -\kappa^2 & \text{for } E < 0 \\ k^2 & \text{for } E > 0, \end{cases}$$

$$\tilde{V} = \frac{2m_0}{\hbar^2} V(r). \quad (10.54)$$

We shall now see what happens to the solution $R(r)$ if we allow r to become very large. We begin with the function

$$R = \frac{u(r)}{r}. \quad (10.55)$$

If we substitute this in (10.53), we obtain

$$\frac{d^2}{dr^2} u(r) + \left[A - \tilde{V}(r) - \frac{l(l+1)}{r^2} \right] u(r) = 0. \quad (10.56)$$

Since both \tilde{V} and $1/r^2$ go to zero at infinity, we neglect these two parameters. The remaining equation has two types of solution:

$$1) E > 0, \quad \text{i.e.} \quad A > 0.$$

In this case the general solution of (10.56) is

$$u = c_1 e^{ikr} + c_2 e^{-ikr} \quad (10.57)$$

and thus the original solution $R(r)$, according to (10.55), is

$$R = \frac{1}{r} (c_1 e^{ikr} + c_2 e^{-ikr}). \quad (10.58)$$

To illustrate the meaning of this solution, let us imagine it to be multiplied by the time-dependence factor $\exp(-i\omega t)$ which would occur in the solution of the time-dependent Schrödinger equation. We see then that $r^{-1} \exp(ikr) \exp(-i\omega t)$ represents a spherical wave propagating outwards, while $r^{-1} \exp(-ikr) \exp(-i\omega t)$ is a spherical wave coming inwards. These spherical waves which come in from infinity and travel outwards again correspond to the hyperbolic orbits in the classical Kepler problem.

Now let us investigate the case

$$2) E < 0, \quad \text{i.e.} \quad A < 0.$$

Then the solution of (10.56) is

$$u = c_1 e^{\kappa r} + c_2 e^{-\kappa r}. \quad (10.59)$$

Since the solution naturally must not become infinite at large distances, which the exponential function $\exp(\kappa r)$ would do, we must require that the coefficient $c_1 = 0$. We then obtain according to (10.55) a solution of the type

$$R = \frac{c}{r} e^{-\kappa r}. \quad (10.60)$$

Since the absolute square of R represents the probability of finding the particle, and this quantity decreases exponentially for increasing r , we see that in (10.60), the electron is localised within a certain area in space. This is the quantum mechanical analogy to the closed elliptical orbits of classical physics (see Sect. 8.9).

10.4 The Radial Wavefunctions of Hydrogen

We will now attack the problem of solving (10.51) for the case of a Coulomb potential

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}. \quad (10.61)$$

For this purpose it is convenient to use dimensionless quantities. We thus introduce a new distance variable

$$\varrho = 2\kappa r \quad (10.62)$$

with κ defined by (10.54). Corresponding to this, we introduce a new function $\tilde{R}(\varrho)$, which is related to $R(r)$ by $R(r) = \tilde{R}(2\kappa r) \equiv \tilde{R}(\varrho)$. We then divide (10.53) by $(4\kappa^2)$ and obtain:

$$\tilde{R}'' + \frac{2}{\varrho}\tilde{R}' + \left(-\frac{1}{4} + \frac{B}{\kappa\varrho} - \frac{l(l+1)}{\varrho^2}\right)\tilde{R} = 0 \quad (10.63)$$

in which we have used the abbreviation

$$B = \frac{m_0 Ze^2}{\hbar^2 4\pi\epsilon_0}. \quad (10.64)$$

The primes on \tilde{R} denote derivatives with respect to ϱ .

Having seen before that the wavefunction decays exponentially at large distances, it would appear reasonable for us to use an exponential function as trial solution. It will later prove useful to adopt the form

$$\tilde{R} = e^{-\varrho/2} v(\varrho). \quad (10.65)$$

If we insert this trial solution in (10.63) and carry out the differentiation of the exponential function and of the function $v(\varrho)$, we obtain

$$v'' + \left(\frac{2}{\varrho} - 1\right)v' + \left[\left(\frac{B}{\kappa} - 1\right)\frac{1}{\varrho} - \frac{l(l+1)}{\varrho^2}\right]v = 0. \quad (10.66)$$

It is shown in the study of differential equations that (10.66) is satisfied by a trial solution in the form of a power series in ϱ , which we will express in the convenient form

$$v = \varrho^\mu \sum_{\nu=0}^{\infty} a_\nu \varrho^\nu \equiv \sum_{\nu=0}^{\infty} a_\nu \varrho^{(\nu+\mu)}, \quad (10.67)$$

in which it is assumed that $a_0 \neq 0$.

In this expression, the exponent μ and the coefficients a_ν are still to be determined. We insert the trial solution (10.67) in (10.66), re-order according to powers of ϱ , and

require that the coefficient of each power of ϱ should be independently equal to zero. The lowest power which occurs is $\varrho^{\mu-2}$. The corresponding coefficient is

$$a_0\mu(\mu-1) + a_02\mu - a_0l(l+1) = 0. \quad (10.68)$$

Since we have assumed that a_0 is nonvanishing, the common factor of a_0 must be zero, i.e.

$$\mu(\mu+1) = l(l+1). \quad (10.69)$$

Of the two possible solutions $\mu = l$ and $\mu = -l-1$, only the first is usable for us, since the other solution leads to a function v which diverges at the origin (10.67), causing the trial solution for \tilde{R} also to diverge (10.65); however, we require the solutions of the Schrödinger equation to be well-behaved in the entire range.

We now investigate the coefficients of the higher powers of ϱ ($v \neq 0$). For ϱ^{v+l-2} we find

$$a_v(v+l)(v+l-1) + a_v2(v+l) - a_vl(l+1) - a_{v-1}(v+l-1) + a_{v-1}(n-1) = 0, \quad (10.70)$$

where the abbreviation

$$n = B/\kappa \quad (10.71)$$

has been employed. Relation (10.70) connects the coefficient a_v with the preceding coefficient a_{v-1} . We thus obtain from (10.70), after an elementary rearrangement, the recursion formula

$$a_v = \frac{v+l-n}{v(v+2l+1)} a_{v-1}. \quad (10.72)$$

This recursion relation permits two quite different types of solutions, depending on whether the chain of the a 's is terminated or not. If it is not, the sum in (10.67) contains infinitely many terms, and it may be shown mathematically that then $v(\varrho)$ is practically equal to an exponential function which diverges at infinity. We must therefore restrict ourselves to the case when the chain of the a 's *does* terminate; this is in fact possible if n is an integer. We then obtain a cutoff for $v = v_0$, where

$$v_0 = n - l. \quad (10.73)$$

Since we must have $v_0 \geq 1$, we obtain from this a condition for l :

$$l \leq n - 1. \quad (10.74)$$

In the following, we shall refer to n as the *principal quantum number* and to l as the *angular momentum quantum number*. According to (10.74), the angular momentum quantum number cannot be larger than $n-1$.

We now calculate the energy value, which, as we will see immediately, is already determined in principle by our assumptions. For this purpose, we express E in terms of κ (10.54); κ is, however, already determined by (10.71).

In (10.71), as we have just seen, n is an integer, $n = 1, 2, \dots$. Furthermore, B is defined in (10.64). We thus obtain for E :

$$E = -\frac{m_0 Z^2 e^4}{2 \hbar^2 (4 \pi \epsilon_0)^2} \cdot \frac{1}{n^2}. \quad (10.75)$$

If we think back through the whole derivation, we see that the energy values E came about through the requirement that the series (10.72) be terminated, or, in order to find the actual solution, that the wavefunction should vanish at infinity. n is allowed to take on integral values 1, 2, 3, ... in (10.75), so that we obtain the energy level diagram of Fig. 8.4. The same energy values have already been derived in Chap. 8, starting with the Bohr postulates.

For $E > 0$, i.e. for non-bound states, the energies form a continuous distribution of values. We will not give the corresponding wavefunction here.

Since the series (10.67) has a cutoff, $v(\varrho)$ is a polynomial. If we recall the trial solution for $\tilde{R}(\varrho)$ and the abbreviation for ϱ , (10.62),

$$\tilde{R} = e^{-\varrho/2} v(\varrho), \quad (10.76)$$

we finally arrive at an expression for the original R of the form

$$R_{n,l}(r) = N_{n,l} \exp(-\kappa_n r) r^l L_{n+1}^{2l+1}(2\kappa_n r). \quad (10.77)$$

The various quantities have the following meanings:

$N_{n,l}$ is the normalisation factor, which is determined by the condition

$$\int_0^\infty R_{n,l}^2(r) r^2 dr = 1. \quad (10.78)$$

(The factor r^2 in the integrand results from the use of spherical polar coordinates.)

κ_n has the dimensions of an inverse radius and is given explicitly by (10.71, 64)

$$\kappa_n = \frac{1}{n} \cdot \frac{m_0 Z e^2}{\hbar^2 4 \pi \epsilon_0}. \quad (10.79)$$

L_{n+1}^{2l+1} is the mathematical symbol for the polynomial which occurs in (10.77), whose coefficients are determined by the recursion formula (10.72). It may be shown that L_{n+1}^{2l+1} can be obtained from the so-called Laguerre Polynomials L_{n+l} by $(2l+1)$ -fold differentiation:

$$L_{n+1}^{2l+1} = d^{2l+1} L_{n+l} / d\varrho^{2l+1}. \quad (10.80)$$

The Laguerre Polynomials, in turn, are obtained from the relation

$$L_{n+l}(\varrho) = e^\varrho d^{n+l} [\exp(-\varrho) \varrho^{n+l}] / d\varrho^{n+l}. \quad (10.81)$$

A series of examples of (10.77) is given in Fig. 10.3 for various values of the quantum numbers. In Fig. 10.3a, the radial wavefunction is plotted as a function of the dimensionless radius variable ϱ (10.62). The parentheses (1, 0), (2, 0) etc. contain the

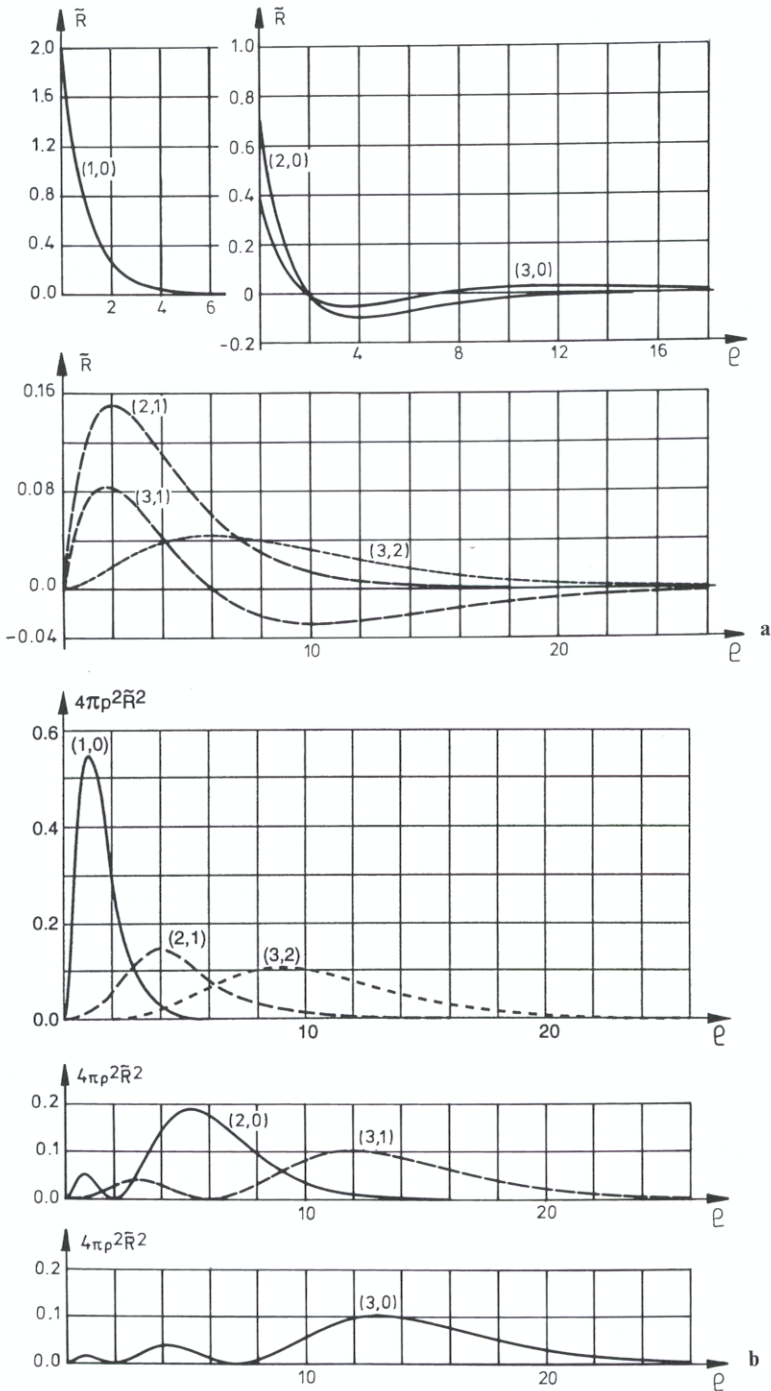


Fig. 10.3. **a)** The radial wavefunctions $\tilde{R}(\rho) = R(r)$ of the hydrogen atom (10.77) are plotted vs the dimensionless coordinate ρ . The indices on the curves, (1, 0), (2, 0) etc. correspond to (n, l) where n is the principal quantum number and l the angular momentum quantum number. **b)** The corresponding probability densities in the radial coordinate, i.e. $4\pi\rho^2\tilde{R}^2(\rho)$ are plotted against the dimensionless coordinate ρ

values of n and l (n, l). In Fig. 10.3 b, $4\pi\rho^2\tilde{R}^2(\rho)$ is plotted for various values of n and l . $\tilde{R}^2(\rho)d\rho$ gives the probability of finding the particle in a particular direction in space in the interval $\rho \dots \rho + d\rho$. If, on the other hand, we wish to know the probability of finding the particle at the distance ρ in the interval $\rho \dots \rho + d\rho$ *independently* of direction, we must integrate over a spherical shell. Since the volume of a spherical shell is just $4\pi\rho^2d\rho$, we are led to the above quantity, $4\pi\rho^2\tilde{R}^2(\rho)$. The maxima of these curves is displaced to regions of greater distance with increasing quantum number n , so that here we see an indication, at least, of the classical orbits.

Let us summarise our results. The wavefunction of the hydrogen atom may be written in the form

$$\psi_{n,l,m}(r, \theta, \phi) = e^{im\phi} P_l^m(\cos \theta) R_{n,l}(r). \quad (10.82)$$

Here n is the principal quantum number, l the angular momentum quantum number, and m the *magnetic* quantum number or *directional* quantum number. These quantum numbers can assume the following values:

$$\begin{aligned} n &= 1, 2, \dots, \\ 0 &\leq l \leq n - 1, \\ -l &\leq m \leq +l. \end{aligned} \quad (10.83)$$

Some examples for the density distribution of the electron (= probability density distribution $|\psi_{n,l,m}(r, \theta, \phi)|^2$) are represented in Fig. 10.4.

The density of points shown here was calculated by computer. It represents the probability density of the electron. Since the hydrogen functions are partially complex, combination of functions which belong to $+m$ and $-m$ yields real functions. These linear combinations are also solutions of the Schrödinger equation of the hydrogen problem. They still have the quantum numbers n and l , but they are no longer eigenfunctions for the z component of the angular momentum, so that this quantum number is lost. Figures 10.4a, b and e represent solutions with $l = 0$, which yield spherically symmetrical distributions. The sections c, d, f and g represent $l = 1$. Here one notices the dumbbell shaped distribution along one axis. There is a further linear combination possible in each case, but not shown here, in which the long axis of the dumbbell would lie along the third coordinate. Sections h and i represent $l = 2$, with $m = 0$ in h, and i represents a linear combination of $m = \pm 1$. Figure 10.4 does not show the wavefunctions with $l = 2, m = \pm 2$.

The energy corresponding to (10.82) is given by (10.75). It clearly depends only on the principal quantum number n . Since each energy level E_n (with the exception of $n = 1$) contains *several* different wavefunctions, these levels are called degenerate. This degeneracy is typical of the hydrogen atom problem with the Coulomb potential.

The degeneracy with respect to l is lifted, i.e. the energy levels become dependent upon l , if the potential no longer has the form $-\text{const}/r$, but is still spherically symmetric (Sect. 11.2). We will be led to consider effective departures from the Coulomb potential for all atoms with more than one electron (see below). The l degeneracy is also lifted even for hydrogen if we treat the problem relativistically, which is necessary for the exact treatment of the spectra (Sect. 12.11). The m degeneracy can only be lifted by superimposing a *non-spherically* symmetric potential on the central potential of the atom, i.e. an electric or a magnetic field (Chaps. 13 and 14).

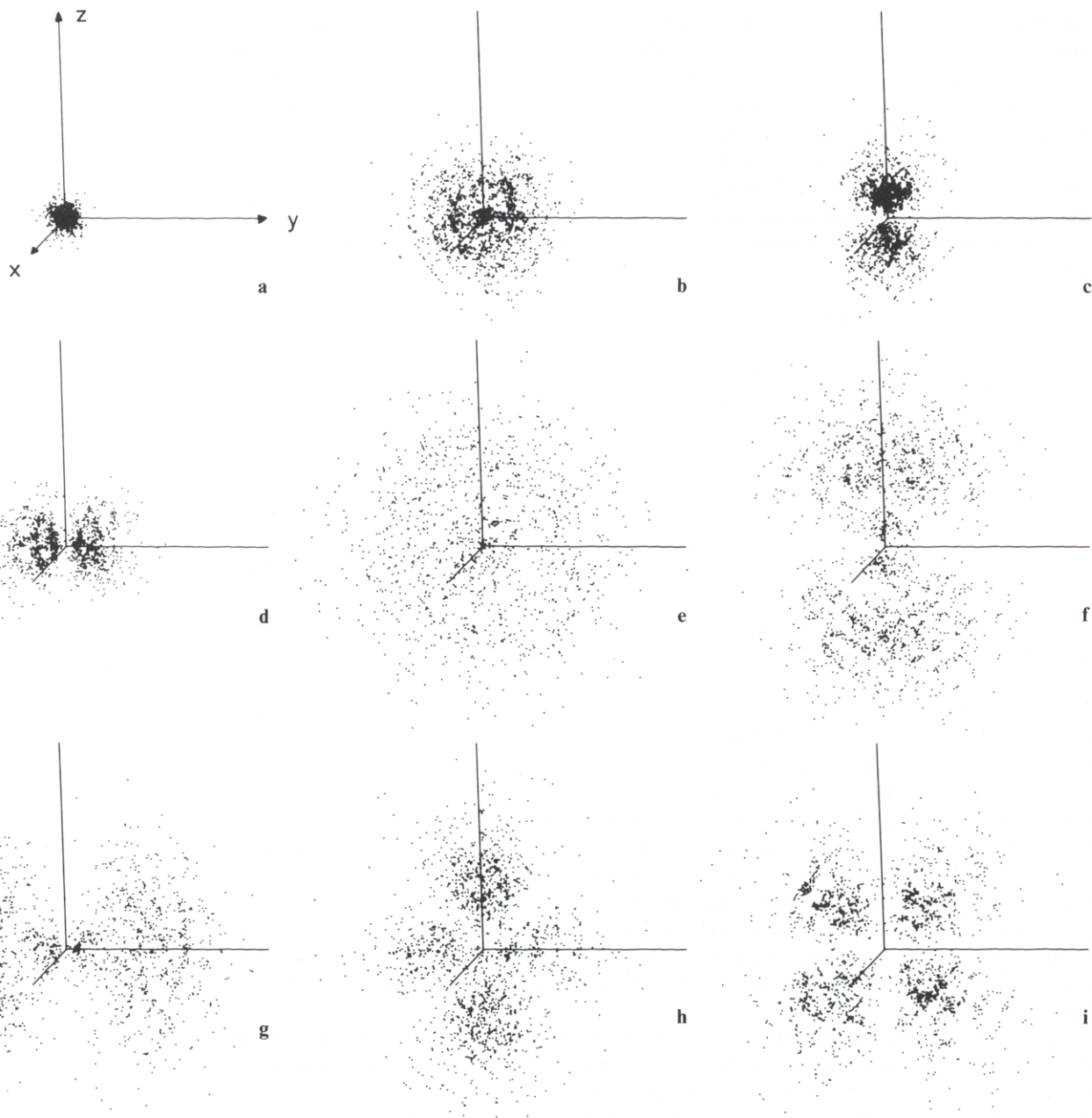


Fig. 10.4a–i. The density distribution (= localisation probability density $|\psi|^2$) of the electron in the H atom represented by the density of dots (according to *H. Ohno*). The wavefunctions represented are:

a) (10.82), $n = 1, l = 0, m = 0$

b) (10.82), $n = 2, l = 0, m = 0$

c) (10.82), $n = 2, l = 1, m = 0$

d) linear combination $(\psi_{2,1,1} + \psi_{2,1,-1}) \frac{i}{\sqrt{2}}$

e) (10.82), $n = 3, l = 0, m = 0$

f) (10.82), $n = 3, l = 1, m = 0$

g) linear combination $(\psi_{3,1,1} + \psi_{3,1,-1}) \frac{i}{\sqrt{2}}$

h) (10.82), $n = 3, l = 2, m = 0$

i) linear combination $(\psi_{3,2,1} + \psi_{3,2,-1}) \frac{i}{\sqrt{2}}$

The linear combinations given are also solutions of the Schrödinger equation of the hydrogen problem with the energies E_n , but they are not eigenfunctions of L_z

Problems

10.1 Calculate the expectation values of the kinetic and potential energies

- a) for the ground state of the hydrogen atom, $n = 1, l = m = 0$,
 b) for the wavefunctions $n = 2, l = 0, m = 0$ and $n = 2, l = 1, m = \pm 1, 0$.

Hint: Use spherical polar coordinates, so that for the volume element dV , $dV = \sin\theta d\theta d\phi r^2 dr$.

10.2 As will be discussed in Sect. 15.2.3, in quantum mechanics dipole matrix elements between two states with the wavefunctions ψ_1 and ψ_2 are defined by

$$\mathbf{D} = \int \psi_1^* e r \psi_2 dx dy dz.$$

Why is \mathbf{D} a vector? Calculate the components of \mathbf{D} when

- a) $\psi_1 = \psi_2 = \psi_{1,0,0}$,
 b) $\psi_1 = \psi_{1,0,0}$; $\psi_2 = \psi_{2,0,0}$
 or $\psi_2 = \psi_{2,1,0}$
 or $\psi_2 = \psi_{2,1,\pm 1}$.

Here $\psi_{n,l,m}$ is the wavefunction of the hydrogen atom with the quantum numbers n, l and m .

10.3 Calculate κ (10.79) and E_n (10.75) numerically for the first three values of n for the hydrogen atom.

10.4 Using the ground state of hydrogen as an example, we discuss here the variation principle of quantum mechanics. This says, in general, that the wavefunction ψ of the ground state of a Schrödinger equation $\mathcal{H}\psi = E\psi$ can be found (aside from solving the equation directly) by minimising the expectation value of the energy by a suitable choice of ψ : $\bar{E} = \int \psi^* \mathcal{H} \psi dx dy dz = \min$. ψ must simultaneously satisfy the additional condition that $\int \psi^* \psi dx dy dz = 1$.

This principle can also be used to estimate wavefunctions, and especially energies.

Problem: a) Take the trial solution $\psi = N \exp(-r^2/r_0^2)$. Calculate the normalisation factor N . Then calculate \bar{E} as a function of r_0 , and minimise \bar{E} by a suitable choice of r_0 . Then compare \bar{E}_{\min} with the exact value of the energy.

b) Repeat the procedure for $\psi = N \exp(-r/r_0)$.

10.5 Solve the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m_0} \frac{d^2 \psi(x)}{dx^2} + \left(-\frac{c_1}{x} + \frac{c_2}{x^2} \right) \psi(x) = E \psi$$

for $x \geq 0$, $c_1 > 0$, $c_2 > 0$, $E < 0$.

Hint: First examine the limiting case $x \rightarrow \infty$ and determine the asymptotic form of $\psi(x)$. Then try the solution

$$\psi(x) = x^\sigma e^{-x\sqrt{\varepsilon}} g(x),$$

where $\sigma = \frac{1}{2} + \sqrt{\frac{1}{4} + \tilde{c}_2}$ with $\tilde{c}_2 = 2m_0 c_2 / \hbar^2$ and $\varepsilon = -2m_0 E / \hbar^2$.

Calculate $g(x)$ with a power series which, however, must be terminated. Why?

11. Lifting of the Orbital Degeneracy in the Spectra of Alkali Atoms

11.1 Shell Structure

After the spectra of atoms with only one electron, the next simplest spectra are those of alkali atoms.

The alkali atoms have a weakly bound outer electron, the so-called valence electron, and all other ($Z - 1$) electrons are in closed shells. What the atomic-physical meaning of a closed shell is, we will discover later. At present we shall only say that even when several electrons are bound to a nucleus, their individual electron states can be characterised by the three quantum numbers n , l and m , but the corresponding energies are strongly modified, with respect to the one-electron problem, by the interactions of the electrons with each other. The Pauli principle (Sect. 17.2) says that a state characterised by specific values of n , l and m can be occupied by at most two electrons. In the ground state of an atom, the states with the lowest energies are naturally the occupied ones. A particular state of occupation of the energy levels or terms of an atom by electrons is called the *electron configuration* of the atom in that state – in this case, the ground state. A closed shell or noble gas configuration occurs whenever the next electron to be added would occupy the s state of the next higher principal quantum number n . It is not necessary that all the states belonging to lower principal quantum numbers be filled; more about this will be said in Chap. 20. The electrons in the closed shells are closer, as a rule, to the nucleus than the valence electron, and are more strongly bound. The total angular momentum of a closed shell vanishes. The closed shell is spherically symmetrical and is especially stable.

How is this known? Firstly, from chemistry: all alkali metal atoms have a valence of one. Each alkali metal is preceded in the periodic system by a noble gas, each of which has one electron fewer and has a particularly stable electron configuration – a closed shell. These gases are chemically inactive. Compared to those of their neighbours in the periodic table, their ionisation potentials are large. The neighbours with one more nuclear charge unit, the alkali metals, have very low ionisation potentials. For example, the ionisation energy of the noble gas helium is 24.46 eV. The next element in the periodic table, the alkali metal lithium, has an ionisation energy of only 5.40 eV. The ionisation energies of the heavier alkali metal atoms are even lower, as can be seen from Table 11.1. The table also shows that the ionisation energy for the removal of the second electron from an alkali metal atom is very large, because the electron configuration of the singly charged positive ion is a closed shell. In Fig. 11.1, the simplified term diagrams of the alkali metals are compared to that of the H atom.

The comparison shows that in the alkali atoms, the l degeneracy is lifted. States with the same principal quantum number n and different orbital angular momentum quantum numbers l have different energies. Relative to the terms of the hydrogen atom, those of the alkalis lie lower – this means a larger (negative) binding energy – and this shift increases, the smaller l is. For larger principal quantum numbers, i.e.

Table 11.1. Work of ionisation for the elements with $Z = 1$ to $Z = 20$. Values are given for the neutral atom, and for singly, doubly and triply charged ions. The ionisation energy is always especially large for a noble gas configuration (closed shell). It is especially low if there is only one electron more than a noble gas configuration which is indicated by bold-face numbers

Element	Work of ionisation [eV] for the transition from the –			
	neutral atom to singly charged	singly to doubly charged	doubly to triply charged	triply to quadruply charged
${}^1_1\text{H}$	13.59	–	–	–
${}^2_2\text{He}$	24.5	54.1	–	–
${}^3_3\text{Li}$	5.4	75	122	–
${}^4_4\text{Be}$	9.3	18.2	154	217
${}^5_5\text{B}$	8.3	25.1	38	259
${}^6_6\text{C}$	11.3	24.5	48	64.5
${}^7_7\text{N}$	14.6	29.6	47	77.4
${}^8_8\text{O}$	13.6	35.2	55	77.4
${}^9_9\text{F}$	17.4	34.9	62.7	87.3
${}^{10}_{10}\text{Ne}$	21.6	41.0	63.9	96.4
${}^{11}_{11}\text{Na}$	5.14	47.3	71.7	98.9
${}^{12}_{12}\text{Mg}$	7.64	15.0	80.2	109.3
${}^{13}_{13}\text{Al}$	5.97	18.8	28.5	120
${}^{14}_{14}\text{Si}$	8.15	16.4	33.5	44.9
${}^{15}_{15}\text{P}$	10.9	19.7	30.2	51.4
${}^{16}_{16}\text{S}$	10.4	23.4	35.1	47.1
${}^{17}_{17}\text{Cl}$	12.9	23.7	39.9	53.5
${}^{18}_{18}\text{Ar}$	15.8	27.5	40.7	ca. 61
${}^{19}_{19}\text{K}$	4.3	31.7	45.5	60.6
${}^{20}_{20}\text{Ca}$	6.1	11.9	51	67

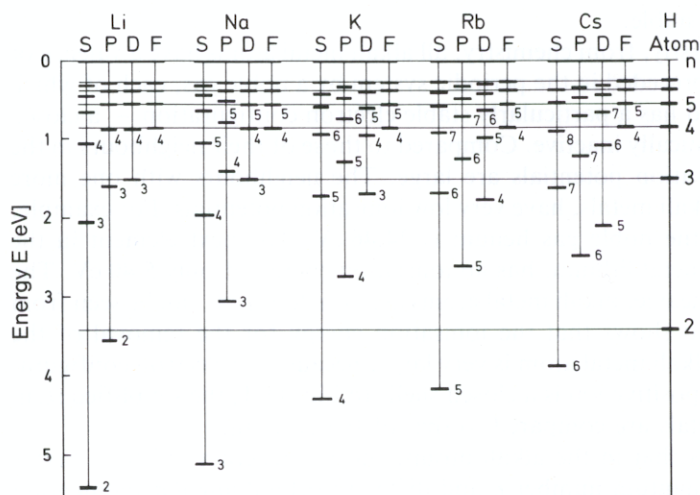


Fig. 11.1. Simplified term diagrams for the alkali metal atoms, showing the empirical positions of the most important energy terms. The principal quantum number n is indicated by numerals, the secondary quantum number l by the letters S , P , D , and F . For comparison, the levels of the H atom are given on the right

greater orbital radii, the terms are only slightly different from those of hydrogen. Here also, however, electrons with small l are more strongly bound and their terms lie lower in the term diagram. This effect becomes stronger with increasing Z . We would like to understand this effect, at least qualitatively.

11.2 Screening

In order to understand the term diagrams of the alkali atoms, we will use the following model (Fig. 11.2):

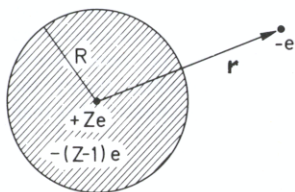


Fig. 11.2. Model of an alkali atom. The valence electron is screened from the nuclear charge $+eZ$ by the $(Z-1)$ inner electrons

A “valence electron” is located at a relatively large distance r from the nucleus. It moves in the electrostatic field of the nuclear charge $+eZ$, which is for the most part screened by the $(Z-1)$ inner electrons. We describe the screening effect of the inner electrons together with the nuclear potential by means of an effective potential $V_{\text{eff}}(r)$ for the valence electron. In this way we reduce the original many-body problem to a single-particle system, and we can treat the energy levels of an alkali atom as terms of a single-electron atom.

The shape of the effective potential $V_{\text{eff}}(r)$ is shown schematically in Fig. 11.3. If the valence electron moves at a great distance from the nucleus, its potential energy is $-e^2/(4\pi\epsilon_0 r)$. The nuclear charge which attracts the valence electron is in this case

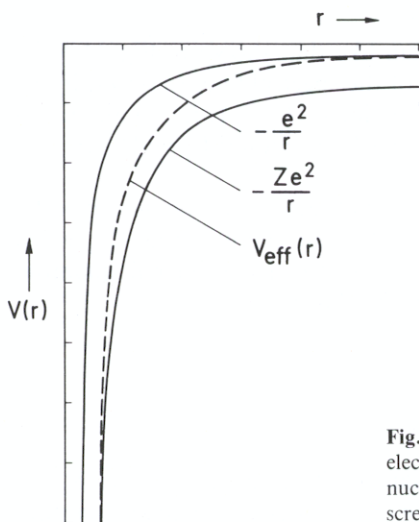


Fig. 11.3. Effective potential $V_{\text{eff}}(r)$ for an alkali atom. At small electron-nuclear distances, V_{eff} has the shape of the unscreened nuclear Coulomb potential; at large distances, the nuclear charge is screened to one unit of charge

compensated down to one unit of charge by the inner electrons. However, the nearer the valence electron approaches the nucleus, the more it experiences the unscreened nuclear potential. The potential energy approaches $V = -Ze^2/(4\pi\epsilon_0 r)$. The effective potential $V_{\text{eff}}(r)$ is no longer proportional to r^{-1} . This proportionality was, as we recall (Chap. 10), responsible for the l degeneracy.

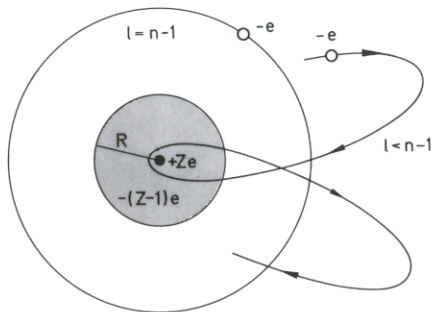


Fig. 11.4. Variation in screening for electrons with different radial probability densities. In the Sommerfeld model it is intuitively clear that electrons with “diving orbits” approach the nucleus closely and are affected at least partially by the unscreened nuclear potential. It has to be remembered, however, that in the modern quantum theory, the electrons are described as charge clouds rather than as orbiting particles

In the Sommerfeld picture, the so-called diving orbits demonstrate especially clearly that electrons with differing orbital angular momenta, i.e. differing orbital shapes, experience different degrees of screening. This is illustrated in Fig. 11.4. Quantum mechanically, this picture remains valid to a large extent. In Chap. 10 it was shown that the probability density of the electrons in the neighbourhood of the nucleus decreases in the order $l = 0, 1, 2, \dots$. The s electrons are thus most strongly affected by the unscreened field of the nucleus. For a given principal quantum number n , the energy terms of the s electrons are therefore shifted the most strongly to negative values relative to the H atom (Fig. 11.1).

11.3 The Term Diagram

For the alkali atoms, we thus obtain a term diagram like that shown in Fig. 11.5 for lithium. This term diagram permits a classification of the spectral lines to series, if one employs the additional selection rule for optical transitions $\Delta l = \pm 1$, i.e. in an optical transition, the quantum number l must change by 1. Such selection rules will be treated in detail in Chap. 16.

The series in the emission spectra of the neutral alkali atoms can be described by series formulae similar to the Balmer series formula. For the energy terms $E_{n,l}$ which are determined by the quantum numbers n and l , an effective principal quantum number n_{eff} may be defined, so that, e.g. for sodium we have

$$E_{n,l} = -R_{\text{Na}}hc \frac{1}{n_{\text{eff}}^2} = -R_{\text{Na}}hc \left\{ \frac{1}{[n - \Delta(n,l)]^2} \right\}.$$

Here the multiplication by the factor hc is necessary if the Rydberg number R_{Na} is measured in cm^{-1} , as is customary. Here $n_{\text{eff}} = n - \Delta(n,l)$ is a principal quantum

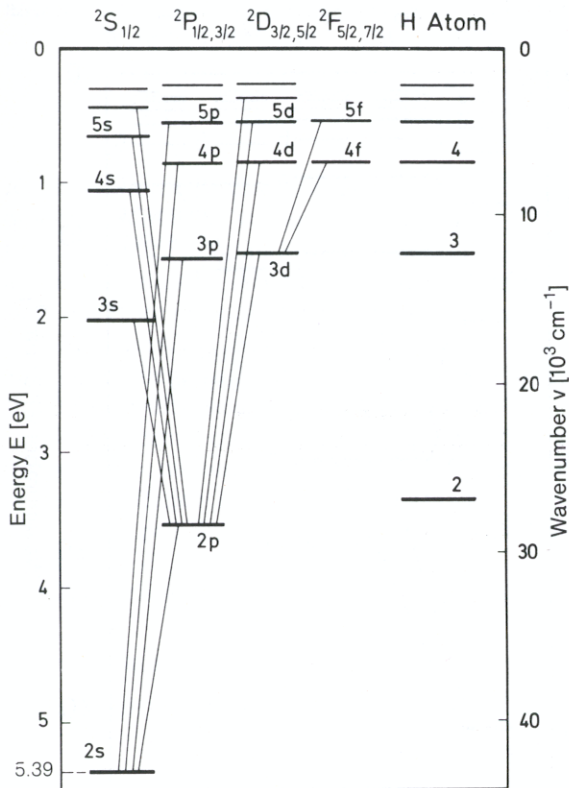


Fig. 11.5. Term diagram of the lithium atom with the most important transitions. This is called a Grotrian diagram. The term symbols given above the figure will be explained in detail in Chaps. 12 and 17. At the right, for comparison, the term scheme of hydrogen is shown

number, in general not an integer, and $\Delta(n, l) = n - n_{\text{eff}}$ is the so-called quantum defect associated with the quantum numbers n and l . The empirically determined numerical values for the quantum defects (see Table 11.2) are largest for s electrons, decrease with increasing orbital angular momentum quantum l , and are largely independent of the principal quantum number n . They increase down the column of alkali atoms from lithium to cesium, or with increasing nuclear charge number Z . These quantum defects are empirical expressions of the different degrees of screening of the s , p , d , etc. electrons by the electrons of the inner shells.

For the sodium atom, the decomposition of the total spectrum into series is represented in Fig. 11.6. Figure 11.7 shows the transitions in the form of a Grotrian

Table 11.2. Quantum defects $\Delta(n, l)$ for the spectra of the Na atom [from F. Richtmyer, E. Kennard, J. Cooper: *Introduction to Modern Physics*, 6th ed. (McGraw-Hill, New York 1969)]. These are empirical values

	Term	$n = 3$	4	5	6	7	8
$l = 0$	s	1.373	1.357	1.352	1.349	1.348	1.351
1	p	0.883	0.867	0.862	0.859	0.858	0.857
2	d	0.010	0.011	0.013	0.011	0.009	0.013
3	f	—	0.000	−0.001	−0.008	−0.012	−0.015

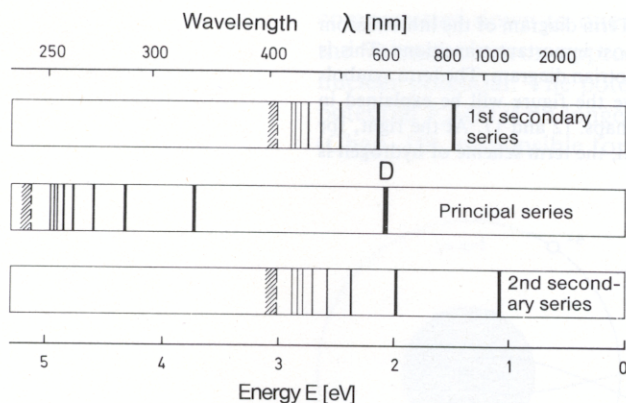


Fig. 11.6. The three shortest-wave spectral series of the sodium atom. The series limits are indicated by shading. The emission spectrum is a composite of these series. In absorption spectra, normally only the principal series is observed, because in the ground state of the Na atom the highest occupied term is the $3s$ term. The yellow colour of sodium lamps is due to the longest-wave resonance line of the main series, the transition $3s \leftrightarrow 3p$. This is the sodium D line, a terminology which has been retained for historical reasons

Fig. 11.7. Term scheme (Grotrian diagram) of the sodium atom. Some of the shortest-wave transitions from the principal series, the two secondary series and the Bergmann series have been included. The numbers in the diagram indicate the wavelength of the transition in Ångstrom units. The term symbols indicated on the upper edge of the figure also represent the quantum numbers for the multiplicity and the total angular momentum. These are explained in Chaps. 12 and 17

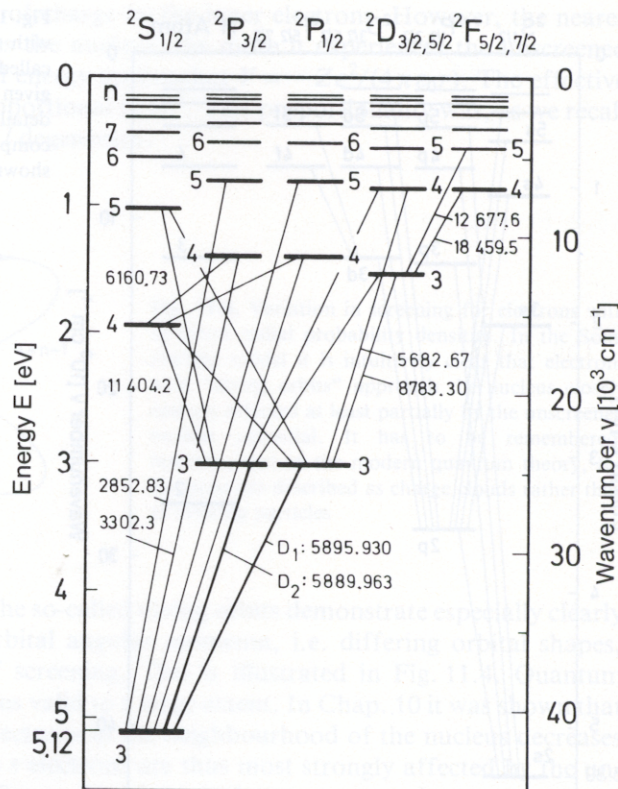


diagram. The most important series are the *principal* series, with transitions from p to s electron terms:

$$\bar{\nu}_p = R_{\text{Na}} \left[\frac{1}{[n_0 - \Delta(n_0, 0)]^2} - \frac{1}{[n - \Delta(n, 1)]^2} \right], \quad n \geq n_0, n_0 = 3,$$

the *sharp* or second secondary series with transitions from s to p electron terms:

$$\bar{\nu}_s = R_{\text{Na}} \left[\frac{1}{[n_0 - \Delta(n_0, 1)]^2} - \frac{1}{[n - \Delta(n, 0)]^2} \right], \quad n \geq n_0 + 1,$$

the *diffuse* or first secondary series with transitions from d to p electron terms:

$$\bar{\nu}_d = R_{\text{Na}} \left[\frac{1}{[n_0 - \Delta(n_0, 1)]^2} - \frac{1}{[n - \Delta(n, 2)]^2} \right], \quad n \geq n_0,$$

and the Bergmann (*fundamental*) series with transitions from f to d electron terms:

$$\bar{\nu}_f = R_{\text{Na}} \left[\frac{1}{[n_0 - \Delta(n_0, 2)]^2} - \frac{1}{[n - \Delta(n, 3)]^2} \right], \quad n \geq n_0 + 1.$$

R_{Na} is again the Rydberg number of the sodium atom and n_0 is the integral principal quantum number of the lowest state. This is 2 for Li, 3 for Na, 4 for K, 5 for Rb and 6 for Cs. We are jumping slightly ahead in saying that the valence electron of the alkali atoms begins a new shell in each element. The principal quantum number of the ground state therefore increases by one in each successive alkali element of the periodic system.

The names for the series and the system of indicating the electrons with orbital angular momentum 0, 1, 2, 3, 4, ... as s, p, d, f, g, \dots are historic. p is for principal, s for sharp, d for diffuse and f for fundamental.

Under normal conditions, only the principal series is observed by absorption spectroscopy, because unless the temperature is extremely high, only the ground state of the atoms is sufficiently populated for transitions into higher states to be observed. The lines of the principal series are thus resonance lines. The best known is the D line of sodium, which is the transition $3s - 3p$. The sum of the s terms can also be designated S , and of the p terms, P , so that the sodium series can be written:

$$\begin{aligned} \text{Principal series} & \quad 3S \leftrightarrow nP \\ \text{Secondary series} & \quad 3P \leftrightarrow nS \\ & \quad 3P \leftrightarrow nD \quad \text{with} \quad n \geq 3. \end{aligned}$$

Capital letters are used for terms which apply to several electrons in an atom, and lower case letters for the terms for individual electrons. In the alkali atoms, which have only one valence electron, the two notations are equivalent.

The screening effect of the inner electrons can be quantitatively calculated, if one knows their charge distribution with sufficient accuracy. Qualitatively, we wish to demonstrate the effect of the nuclear charge on a single $3d$ or $4s$ electron in the atoms H ($Z = 1$) and K ($Z = 19$).

In the H atom, the charge cloud of a $3d$ electron is, on the average, closer to the nucleus than that of a $4s$ electron (Fig. 11.8). Therefore, the $3d$ electron is more strongly bound to the H atom. It is different, however, in the K atom. The configuration of the atomic core, i.e. the noble gas configuration of Ar, consists of two s electrons with $n = 1$ (symbol $1s^2$), two s electrons with $n = 2$ (symbol $2s^2$), six p electrons

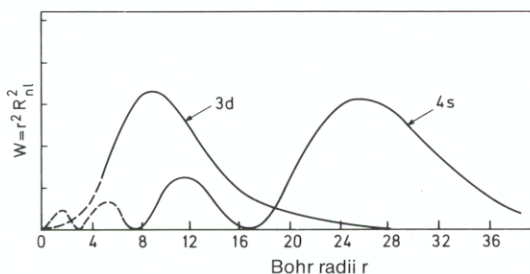


Fig. 11.8. Radial probability densities for a $4s$ and a $3d$ electron in the H atom. The $4s$ electron is, on the average, farther from the nucleus, but the probability of finding it near the nucleus is greater than the probability of finding the $3d$ electron there

with $n = 2$ (symbol $2p^6$), two s electrons with $n = 3$ (symbol $3s^2$) and six p electrons with $n = 3$ (symbol $3p^6$):

$$1s^2 2s^2 2p^6 3s^2 3p^6 - \text{ or } [\text{Ar}] \text{ for argon.}$$

Now the question is, does K, with one more electron, have the configuration $[\text{Ar}]4s^1$, or does $[\text{Ar}]3d^1$ have a greater binding energy? Is the 19th electron added as a $4s$ or a $3d$ electron?

From our consideration of the H atom, we would predict that the $[\text{Ar}]3d^1$ configuration is more stable. However, it must now be determined what the effects of shielding are on the $3d$ and $4s$ electrons. Because the $4s$ electron has a higher probability of being very close to the nucleus, and thus unscreened, it turns out that the $4s$ energy level is energetically somewhat lower than the $3d$. The 20th electron is also an s electron; see Table 3.1. The element following potassium in the periodic table, calcium, has the configuration $[\text{Ar}]4s^2$. It thus becomes clear how decisively the screening affects the binding energies of the outer electrons, in a manner dependent on the orbital angular momentum quantum number l .

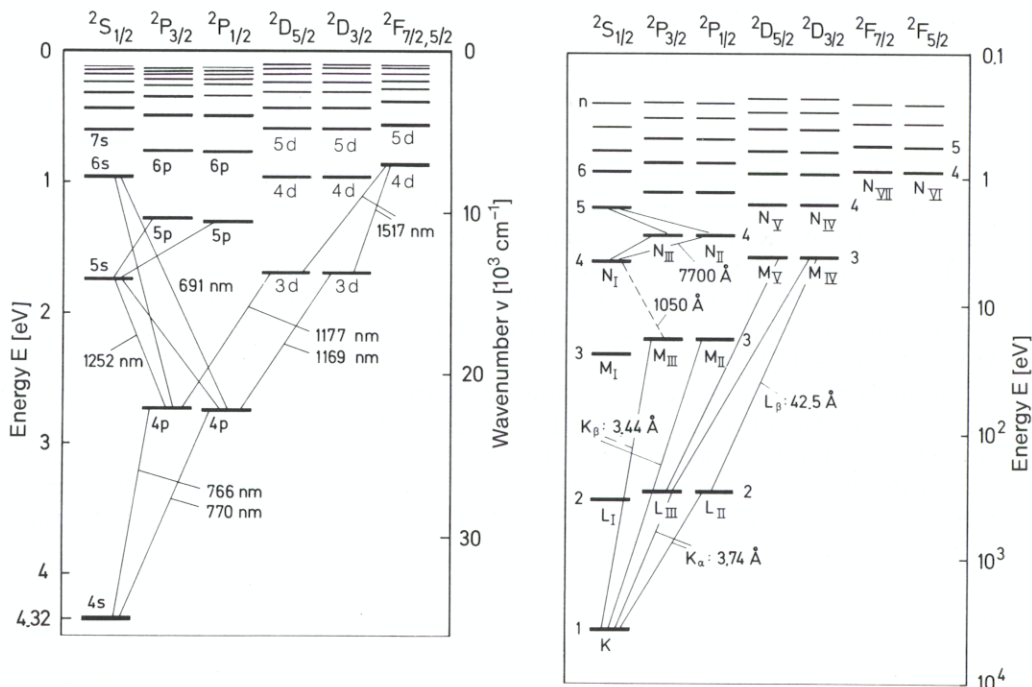


Fig. 11.9. *Left.* Grotrian diagram for the neutral potassium atom in the visible and infrared regions. The wavelengths for a few transitions (in nm) are indicated. The term symbols on the upper edge of the diagram are explained in Sect. 12.8 and Chap. 17. *Right.* Term scheme for the potassium atom in the infrared, visible, ultraviolet and x-ray regions. The term symbols used in this diagram are explained in Chaps. 12 and 17. (One should observe that the energy ranges in the two halves of the figure are different.) The x-ray spectrum also includes terms with lower principal quantum numbers than the visible spectrum. Terms with $n = 1, 2, 3, \dots$ are referred to in the x-ray region as the K, L, M, \dots shells, see Chap. 18

11.4 Inner Shells

So far we have treated only the optical spectra of the alkali atoms. The valence electron could only have the principal quantum number $n \geq 2$ for Li, ≥ 3 for Na, ≥ 4 for K, etc. The states with lower principal quantum numbers were completely occupied. Transitions involving these inner electrons were not discussed. However, they are also possible. Since the inner electrons are more strongly bound, such transitions take place at higher energies. We will introduce such transitions later, in the discussion of x-ray spectra (Chap. 18).

Figure 11.9 shows, in addition to the optical term scheme for the valence electron of the K atom, a complete term scheme. This includes the transitions in the x-ray region of the spectrum, in which an electron is removed from a closed inner shell and replaced by an electron from further out.

Problems

11.1 The energy levels of the valence electrons of an alkali atom are given, to a good approximation, by the expression

$$E_n = -Rhc \cdot 1/[n - \Delta(n, l)]^2.$$

Here $\Delta(n, l)$ is the quantum defect (which depends on the values of n and l of the valence electron in question). For lithium and sodium, $\Delta(n, l)$ have been measured:

	<i>s</i>	<i>p</i>	<i>d</i>
Li ($Z = 3$)	0.40	0.04	0.00
Na ($Z = 11$)	1.37	0.88	0.01

Calculate the energy of the ground state and the first two excited states of the valence electron in lithium and sodium.

11.2 The ionisation energy of the Li atom is 5.3913 eV, and the resonance line ($2s \leftrightarrow 2p$) is observed at 6710 Å. Lithium vapour is selectively excited so that only the $3p$ level is occupied. Which spectral lines are emitted by this vapour, and what are their wavelengths?

Hint: Start from the fact that the quantum defect is independent of n , the principal quantum number.

11.3 Explain the symbols for the $3^2D \rightarrow 3^2P$ transition in sodium. How many lines can be expected in the spectrum?