The previous equation can also be written in the coordinate-free form

$$\mathbf{n}\cdot\mathbf{r} = d, \tag{3.6}$$

where $\mathbf{n} = (1,\, 0,\, 0)$ is a unit vector directed along the positive x-axis, and $\mathbf{r} = (x,\, y,\, z)$ represents the vector displacement of a general point from the origin. Since there is nothing special about the x-direction, it follows that if $\mathbf{n}$ is re-interpreted as a unit vector pointing in an *arbitrary* direction then (3.6) can be re-interpreted as the general equation of a plane. As before, the plane is normal to $\mathbf{n}$, and its distance of closest approach to the origin is d. See Fig. 3.1. This observation allows us to write the three-dimensional equivalent to the wavefunction (3.3) as

$$\psi(x, y, z, t) = A\,\cos(\mathbf{k}\cdot\mathbf{r} - \omega\,t + \varphi), \tag{3.7}$$

where the constant vector $\mathbf{k} = (k_x,\, k_y,\, k_z) = k\,\mathbf{n}$ is called the *wavevector*. The wave represented above is conventionally termed a *three-dimensional plane wave*. It is three-dimensional because its wavefunction, $\psi(x, y, z, t)$, depends on all three Cartesian coordinates. Moreover, it is a plane wave because the wave maxima are located at

$$\mathbf{k}\cdot\mathbf{r} - \omega\,t + \varphi = j\,2\pi, \tag{3.8}$$

or

$$\mathbf{n}\cdot\mathbf{r} = (j - \varphi/2\pi)\,\lambda + v\,t, \tag{3.9}$$

where $\lambda = 2\pi/k$, and $v = \omega/k$. Note that the wavenumber, k, is the *magnitude* of the wavevector, $\mathbf{k}$: *i.e.*, $k \equiv |\mathbf{k}|$. It follows, by comparison with Eq. (3.6), that the wave maxima consist of a series of parallel planes, normal to the wavevector, which are equally spaced a distance λ apart, and which propagate in the $\mathbf{k}$-direction at the velocity v. See Fig. 3.2. Hence, the direction of the wavevector specifies the wave propagation direction, whereas its magnitude determines the wavenumber, k, and, thus, the wavelength, $\lambda = 2\pi/k$.

3.4 Representation of Waves via Complex Functions

In mathematics, the symbol i is conventionally used to represent the *square-root of minus one*: *i.e.*, one of the solutions of $i^2 = -1$. Now, a *real number*, x (say), can take any value in a continuum of different values lying between $-\infty$ and $+\infty$. On the other hand, an *imaginary number* takes the general form $i\,y$, where y is a real number. It follows that the square of a real number is a positive real number, whereas the square of an imaginary number is a negative real number. In addition, a general *complex number* is written

$$z = x + i\,y, \tag{3.10}$$

where x and y are real numbers. In fact, x is termed the *real part* of z, and y the *imaginary part* of z. This is written mathematically as $x = \mathrm{Re}(z)$ and $y = \mathrm{Im}(z)$. Finally, the *complex conjugate* of z is defined $z^* = x - i\,y$.

Thus, the wave maxima and minima propagate in the x-direction at the fixed velocity

$$\frac{dx}{dt} = c. \tag{3.27}$$

An expression, such as (3.24), which determines the wave angular frequency as a function of the wavenumber, is generally termed a *dispersion relation*. As we have already seen, and as is apparent from Eq. (3.25), the maxima and minima of a plane wave propagate at the characteristic velocity

$$v_p = \frac{\omega}{k}, \tag{3.28}$$

which is known as the *phase velocity*. Hence, the dispersion relation (3.24) is effectively saying that the phase velocity of a plane light wave propagating through a vacuum always takes the fixed value c, irrespective of its wavelength or frequency.

Now, from standard electromagnetic theory, the *energy density* (*i.e.*, the energy per unit volume) of a light wave is

$$U = \frac{E_y^{\,2}}{\epsilon_0}, \tag{3.29}$$

where $\epsilon_0 = 8.85 \times 10^{-12}\,\mathrm{F/m}$ is the *permittivity of free space*. Hence, it follows from Eqs. (3.20) and (3.22) that

$$U \propto |\psi|^2. \tag{3.30}$$

Furthermore, a light wave possesses linear *momentum*, as well as energy. This momentum is directed along the wave's direction of propagation, and is of density

$$G = \frac{U}{c}. \tag{3.31}$$

3.6 Photoelectric Effect

The so-called *photoelectric effect*, by which a polished metal surface emits electrons when illuminated by visible and ultra-violet light, was discovered by Heinrich Hertz in 1887. The following facts regarding this effect can be established via careful observation. First, a given surface only emits electrons when the *frequency* of the light with which it is illuminated exceeds a certain threshold value, which is a property of the metal. Second, the current of photoelectrons, when it exists, is proportional to the *intensity* of the light falling on the surface. Third, the energy of the photoelectrons is independent of the light intensity, but varies *linearly* with the light frequency. These facts are inexplicable within the framework of classical physics.

In 1905, Albert Einstein proposed a radical new theory of light in order to account for the photoelectric effect. According to this theory, light of fixed frequency ν consists of a collection of indivisible discrete packages, called *quanta*,[1] whose energy is

$$E = h\,\nu. \tag{3.32}$$

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[1] Plural of *quantum*: Latin neuter of *quantus*: how much?

The complex conjugate of this expression yields

$$\psi\,\frac{\partial\psi^*}{\partial t} = -\frac{i\,\hbar}{2\,m}\,\psi\,\frac{\partial^2\psi^*}{\partial x^2} + \frac{i}{\hbar}\,V\,|\psi|^2 \tag{4.14}$$

[since $(A\,B)^* = A^*\,B^*$, $A^{**} = A$, and $i^* = -i$]. Summing the previous two equations, we get

$$\frac{\partial\psi^*}{\partial t}\,\psi + \psi^*\,\frac{\partial\psi}{\partial t} = \frac{i\,\hbar}{2\,m}\left(\psi^*\,\frac{\partial^2\psi}{\partial x^2} - \psi\,\frac{\partial^2\psi^*}{\partial x^2}\right) = \frac{i\,\hbar}{2\,m}\,\frac{\partial}{\partial x}\left(\psi^*\,\frac{\partial\psi}{\partial x} - \psi\,\frac{\partial\psi^*}{\partial x}\right). \tag{4.15}$$

Equations (4.12) and (4.15) can be combined to produce

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2\,dx = \frac{i\,\hbar}{2\,m}\left[\psi^*\,\frac{\partial\psi}{\partial x} - \psi\,\frac{\partial\psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{4.16}$$

The above equation is satisfied provided

$$|\psi| \rightarrow 0 \quad \text{as} \quad |x| \rightarrow \infty. \tag{4.17}$$

However, this is a necessary condition for the integral on the left-hand side of Eq. (4.4) to converge. Hence, we conclude that all wavefunctions which are *square-integrable* [*i.e.*, are such that the integral in Eq. (4.4) converges] have the property that if the normalization condition (4.4) is satisfied at one instant in time then it is satisfied at all subsequent times.

It is also possible to demonstrate, via very similar analysis to the above, that

$$\frac{dP_{x\,\in\,a:b}}{dt} + j(b,t) - j(a,t) = 0, \tag{4.18}$$

where $P_{x\,\in\,a:b}$ is defined in Eq. (4.2) and

$$j(x,t) = \frac{i\,\hbar}{2\,m}\left(\psi\,\frac{\partial\psi^*}{\partial x} - \psi^*\,\frac{\partial\psi}{\partial x}\right) \tag{4.19}$$

is known as the *probability current*. Note that j is real. Equation (4.18) is a *probability conservation equation*. According to this equation, the probability of a measurement of x lying in the interval a to b evolves in time due to the difference between the flux of probability into the interval [*i.e.*, $j(a,t)$], and that out of the interval [*i.e.*, $j(b,t)$]. Here, we are interpreting $j(x,t)$ as the *flux* of probability in the $+x$-direction at position x and time t.

Note, finally, that not all wavefunctions can be normalized according to the scheme set out in Eq. (4.4). For instance, a plane wave wavefunction

$$\psi(x,t) = \psi_0\,e^{\,i\,(k\,x-\omega\,t)} \tag{4.20}$$

is not square-integrable, and, thus, cannot be normalized. For such wavefunctions, the best we can say is that

$$P_{x\,\in\,a:b}(t) \propto \int_a^b |\psi(x,t)|^2\,dx. \tag{4.21}$$

In the following, all wavefunctions are assumed to be square-integrable and normalized, unless otherwise stated.

It is a reasonable guess that the operator corresponding to energy (which is called the Hamiltonian, and conventionally denoted H) takes the form

$$H \equiv \frac{p^2}{2\,m} + V(x). \tag{4.59}$$

Note that H is Hermitian. Now, it follows from Eq. (4.55) that

$$H \equiv -\frac{\hbar^2}{2\,m}\,\frac{\partial^2}{\partial x^2} + V(x). \tag{4.60}$$

However, according to Schrödinger's equation, (4.1), we have

$$-\frac{\hbar^2}{2\,m}\,\frac{\partial^2}{\partial x^2} + V(x) = \mathrm{i}\,\hbar\,\frac{\partial}{\partial t}, \tag{4.61}$$

so

$$H \equiv \mathrm{i}\,\hbar\,\frac{\partial}{\partial t}. \tag{4.62}$$

Thus, the time-dependent Schrödinger equation can be written

$$\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t} = H\,\psi. \tag{4.63}$$

Finally, if $O(x, p, E)$ is a classical dynamical variable which is a function of displacement, momentum, and energy, then a reasonable guess for the corresponding operator in quantum mechanics is $(1/2)\,[O(x, p, H) + O^\dagger(x, p, H)]$, where $p = -\mathrm{i}\,\hbar\,\partial/\partial x$, and $H = \mathrm{i}\,\hbar\,\partial/\partial t$.

4.7 Momentum Representation

Fourier's theorerm (see Sect. 3.12), applied to one-dimensional wavefunctions, yields

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\bar{\psi}(k, t)\,e^{+\mathrm{i}\,k\,x}\,dk, \tag{4.64}$$

$$\bar{\psi}(k, t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\psi(x, t)\,e^{-\mathrm{i}\,k\,x}\,dx, \tag{4.65}$$

where k represents wavenumber. However, $p = \hbar\,k$. Hence, we can also write

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\,\hbar}}\int_{-\infty}^{\infty}\phi(p, t)\,e^{+\mathrm{i}\,p\,x/\hbar}\,dp, \tag{4.66}$$

$$\phi(p, t) = \frac{1}{\sqrt{2\pi\,\hbar}}\int_{-\infty}^{\infty}\psi(x, t)\,e^{-\mathrm{i}\,p\,x/\hbar}\,dx, \tag{4.67}$$

where $\phi(p, t) = \bar{\psi}(k, t)/\sqrt{\hbar}$ is the momentum-space equivalent to the real-space wavefunction $\psi(x, t)$.

4.12 Stationary States

An eigenstate of the energy operator $H \equiv i\,\hbar\,\partial/\partial t$ corresponding to the eigenvalue E_i satisfies

$$i\,\hbar\,\frac{\partial\psi_E(x,t,E_i)}{\partial t} = E_i\,\psi_E(x,t,E_i). \tag{4.157}$$

It is evident that this equation can be solved by writing

$$\psi_E(x,t,E_i) = \psi_i(x)\,e^{-i\,E_i\,t/\hbar}, \tag{4.158}$$

where $\psi_i(x)$ is a properly normalized stationary (*i.e.*, non-time-varying) wavefunction. The wavefunction $\psi_E(x,t,E_i)$ corresponds to a so-called *stationary state*, since the probability density $|\psi_E|^2$ is non-time-varying. Note that a stationary state is associated with a *unique* value for the energy. Substitution of the above expression into Schrödinger's equation (4.1) yields the equation satisfied by the stationary wavefunction:

$$\frac{\hbar^2}{2\,m}\,\frac{d^2\psi_i}{dx^2} = [V(x) - E_i]\,\psi_i. \tag{4.159}$$

This is known as the *time-independent Schrödinger equation*. More generally, this equation takes the form

$$H\,\psi_i = E_i\,\psi_i, \tag{4.160}$$

where H is assumed not to be an explicit function of t. Of course, the ψ_i satisfy the usual orthonormality condition:

$$\int_{-\infty}^{\infty}\psi_i^*\,\psi_j\,dx = \delta_{ij}. \tag{4.161}$$

Moreover, we can express a general wavefunction as a linear combination of energy eigenstates:

$$\psi(x,t) = \sum_i c_i\,\psi_i(x)\,e^{-i\,E_i\,t/\hbar}, \tag{4.162}$$

where

$$c_i = \int_{-\infty}^{\infty}\psi_i^*(x)\,\psi(x,0)\,dx. \tag{4.163}$$

Here, $|c_i|^2$ is the probability that a measurement of the energy will yield the eigenvalue E_i. Furthermore, immediately after such a measurement, the system is left in the corresponding energy eigenstate. The generalization of the above results to the case where H has continuous eigenvalues is straightforward.

If a dynamical variable is represented by some Hermitian operator A which commutes with H (so that it has simultaneous eigenstates with H), and contains no specific time dependence, then it is evident from Eqs. (4.161) and (4.162) that the expectation value and variance of A are *time independent*. In this sense, the dynamical variable in question is a constant of the motion.

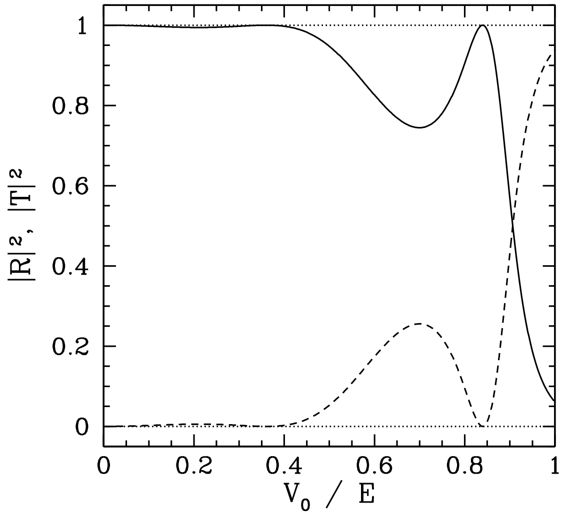

Figure 5.1: *Transmission (solid-curve) and reflection (dashed-curve) probabilities for a square potential barrier of width* $a = 1.25\,\lambda$*, where* λ *is the free-space de Broglie wavelength, as a function of the ratio of the height of the barrier,* V_0*, to the energy,* E*, of the incident particle.*

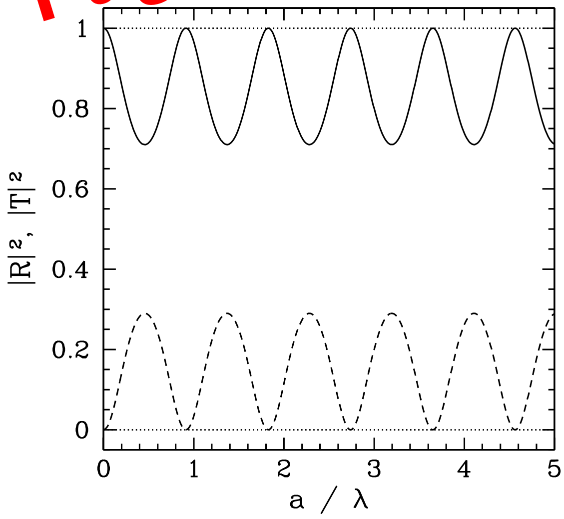

Figure 5.2: *Transmission (solid-curve) and reflection (dashed-curve) probabilities for a particle of energy* E *incident on a square potential barrier of height* $V_0 = 0.75\,E$*, as a function of the ratio of the width of the barrier,* a*, to the free-space de Broglie wavelength,* λ*.*

5.4 WKB Approximation

Consider a particle of mass m and energy $E > 0$ moving through some *slowly varying* potential $V(x)$. The particle's wavefunction satisfies

$$\frac{d^2\psi(x)}{dx^2} = -k^2(x)\,\psi(x), \tag{5.38}$$

where

$$k^2(x) = \frac{2\,m\,[E - V(x)]}{\hbar^2}. \tag{5.39}$$

Let us try a solution to Eq. (5.38) of the form

$$\psi(x) = \psi_0 \exp\left(\int_0^x i\,k(x')\,dx'\right), \tag{5.40}$$

where ψ_0 is a complex constant. Note that this solution represents a particle propagating in the positive x-direction [since the full wavefunction is multiplied by $\exp(-i\,\omega\,t)$, where $\omega = E/\hbar > 0$] with the continuously varying wavenumber $k(x)$. It follows that

$$\frac{d\psi(x)}{dx} = i\,k(x)\,\psi(x), \tag{5.41}$$

and

$$\frac{d^2\psi(x)}{dx^2} = i\,k'(x)\,\psi(x) - k^2(x)\,\psi(x), \tag{5.42}$$

where $k' \equiv dk/dx$. A comparison of Eqs. (5.38) and (5.42) reveals that Eq. (5.40) represents an approximate solution to Eq. (5.38) provided that the first term on its right-hand side is negligible compared to the second. This yields the validity criterion $|k'| \ll k^2$, or

$$\frac{k}{|k'|} \gg k^{-1}. \tag{5.43}$$

In other words, the variation length-scale of $k(x)$, which is approximately the same as the variation length-scale of $V(x)$, must be *much greater* than the particle's de Broglie wavelength (which is of order k^{-1}). Let us suppose that this is the case. Incidentally, the approximation involved in dropping the first term on the right-hand side of Eq. (5.42) is generally known as the *WKB approximation.*[1] Similarly, Eq. (5.40) is termed a WKB solution.

According to the WKB solution (5.40), the probability density remains constant: *i.e.*,

$$|\psi(x)|^2 = |\psi_0|^2, \tag{5.44}$$

as long as the particle moves through a region in which $E > V(x)$, and $k(x)$ is consequently real (*i.e.*, an allowed region according to classical physics). Suppose, however, that the

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[1] After G. Wentzel, H.A. Kramers, and L. Brillouin.

This reduces to

$$|T|^2 = \exp\left(-2\sqrt{2}\,\frac{m^{1/2}\,W^{3/2}}{\hbar\,e\,\mathcal{E}}\int_0^1\sqrt{1-y}\,dy\right), \tag{5.52}$$

or

$$|T|^2 = \exp\left(-\frac{4\sqrt{2}}{3}\,\frac{m^{1/2}\,W^{3/2}}{\hbar\,e\,\mathcal{E}}\right). \tag{5.53}$$

The above result is known as the *Fowler-Nordheim* formula. Note that the probability of emission increases *exponentially* as the electric field-strength above the surface of the metal increases.

The cold emission of electrons from a metal surface is the basis of an important device known as a *scanning tunneling microscope*, or an STM. An STM consists of a very sharp conducting probe which is scanned over the surface of a metal (or any other solid conducting medium). A large voltage difference is applied between the probe and the surface. Now, the surface electric field-strength immediately below the probe tip is proportional to the applied potential difference, and inversely proportional to the spacing between the tip and the surface. Electrons tunneling between the surface and the probe tip give rise to a weak electric current. The magnitude of this current is proportional to the tunneling probability (5.53). It follows that the current is an *extremely sensitive* function of the surface electric field-strength, and, hence, of the spacing between the tip and the surface (assuming that the potential difference is held constant). An STM can thus be used to construct a very accurate contour map of the surface under investigation. In fact, STMs are capable of achieving sufficient resolution to image individual atoms

5.6 Alpha Decay

Many types of heavy atomic nucleus spontaneously decay to produce daughter nucleii via the emission of α-particles (*i.e.*, helium nucleii) of some characteristic energy. This process is know as α-decay. Let us investigate the α-decay of a particular type of atomic nucleus of radius R, charge-number Z, and mass-number A. Such a nucleus thus decays to produce a daughter nucleus of charge-number $Z_1 = Z - 2$ and mass-number $A_1 = A - 4$, and an α-particle of charge-number $Z_2 = 2$ and mass-number $A_2 = 4$. Let the characteristic energy of the α-particle be E. Incidentally, nuclear radii are found to satisfy the empirical formula

$$R = 1.5\times 10^{-15}\,A^{1/3}\,\mathrm{m} = 2.0\times 10^{-15}\,Z_1^{1/3}\,\mathrm{m} \tag{5.54}$$

for $Z \gg 1$.

In 1928, George Gamov proposed a very successful theory of α-decay, according to which the α-particle moves freely inside the nucleus, and is emitted after *tunneling* through the potential barrier between itself and the daughter nucleus. In other words, the α-particle, whose energy is E, is trapped in a potential well of radius R by the potential barrier

$$V(r) = \frac{Z_1\,Z_2\,e^2}{4\pi\,\epsilon_0\,r} \tag{5.55}$$

Assuming that the ψ_n are properly normalized (and real), we have

$$\int_{-\infty}^{\infty} \psi_n\, \psi_m\, dx = \delta_{nm}. \tag{5.107}$$

Now, Eq. (5.94) can be written

$$\left(-\frac{d^2}{dy^2} + y^2\right) \psi_n = (2n+1)\, \psi_n, \tag{5.108}$$

where $x = d\, y$, and $d = \sqrt{\hbar/m\,\omega}$. It is helpful to define the operators

$$a_\pm = \frac{1}{\sqrt{2}} \left(\mp \frac{d}{dy} + y\right). \tag{5.109}$$

As is easily demonstrated, these operators satisfy the commutation relation

$$[a_+, a_-] = -1. \tag{5.110}$$

Using these operators, Eq. (5.108) can also be written in the forms

$$a_+\, a_-\, \psi_n = n\, \psi_n, \tag{5.111}$$

or

$$a_-\, a_+\, \psi_n = (n+1)\, \psi_n. \tag{5.112}$$

The above two equations imply that

$$\begin{aligned} a_+\, \psi_n &= \sqrt{n+1}\, \psi_{n+1}, & (5.113)\\ a_-\, \psi_n &= \sqrt{n}\, \psi_{n-1}. & (5.114) \end{aligned}$$

We conclude that a_+ and a_- are *raising and lowering operators*, respectively, for the harmonic oscillator: *i.e.*, operating on the wavefunction with a_+ causes the quantum number n to increase by unity, and *vice versa*. The Hamiltonian for the harmonic oscillator can be written in the form

$$H = \hbar\, \omega \left(a_+\, a_- + \frac{1}{2}\right), \tag{5.115}$$

from which the result

$$H\, \psi_n = (n + 1/2)\, \hbar\, \omega\, \psi_n = E_n\, \psi_n \tag{5.116}$$

is readily deduced. Finally, Eqs. (5.107), (5.113), and (5.114) yield the useful expression

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_m\, x\, \psi_n\, dx &= \frac{d}{\sqrt{2}} \int_{-\infty}^{\infty} \psi_m\, (a_+ + a_-)\, \psi_n\, dx & (5.117)\\ &= \sqrt{\frac{\hbar}{2\, m\, \omega}} \left(\sqrt{m}\, \delta_{m,n+1} + \sqrt{n}\, \delta_{m,n-1}\right). \end{aligned}$$

Since the x_i are *independent* variables (*i.e.*, $\partial x_i/\partial x_j = \delta_{ij}$), we conclude that the various position and momentum operators satisfy the following commutation relations:

$$[x_i, x_j] = 0, \tag{6.4}$$

$$[p_i, p_j] = 0, \tag{6.5}$$

$$[x_i, p_j] = i\,\hbar\,\delta_{ij}. \tag{6.6}$$

Now, we know, from Sect. 4.10, that two dynamical variables can only be (exactly) measured *simultaneously* if the operators which represent them in quantum mechanics *commute* with one another. Thus, it is clear, from the above commutation relations, that the only restriction on measurement in a one-dimensional multi-particle system is that it is impossible to simultaneously measure the position and momentum of the *same* particle. Note, in particular, that a knowledge of the position or momentum of a given particle does not in any way preclude a similar knowledge for a different particle. The commutation relations (6.4)–(6.6) illustrate an important point in quantum mechanics: namely, that operators corresponding to *different degrees of freedom* of a dynamical system tend to *commute* with one another. In this case, the different degrees of freedom correspond to the different motions of the various particles making up the system.

Finally, if $H(x_1, x_2, \ldots, x_N, t)$ is the Hamiltonian of the system then the multi-particle wavefunction $\psi(x_1, x_2, \ldots, x_N, t)$ satisfies the usual time-dependent Schrödinger equation [see Eq. (4.63)]

$$i\,\hbar\,\frac{\partial\psi}{\partial t} = H\,\psi. \tag{6.7}$$

Likewise, a multi-particle state of definite energy E (*i.e.*, an eigenstate of the Hamiltonian with eigenvalue E) is written (see Sect. 4.12)

$$\psi(x_1, x_2, \ldots, x_N, t) = \psi_E(x_1, x_2, \ldots, x_N)\,e^{-i\,E\,t/\hbar}, \tag{6.8}$$

where the stationary wavefunction ψ_E satisfies the time-independent Schrödinger equation [see Eq. (4.160)]

$$H\,\psi_E = E\,\psi_E. \tag{6.9}$$

Here, H is assumed not to be an explicit function of t.

6.3 Non-Interacting Particles

In general, we expect the Hamiltonian of a multi-particle system to take the form

$$H(x_1, x_2, \ldots, x_N, t) = \sum_{i=1,N} \frac{p_i^2}{2\,m_i} + V(x_1, x_2, \ldots, x_N, t). \tag{6.10}$$

Here, the first term on the right-hand side represents the total kinetic energy of the system, whereas the potential V specifies the nature of the interaction between the various particles making up the system, as well as the interaction of the particles with any external forces.

Suppose that the particles do not interact with one another. This implies that each particle moves in a common potential: *i.e.*,

$$V(x_1, x_2, \ldots, x_N, t) = \sum_{i=1,N} V(x_i, t). \tag{6.11}$$

Hence, we can write

$$H(x_1, x_2, \ldots, x_N, t) = \sum_{i=1,N} H_i(x_i, t), \tag{6.12}$$

where

$$H_i = \frac{p_i^2}{2\,m_i} + V(x_i, t). \tag{6.13}$$

In other words, for the case of non-interacting particles, the multi-particle Hamiltonian of the system can be written as the sum of N independent single-particle Hamiltonians. Here, H_i represents the energy of the ith particle, and is completely unaffected by the energies of the other particles. Furthermore, given that the various particles which make up the system are non-interacting, we expect their instantaneous positions to be completely *uncorrelated* with one another. This immediately implies that the multi-particle wavefunction $\psi(x_1, x_2, \ldots x_N, t)$ can be written as the product of N independent single-particle wavefunctions: *i.e.*,

$$\psi(x_1, x_2, \ldots, x_N, t) = \psi_1(x_1, t)\,\psi_2(x_2, t)\ldots\psi_N(x_N, t). \tag{6.14}$$

Here, $|\psi_i(x_i, t)|^2\,dx_i$ is the probability of finding the ith particle between x_i and $x_i + dx_i$ at time t. This probability is completely unaffected by the positions of the other particles. It is evident that $\psi_i(x_i, t)$ must satisfy the normalization constraint

$$\int_{-\infty}^{\infty} |\psi_i(x_i, t)|^2\,dx_i = 1. \tag{6.15}$$

If this is the case then the normalization constraint (6.2) for the multi-particle wavefunction is automatically satisfied. Equation (6.14) illustrates an important point in quantum mechanics: namely, that we can generally write the total wavefunction of a many degree of freedom system as a product of different wavefunctions corresponding to each degree of freedom.

According to Eqs. (6.12) and (6.14), the time-dependent Schrödinger equation (6.7) for a system of N non-interacting particles factorizes into N independent equations of the form

$$i\,\hbar\,\frac{\partial\psi_i}{\partial t} = H_i\,\psi_i. \tag{6.16}$$

Assuming that $V(x, t) \equiv V(x)$, the time-independent Schrödinger equation (6.9) also factorizes to give

$$H_i\,\psi_{E_i} = E_i\,\psi_{E_i}, \tag{6.17}$$

further apart than two similar distinguishable particles. However, the strength of this effect depends on square of the magnitude of $\langle x\rangle_{ab}$, which measures the *overlap* between the wavefunctions $\psi(x, E_a)$ and $\psi(x, E_b)$. It is evident, then, that if these two wavefunctions do not overlap to any great extent then identical bosons or fermions will act very much like distinguishable particles.

For a system containing N identical and non-interacting fermions, the anti-symmetric stationary wavefunction of the system is written

$$\psi_E(x_1, x_2, \ldots x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi(x_1, E_1) & \psi(x_2, E_1) & \ldots & \psi(x_N, E_1) \\ \psi(x_1, E_2) & \psi(x_2, E_2) & \ldots & \psi(x_N, E_2) \\ \vdots & \vdots & \vdots & \vdots \\ \psi(x_1, E_N) & \psi(x_2, E_N) & \ldots & \psi(x_N, E_N) \end{vmatrix}. \tag{6.50}$$

This expression is known as the *Slater determinant*, and automatically satisfies the symmetry requirements on the wavefunction. Here, the energies of the particles are $E_1, E_2, \ldots, E_N$. Note, again, that if any two particles in the system have the same energy (*i.e.*, if $E_i = E_j$ for some $i \neq j$) then the total wavefunction is null. We conclude that it is impossible for any two identical fermions in a multi-particle system to occupy the same single-particle stationary state. This important result is known as the *Pauli exclusion principle*.

Exercises (N.B. Neglect spin in the following questions.)

1. Consider a system consisting of two non-interacting particles, and three one-particle states, $\psi_a(x)$, $\psi_b(x)$, and $\psi_c(x)$. How many different two-particle states can be constructed if the particles are (a) distinguishable, (b) indistinguishable bosons, or (c) indistinguishable fermions?

2. Consider two non-interacting particles, each of mass m, in a one-dimensional harmonic oscillator potential of classical oscillation frequency ω. If one particle is in the ground-state, and the other in the first excited state, calculate $\langle (x_1 - x_2)^2\rangle$ assuming that the particles are (a) distinguishable, (b) indistinguishable bosons, or (c) indistinguishable fermions.

3. Two non-interacting particles, with the same mass m, are in a one-dimensional box of length a. What are the four lowest energies of the system? What are the degeneracies of these energies if the two particles are (a) distinguishable, (b) indistinguishable bosons, or (c) indistingishable fermions?

4. Two particles in a one-dimensional box of length a occupy the $n = 4$ and $n' = 3$ states. Write the properly normalized wavefunctions if the particles are (a) distinguishable, (b) indistinguishable bosons, or (c) indistinguishable fermions.

numbers) can occupy a single-particle energy level corresponding to a particular set of values of l_x, l_y, and l_z. Note, from Eqs. (7.38) and (7.39), that the associated particle energy is proportional to $l^2 = l_x^2 + l_y^2 + l_z^2$.

Suppose that our electrons are *cold*: *i.e.*, they have comparatively little thermal energy. In this case, we would expect them to fill the lowest single-particle energy levels available to them. We can imagine the single-particle energy levels as existing in a sort of three-dimensional quantum number space whose Cartesian coordinates are l_x, l_y, and l_z. Thus, the energy levels are uniformly distributed in this space on a cubic lattice. Moreover, the distance between nearest neighbour energy levels is unity. This implies that the number of energy levels per unit volume is also unity. Finally, the energy of a given energy level is proportional to its distance, $l^2 = l_x^2 + l_y^2 + l_z^2$, from the origin.

Since we expect cold electrons to occupy the lowest energy levels available to them, but only two electrons can occupy a given energy level, it follows that if the number of electrons, N, is very large then the filled energy levels will be approximately distributed in a *sphere* centered on the origin of quantum number space. The number of energy levels contained in a sphere of radius l is approximately equal to the volume of the sphere—since the number of energy levels per unit volume is unity. It turns out that this is not quite correct, because we have forgotten that the quantum numbers l_x, l_y, and l_z can only take *positive* values. Hence, the filled energy levels actually only occupy one *octant* of a sphere. The radius l_F of the octant of filled energy levels in quantum number space can be calculated by equating the number of energy levels it contains to the number of electrons, N. Thus, we can write

$$N = 2\times\frac{1}{8}\times\frac{4\pi}{3}\,l_F^{3}. \tag{7.40}$$

Here, the factor 2 is to take into account the two spin states of an electron, and the factor 1/8 is to take account of the fact that l_x, l_y, and l_z can only take positive values. Thus,

$$l_F = \left(\frac{3\,N}{\pi}\right)^{1/3}. \tag{7.41}$$

According to Eq. (7.38), the energy of the most energetic electrons—which is known as the *Fermi energy*—is given by

$$E_F = \frac{l_F^2\,\pi^2\,\hbar^2}{2\,m_e\,a^2} = \frac{\pi^2\,\hbar^2}{2\,m\,a^2}\left(\frac{3\,N}{\pi}\right)^{2/3}, \tag{7.42}$$

where m_e is the electron mass. This can also be written as

$$E_F = \frac{\pi^2\,\hbar^2}{2\,m_e}\left(\frac{3\,n}{\pi}\right)^{2/3}, \tag{7.43}$$

where $n = N/a^3$ is the number of electrons per unit volume (in real space). Note that the Fermi energy only depends on the *number density* of the confined electrons.

8 Orbital Angular Momentum

8.1 Introduction

As is well-known, angular momentum plays a vitally important role in the classical description of three-dimensional motion. Let us now investigate the role of angular momentum in the quantum mechanical description of such motion.

8.2 Angular Momentum Operators

In classical mechanics, the vector angular momentum, **L**, of a particle of position vector **r** and linear momentum **p** is defined as

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}. \tag{8.1}$$

It follows that

$$L_x = y\,p_z - z\,p_y, \tag{8.2}$$

$$L_y = z\,p_x - x\,p_z, \tag{8.3}$$

$$L_z = x\,p_y - y\,p_x. \tag{8.4}$$

Let us, first of all, consider whether it is possible to use the above expressions as the definitions of the operators corresponding to the components of angular momentum in quantum mechanics, assuming that the x_i and p_i (where $x_1 \equiv x$, $p_1 \equiv p_x$, $x_2 \equiv y$, *etc.*) correspond to the appropriate quantum mechanical position and momentum operators. The first point to note is that expressions (8.2)–(8.4) are *unambiguous* with respect to the order of the terms in multiplicative factors, since the various position and momentum operators appearing in them all *commute* with one another [see Eqs. (7.17)]. Moreover, given that the x_i and the p_i are Hermitian operators, it is easily seen that the L_i are also *Hermitian*. This is important, since only Hermitian operators can represent physical variables in quantum mechanics (see Sect. 4.6). We, thus, conclude that Eqs. (8.2)–(8.4) are plausible definitions for the quantum mechanical operators which represent the components of angular momentum.

Let us now derive the commutation relations for the L_i. For instance,

$$\begin{aligned}[L_x, L_y] &= [y\,p_z - z\,p_y, z\,p_x - x\,p_z] = y\,p_x\,[p_z, z] + x\,p_y\,[z, p_z] \\ &= i\,\hbar\,(x\,p_y - y\,p_x) = i\,\hbar\,L_z, \end{aligned} \tag{8.5}$$

where use has been made of the definitions of the L_i [see Eqs. (8.2)–(8.4)], and commutation relations (7.15)–(7.17) for the x_i and p_i. There are two similar commutation as well as

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \tag{8.29}$$

and

$$L_\pm = \hbar\, e^{\pm i\,\phi}\left(\pm\frac{\partial}{\partial\theta} + i\,\cot\theta\,\frac{\partial}{\partial\phi}\right). \tag{8.30}$$

We, thus, conclude that all of our angular momentum operators can be represented as differential operators involving the *angular* spherical coordinates, θ and ϕ, but not involving the *radial* coordinate, r.

8.4 Eigenstates of Angular Momentum

Let us find the simultaneous eigenstates of the angular momentum operators L_z and L^2. Since both of these operators can be represented as purely angular differential operators, it stands to reason that their eigenstates only depend on the angular coordinates θ and ϕ. Thus, we can write

$$L_z\,Y_{l,m}(\theta,\phi) = m\,\hbar\,Y_{l,m}(\theta,\phi), \tag{8.31}$$

$$L^2\,Y_{l,m}(\theta,\phi) = l\,(l+1)\,\hbar^2\,Y_{l,m}(\theta,\phi). \tag{8.32}$$

Here, the $Y_{l,m}(\theta,\phi)$ are the eigenstates in question, whereas the dimensionless quantities m and l parameterize the eigenvalues of L_z and L^2, which are $m\,\hbar$ and $l\,(l+1)\,\hbar^2$, respectively. Of course, we expect the $Y_{l,m}$ to be both mutually orthogonal and properly normalized (see Sect. 4.9), so that

$$\oint Y^*_{l',m'}(\theta,\phi)\,Y_{l,m}(\theta,\phi)\,d\Omega = \delta_{ll'}\,\delta_{mm'}, \tag{8.33}$$

where $d\Omega = \sin\theta\,d\theta\,d\phi$ is an element of solid angle, and the integral is over all solid angle.

Now,

$$\begin{aligned} L_z\,(L_+\,Y_{l,m}) &= (L_+\,L_z + [L_z, L_+])\,Y_{l,m} = (L_+\,L_z + \hbar\,L_+)\,Y_{l,m} \\ &= (m+1)\,\hbar\,(L_+\,Y_{l,m}), \end{aligned} \tag{8.34}$$

where use has been made of Eq. (8.18). We, thus, conclude that when the operator L_+ operates on an eigenstate of L_z corresponding to the eigenvalue $m\,\hbar$ it converts it to an eigenstate corresponding to the eigenvalue $(m+1)\,\hbar$. Hence, L_+ is known as the *raising operator* (for L_z). It is also easily demonstrated that

$$L_z\,(L_-\,Y_{l,m}) = (m-1)\,\hbar\,(L_-\,Y_{l,m}). \tag{8.35}$$

Thus, $\epsilon_{123} = \epsilon_{231} = 1$, $\epsilon_{321} = \epsilon_{132} = -1$, and $\epsilon_{112} = \epsilon_{131} = 0$, *etc.* Equation (9.6) also makes use of the *Einstein summation convention*, according to which repeated indices are summed (from 1 to 3). For instance, $a_i\, b_i \equiv a_1\, b_1 + a_2\, b_2 + a_3\, b_3$. Making use of this convention, as well as Eq. (9.7), it is easily seen that Eqs. (9.5) and (9.6) are indeed equivalent.

Let us calculate the value of L^2 using Eq. (9.6). According to our new notation, L^2 is the same as $L_i\, L_i$. Thus, we obtain

$$L^2 = \epsilon_{ijk}\, x_j\, p_k\, \epsilon_{ilm}\, x_l\, p_m = \epsilon_{ijk}\, \epsilon_{ilm}\, x_j\, p_k\, x_l\, p_m. \tag{9.8}$$

Note that we are able to shift the position of ϵ_{ilm} because its elements are just numbers, and, therefore, commute with all of the x_i and the p_i. Now, it is easily demonstrated that

$$\epsilon_{ijk}\, \epsilon_{ilm} \equiv \delta_{jl}\, \delta_{km} - \delta_{jm}\, \delta_{kl}. \tag{9.9}$$

Here δ_{ij} is the usual *Kronecker delta*, whose elements are determined according to the rule

$$\delta_{ij} = \begin{cases} 1 & \text{if } i \text{ and } j \text{ the same} \\ 0 & \text{if } i \text{ and } j \text{ different} \end{cases}. \tag{9.10}$$

It follows from Eqs. (9.8) and (9.9) that

$$L^2 = x_i\, p_j\, x_i\, p_j - x_i\, p_j\, x_j\, p_i. \tag{9.11}$$

Here, we have made use of the fairly self-evident result that $\delta_{ij}\, a_i\, b_j \equiv a_i\, b_i$. We have also been careful to preserve the order of the various terms on the right-hand side of the above expression, since the x_i and the p_i do not necessarily commute with one another.

We now need to rearrange the order of the terms on the right-hand side of Eq. (9.11). We can achieve this by making use of the fundamental commutation relation for the x_i and the p_i [see Eq. (7.17)]:

$$[x_i, p_j] = i\,\hbar\,\delta_{ij}. \tag{9.12}$$

Thus,

$$\begin{aligned} L^2 &= x_i\,(x_i\, p_j - [x_i, p_j])\, p_j - x_i\, p_j\, (p_i\, x_j + [x_j, p_i]) \\ &= x_i\, x_i\, p_j\, p_j - i\,\hbar\,\delta_{ij}\, x_i\, p_j - x_i\, p_j\, p_i\, x_j - i\,\hbar\,\delta_{ij}\, x_i\, p_j \\ &= x_i\, x_i\, p_j\, p_j - x_i\, p_i\, p_j\, x_j - 2\,i\,\hbar\, x_i\, p_i. \end{aligned} \tag{9.13}$$

Here, we have made use of the fact that $p_j\, p_i = p_i\, p_j$, since the p_i commute with one another [see Eq. (7.16)]. Next,

$$L^2 = x_i\, x_i\, p_j\, p_j - x_i\, p_i\,(x_j\, p_j - [x_j, p_j]) - 2\,i\,\hbar\, x_i\, p_i. \tag{9.14}$$

Now, according to (9.12),

$$[x_j, p_j] \equiv [x_1, p_1] + [x_2, p_2] + [x_3, p_3] = 3\,i\,\hbar. \tag{9.15}$$

Hence, we obtain

$$L^2 = x_i\, x_i\, p_j\, p_j - x_i\, p_i\, x_j\, p_j + i\,\hbar\, x_i\, p_i. \tag{9.16}$$

When expressed in more conventional vector notation, the above expression becomes

$$L^2 = r^2\, p^2 - (\mathbf{r}\cdot\mathbf{p})^2 + i\,\hbar\,\mathbf{r}\cdot\mathbf{p}. \tag{9.17}$$

Note that if we had attempted to derive the above expression directly from Eq. (9.5), using standard vector identities, then we would have missed the final term on the right-hand side. This term originates from the lack of commutation between the x_i and p_i operators in quantum mechanics. Of course, standard vector analysis assumes that all terms commute with one another.

Equation (9.17) can be rearranged to give

$$p^2 = r^{-2}\left[(\mathbf{r}\cdot\mathbf{p})^2 - i\,\hbar\,\mathbf{r}\cdot\mathbf{p} + L^2\right]. \tag{9.18}$$

Now,

$$\mathbf{r}\cdot\mathbf{p} = r\, p_r = -i\,\hbar\, r\,\frac{\partial}{\partial r}, \tag{9.19}$$

where use has been made of Eq. (9.4). Hence, we obtain

$$p^2 = -\hbar^2\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\frac{\partial}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2\, r^2}\right]. \tag{9.20}$$

Finally, the above equation can be combined with Eq. (9.2) to give the following expression for the Hamiltonian:

$$H = -\frac{\hbar^2}{2\,m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2\, r^2}\right) + V(r). \tag{9.21}$$

Let us now consider whether the above Hamiltonian commutes with the angular momentum operators L_z and L^2. Recall, from Sect. 8.3, that L_z and L^2 are represented as differential operators which depend solely on the angular spherical polar coordinates, θ and ϕ, and do not contain the radial polar coordinate, r. Thus, any function of r, or any differential operator involving r (but not θ and ϕ), will automatically commute with L^2 and L_z. Moreover, L^2 commutes both with itself, and with L_z (see Sect. 8.2). It is, therefore, clear that the above Hamiltonian commutes with both L_z and L^2.

Now, according to Sect. 4.10, if two operators commute with one another then they possess simultaneous eigenstates. We thus conclude that *for a particle moving in a central potential the eigenstates of the Hamiltonian are simultaneous eigenstates of* L_z *and* L^2. Now, we have already found the simultaneous eigenstates of L_z and L^2—they are the spherical harmonics, $Y_{l,m}(\theta,\phi)$, discussed in Sect. 8.7. It follows that the spherical harmonics are also eigenstates of the Hamiltonian. This observation leads us to try the following separable form for the stationary wavefunction:

$$\psi(r,\theta,\phi) = R(r)\, Y_{l,m}(\theta,\phi). \tag{9.22}$$

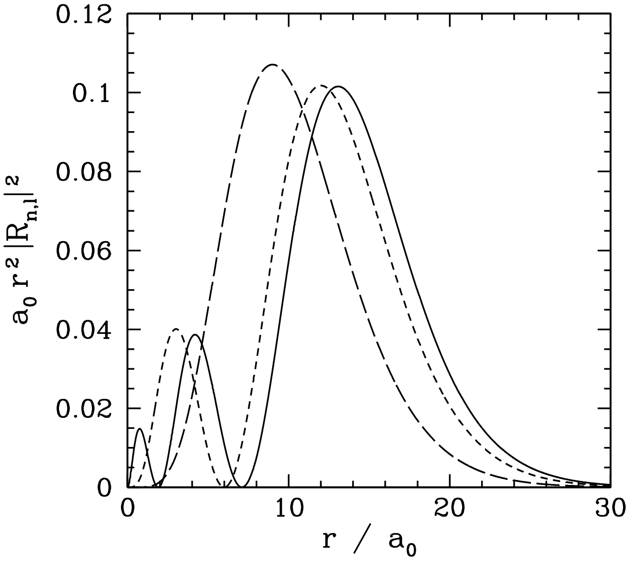

Figure 9.3: *The* $a_0\, r^2\, |R_{n,l}(r)|^2$ *plotted as a functions of* r/a_0. *The solid, short-dashed, and long-dashed curves correspond to* $n, l = 3, 0$, *and* $3, 1$, *and* $3, 2$, *respectively.*

where the angle-brackets denote an expectation value. For instance, it can be demonstrated (after much tedious algebra) that

$$\langle r^2\rangle = \frac{a_0^{\,2}\, n^2}{2}\,[5\, n^2 + 1 - 3\, l\, (l+1)], \tag{9.72}$$

$$\langle r\rangle = \frac{a_0}{2}\,[3\, n^2 - l\, (l+1)], \tag{9.73}$$

$$\left\langle \frac{1}{r}\right\rangle = \frac{1}{n^2\, a_0}, \tag{9.74}$$

$$\left\langle \frac{1}{r^2}\right\rangle = \frac{1}{(l+1/2)\, n^3\, a_0^{\,2}}, \tag{9.75}$$

$$\left\langle \frac{1}{r^3}\right\rangle = \frac{1}{l\,(l+1/2)\,(l+1)\, n^3\, a_0^{\,3}}. \tag{9.76}$$

According to Eq. (9.55), the energy levels of the bound-states of a hydrogen atom only depend on the radial quantum number n. It turns out that this is a special property of a $1/r$ potential. For a general central potential, $V(r)$, the quantized energy levels of a bound-state depend on both n and l (see Sect. 9.3).

The fact that the energy levels of a hydrogen atom only depend on n, and not on l and m, implies that the energy spectrum of a hydrogen atom is *highly degenerate*: *i.e.*, there are many different states which possess the same energy. According to the inequality (9.61) (and the fact that n, l, and m are integers), for a given value of l, there are $2\, l+1$ different allowed values of m (*i.e.*, $-l, -l+1, \cdots, l-1, l$). Likewise, for a given value of n, there leads to the null state [see Eq. (10.31)]. If this is not the case then we will inevitably obtain eigenstates of S_z corresponding to $m_s > s$, which we have already demonstrated is impossible.

It follows, from the above argument, that

$$m_{s\,max} - m_{s\,min} = 2\,s = k, \tag{10.32}$$

where k is a positive integer. Hence, the quantum number s can either take *positive integer* or *positive half-integer* values. Up to now, our analysis has been very similar to that which we used earlier to investigate orbital angular momentum (see Sect. 8). Recall, that for orbital angular momentum the quantum number m, which is analogous to m_s, is restricted to take *integer* values (see Cha. 8.5). This implies that the quantum number l, which is analogous to s, is also restricted to take integer values. However, the origin of these restrictions is the representation of the orbital angular momentum operators as differential operators in real space (see Sect. 8.3). There is no equivalent representation of the corresponding spin angular momentum operators. Hence, we conclude that there is no reason why the quantum number s cannot take half-integer, as well as integer, values.

In 1940, Wolfgang Pauli proved the so-called *spin-statistics theorem* using relativistic quantum mechanics. According to this theorem, all *fermions* possess *half-integer spin* (*i.e.*, a half-integer value of s), whereas all *bosons* possess *integer spin* (*i.e.*, an integer value of s). In fact, all presently known fermions, including electrons and protons, possess *spin one-half*. In other words, electrons and protons are characterized by $s = 1/2$ and $m_s = \pm 1/2$.

10.5 Pauli Representation

Let us denote the two independent spin eigenstates of an electron as

$$\chi_\pm \equiv \chi_{1/2,\pm 1/2}. \tag{10.33}$$

It thus follows, from Eqs. (10.16) and (10.17), that

$$S_z\,\chi_\pm = \pm\frac{1}{2}\,\hbar\,\chi_\pm, \tag{10.34}$$

$$S^2\,\chi_\pm = \frac{3}{4}\,\hbar^2\,\chi_\pm. \tag{10.35}$$

Note that χ_+ corresponds to an electron whose spin angular momentum vector has a positive component along the z-axis. Loosely speaking, we could say that the spin vector points in the $+z$-direction (or its spin is “up”). Likewise, χ_- corresponds to an electron whose spin points in the $-z$-direction (or whose spin is “down”). These two eigenstates satisfy the orthonormality requirements

$$\chi_+^\dagger\,\chi_+ = \chi_-^\dagger\,\chi_- = 1, \tag{10.36}$$

	$-1,-1/2$	$-1,1/2$	$0,-1/2$	$0,1/2$	$1,-1/2$	$1,1/2$	m, m_s
$3/2,-3/2$	1						
$3/2,-1/2$		$\sqrt{1/3}$	$\sqrt{2/3}$				
$1/2,-1/2$		$\sqrt{2/3}$	$-\sqrt{1/3}$				
$3/2,1/2$				$\sqrt{2/3}$	$\sqrt{1/3}$		
$1/2,1/2$				$\sqrt{1/3}$	$-\sqrt{2/3}$		
$3/2,3/2$						1	
j, m_j							

Table 11.2: *Clebsch-Gordon coefficients for adding spin one-half to spin one. Only non-zero coefficients are shown.*

$$\psi^{(1)}_{1,-1/2} = \sqrt{\frac{1}{3}}\,\psi^{(2)}_{3/2,1/2} - \sqrt{\frac{2}{3}}\,\psi^{(2)}_{1/2,1/2}, \tag{11.57}$$

$$\psi^{(1)}_{0,1/2} = \sqrt{\frac{2}{3}}\,\psi^{(2)}_{3/2,1/2} + \sqrt{\frac{1}{3}}\,\psi^{(2)}_{1/2,1/2}, \tag{11.58}$$

$$\psi^{(1)}_{0,-1/2} = \sqrt{\frac{2}{3}}\,\psi^{(2)}_{3/2,-1/2} - \sqrt{\frac{1}{3}}\,\psi^{(2)}_{1/2,-1/2}, \tag{11.59}$$

$$\psi^{(1)}_{-1,1/2} = \sqrt{\frac{1}{3}}\,\psi^{(2)}_{3/2,-1/2} + \sqrt{\frac{2}{3}}\,\psi^{(2)}_{1/2,-1/2}, \tag{11.60}$$

Thus, if we know that an electron in a hydrogen atom is in an $l = 1$ state characterized by $m = 0$ and $m_s = 1/2$ [*i.e.*, the state represented by $\psi^{(1)}_{0,1/2}$] then, according to Eq. (11.58), a measurement of the total angular momentum will yield $j = 3/2$, $m_j = 1/2$ with probability $2/3$, and $j = 1/2$, $m_j = 1/2$ with probability $1/3$. Suppose that we make such a measurement, and obtain the result $j = 3/2$, $m_j = 1/2$. As a result of the measurement, the electron is thrown into the corresponding eigenstate, $\psi^{(2)}_{3/2,1/2}$. It thus follows from Eq. (11.52) that a subsequent measurement of L_z and S_z will yield $m = 0$, $m_s = 1/2$ with probability $2/3$, and $m = 1$, $m_s = -1/2$ with probability $1/3$.

The information contained in Eqs. (11.51)–(11.59) is neatly summed up in Table 11.2. Note that each row and column of this table has unit norm, and also that the different rows and different columns are mutually orthogonal. Of course, this is because the $\psi^{(1)}$ and $\psi^{(2)}$ eigenstates are orthonormal.

11.4 Two Spin One-Half Particles

Consider a system consisting of two spin one-half particles. Suppose that the system does not possess any orbital angular momentum. Let $\mathbf{S}_1$ and $\mathbf{S}_2$ be the spin angular momentum

(a) In the spin singlet state.

(b) In the spin triplet state.

3. Consider two electrons in a spin singlet state.

   (a) If a measurement of the spin of one of the electrons shows that it is in the state with $S_z = \hbar/2$, what is the probability that a measurement of the z-component of the spin of the other electron yields $S_z = \hbar/2$?

   (b) If a measurement of the spin of one of the electrons shows that it is in the state with $S_y = \hbar/2$, what is the probability that a measurement of the x-component of the spin of the other electron yields $S_x = -\hbar/2$?

   Finally, if electron 1 is in a spin state described by $\cos\alpha_1\,\chi_+ + \sin\alpha_1\,e^{i\beta_1}\,\chi_-$, and electron 2 is in a spin state described by $\cos\alpha_2\,\chi_+ + \sin\alpha_2\,e^{i\beta_2}\,\chi_-$, what is the probability that the two-electron spin state is a triplet state?

Finally, if ψ is a spinor then we have

$$A_{ij} = \psi_i^\dagger\, A\, \psi_j. \tag{12.17}$$

We can represent all of the above possibilities by writing

$$A_{ij} = \langle \psi_i | A | \psi_j \rangle \equiv \langle i | A | j \rangle. \tag{12.18}$$

The expansion (12.14) thus becomes

$$\langle A \rangle \equiv \langle a | A | a \rangle = \sum_{i,j} \langle a | i \rangle \langle i | A | j \rangle \langle j | a \rangle. \tag{12.19}$$

Incidentally, it follows that [see Eq. (4.58)]

$$\langle i | A | j \rangle^* = \langle j | A^\dagger | i \rangle. \tag{12.20}$$

Finally, it is clear from Eq. (12.19) that

$$\sum_i |i\rangle\langle i| \equiv 1, \tag{12.21}$$

where the ψ_i are a *complete* set of eigenstates, and 1 is the identity operator.

12.3 Two-State System

Consider the simplest possible non-trivial quantum mechanical system. In such a system, there are only *two* independent eigenstates of the unperturbed Hamiltonian: *i.e.*,

$$H_0\, \psi_1 = E_1\, \psi_1, \tag{12.22}$$

$$H_0\, \psi_2 = E_2\, \psi_2. \tag{12.23}$$

It is assumed that these states, and their associated eigenvalues, are known. We also expect the states to be orthonormal, and to form a complete set.

Let us now try to solve the modified energy eigenvalue problem

$$(H_0 + H_1)\, \psi_E = E\, \psi_E. \tag{12.24}$$

We can, in fact, solve this problem exactly. Since the eigenstates of H_0 form a complete set, we can write [see Eq. (12.12)]

$$\psi_E = \langle 1 | E \rangle\, \psi_1 + \langle 2 | E \rangle\, \psi_2. \tag{12.25}$$

It follows from (12.24) that

$$\langle i | H_0 + H_1 | E \rangle = E\, \langle i | E \rangle, \tag{12.26}$$

where $i = 1$ or 2. Equations (12.22), (12.23), (12.25), (12.26), and the orthonormality condition

$$\langle i|j\rangle = \delta_{ij}, \tag{12.27}$$

yield two coupled equations which can be written in matrix form:

$$\left(\begin{array}{cc} E_1 - E + e_{11} & e_{12} \\ e_{12}^{*} & E_2 - E + e_{22} \end{array}\right)\left(\begin{array}{c} \langle 1|E\rangle \\ \langle 2|E\rangle \end{array}\right) = \left(\begin{array}{c} 0 \\ 0 \end{array}\right), \tag{12.28}$$

where

$$\begin{aligned} e_{11} &= \langle 1|H_1|1\rangle, &(12.29)\\ e_{22} &= \langle 2|H_1|2\rangle, &(12.30)\\ e_{12} &= \langle 1|H_1|2\rangle = \langle 2|H_1|1\rangle^{*}. &(12.31) \end{aligned}$$

Here, use has been made of the fact that H_1 is an Hermitian operator.

Consider the special (but not uncommon) case of a perturbing Hamiltonian whose diagonal matrix elements are zero, so that

$$e_{11} = e_{22} = 0. \tag{12.32}$$

The solution of Eq. (12.28) (obtained by setting the determinant of the matrix to zero) is

$$E = \frac{(E_1 + E_2) \pm \sqrt{(E_1 - E_2)^2 + 4\,|e_{12}|^2}}{2}. \tag{12.33}$$

Let us expand in the supposedly small parameter

$$\epsilon = \frac{|e_{12}|}{|E_1 - E_2|}. \tag{12.34}$$

We obtain

$$E \simeq \frac{1}{2}\,(E_1 + E_2) \pm \frac{1}{2}\,(E_1 - E_2)(1 + 2\,\epsilon^2 + \cdots). \tag{12.35}$$

The above expression yields the modification of the energy eigenvalues due to the perturbing Hamiltonian:

$$\begin{aligned} E_1' &= E_1 + \frac{|e_{12}|^2}{E_1 - E_2} + \cdots, &(12.36)\\ E_2' &= E_2 - \frac{|e_{12}|^2}{E_1 - E_2} + \cdots. &(12.37) \end{aligned}$$

Note that H_1 causes the upper eigenvalue to rise, and the lower to fall. It is easily demonstrated that the modified eigenstates take the form

$$\begin{aligned} \psi_1' &= \psi_1 + \frac{e_{12}^{*}}{E_1 - E_2}\,\psi_2 + \cdots, &(12.38)\\ \psi_2' &= \psi_2 - \frac{e_{12}}{E_1 - E_2}\,\psi_1 + \cdots. &(12.39) \end{aligned}$$

The $\psi^{(1)}_{nlm}$ are also chosen so as to be orthonormal: *i.e.*,

$$\langle n, l'^{(1)}, m|n, l^{(1)}, m\rangle = \delta_{ll'}. \tag{12.94}$$

It follows that

$$\langle n, l'^{(1)}, m|H_1|n, l^{(1)}, m\rangle = \lambda_{nl}\,\delta_{ll'}. \tag{12.95}$$

Thus, if we use the new eigenstates, instead of the old ones, then we can employ Eqs. (12.88) and (12.89) directly, since all of the singular terms vanish. The only remaining difficulty is to determine the new eigenstates in terms of the original ones.

Now [see Eq. (12.21)]

$$\sum_{l=1,N_n} |n, l, m\rangle\langle n, l, m| \equiv 1, \tag{12.96}$$

where 1 denotes the identity operator in the sub-space of all coupled unperturbed eigenstates corresponding to the eigenvalue E_n. Using this completeness relation, the eigenvalue equation (12.93) can be transformed into a straightforward matrix equation:

$$\sum_{l''=1,N_n} \langle n, l', m|H_1|n, l'', m\rangle\, \langle n, l'', m|n, l^{(1)}, m\rangle = \lambda_{nl}\, \langle n, l', m|n, l^{(1)}, m\rangle. \tag{12.97}$$

This can be written more transparently as

$$\mathbf{U}\,\mathbf{x} = \lambda\,\mathbf{x}, \tag{12.98}$$

where the elements of the $N_n \times N_n$ Hermitian matrix $\mathbf{U}$ are

$$U_{jk} = \langle n, j, m|H_1|n, k, m\rangle. \tag{12.99}$$

Provided that the determinant of $\mathbf{U}$ is non-zero, Eq. (12.98) can always be solved to give N_n eigenvalues λ_{nl} (for $l = 1$ to N_n), with N_n corresponding eigenvectors $\mathbf{x}_{nl}$. The normalized eigenvectors specify the weights of the new eigenstates in terms of the original eigenstates: *i.e.*,

$$(\mathbf{x}_{nl})_k = \langle n, k, m|n, l^{(1)}, m\rangle, \tag{12.100}$$

for $k = 1$ to N_n. In our new scheme, Eqs. (12.88) and (12.89) yield

$$E'_{nl} = E_n + \lambda_{nl} + \sum_{n'\neq n, l'=l\pm 1} \frac{|e_{n'l'nl}|^2}{E_n - E_{n'}}, \tag{12.101}$$

and

$$\psi^{(1)'}_{nlm} = \psi^{(1)}_{nlm} + \sum_{n'\neq n, l'=l\pm 1} \frac{e_{n'l'nl}}{E_n - E_{n'}}\,\psi_{n'l'm}. \tag{12.102}$$

There are no singular terms in these expressions, since the summations are over $n' \neq n$: *i.e.*, they specifically exclude the problematic, degenerate, unperturbed energy eigenstates corresponding to the eigenvalue E_n. Note that the first-order energy shifts are equivalent to the eigenvalues of the matrix equation (12.98).

However, Schrödinger's equation for a unperturbed hydrogen atom can be written

$$p^2\,\psi_{n,l,m} = 2\,m_e\,(E_n - V)\,\psi_{n,l,m}, \tag{12.118}$$

where $V = -e^2/(4\pi\epsilon_0\,r)$. Since p^2 is an Hermitian operator, it follows that

$$\begin{aligned}\Delta E_{nlm} &= -\frac{1}{2\,m_e\,c^2}\,\langle n,l,m|(E_n-V)^2|n,l,m\rangle\\ &= -\frac{1}{2\,m_e\,c^2}\left(E_n^{\,2} - 2\,E_n\,\langle n,l,m|V|n,l,m\rangle + \langle n,l,m|V^2|n,l,m\rangle\right)\\ &= -\frac{1}{2\,m_e\,c^2}\left[E_n^{\,2} + 2\,E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right].\end{aligned} \tag{12.119}$$

It follows from Eqs. (9.74) and (9.75) that

$$\Delta E_{nlm} = -\frac{1}{2\,m_e\,c^2}\left[E_n^{\,2} + 2\,E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{n^2\,a_0} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{(l+1/2)\,n^3\,a_0^2}\right]. \tag{12.120}$$

Finally, making use of Eqs. (9.55), (9.57), and (9.58), the above expression reduces to

$$\Delta E_{nlm} = E_n\,\frac{\alpha^2}{n^2}\left(\frac{n}{l+1/2} - \frac{3}{4}\right), \tag{12.121}$$

where

$$\alpha = \frac{e^2}{4\pi\epsilon_0\,\hbar\,c} \simeq \frac{1}{137} \tag{12.122}$$

is the dimensionless *fine structure constant*.

Note that the above derivation implicitly assumes that p^4 is an Hermitian operator. It turns out that this is not the case for $l = 0$ states. However, somewhat fortuitously, our calculation still gives the correct answer when $l = 0$. Note, also, that we are able to use *non-degenerate* perturbation theory in the above calculation, using the ψ_{nlm} eigenstates, because the perturbing Hamiltonian commutes with both L^2 and L_z. It follows that there is no coupling between states with different l and m quantum numbers. Hence, all coupled states have different n quantum numbers, and therefore have different energies.

Now, an electron in a hydrogen atom experiences an electric field

$$\mathbf{E} = \frac{e\,\mathbf{r}}{4\pi\epsilon_0\,r^3} \tag{12.123}$$

due to the charge on the nucleus. However, according to electromagnetic theory, a non-relativistic particle moving in a electric field $\mathbf{E}$ with velocity $\mathbf{v}$ also experiences an effective magnetic field

$$\mathbf{B} = -\frac{\mathbf{v}\times\mathbf{E}}{c^2}. \tag{12.124}$$

where $\mathbf{A}(\mathbf{r})$ is the vector potential, and $\phi(\mathbf{r})$ the scalar potential. Note that

$$\mathbf{E} = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}, \tag{13.67}$$

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{13.68}$$

This prescription also works in quantum mechanics. Thus, the Hamiltonian of an atomic electron placed in an electromagnetic field is

$$H = \frac{(\mathbf{p} - e\,\mathbf{A})^2}{2\,m_e} + e\,\phi + V_0(r), \tag{13.69}$$

where $\mathbf{A}$ and ϕ are functions of the position operators. The above equation can be written

$$H = \frac{\left(p^2 - e\,\mathbf{A}\cdot\mathbf{p} - e\,\mathbf{p}\cdot\mathbf{A} + e^2 A^2\right)}{2\,m_e} + e\,\phi + V_0(r). \tag{13.70}$$

Now,

$$\mathbf{p}\cdot\mathbf{A} = \mathbf{A}\cdot\mathbf{p}, \tag{13.71}$$

provided that we adopt the gauge $\nabla\cdot\mathbf{A} = 0$. Hence,

$$H = \frac{p^2}{2\,m_e} - \frac{e\,\mathbf{A}\cdot\mathbf{p}}{m_e} + \frac{e^2 A^2}{2\,m_e} + e\,\phi + V_0(r). \tag{13.72}$$

Suppose that the perturbation corresponds to a linearly polarized, monochromatic, plane-wave. In this case,

$$\phi = 0, \tag{13.73}$$

$$\mathbf{A} = A_0\,\boldsymbol{\epsilon}\,\cos(\mathbf{k}\cdot\mathbf{r} - \omega t), \tag{13.74}$$

where $\mathbf{k}$ is the wavevector (note that $\omega = k\,c$), and $\boldsymbol{\epsilon}$ a unit vector which specifies the direction of polarization (*i.e.*, the direction of $\mathbf{E}$). Note that $\boldsymbol{\epsilon}\cdot\mathbf{k} = 0$. The Hamiltonian becomes

$$H = H_0 + H_1(t), \tag{13.75}$$

with

$$H_0 = \frac{p^2}{2\,m_e} + V_0(r), \tag{13.76}$$

and

$$H_1 \simeq -\frac{e\,\mathbf{A}\cdot\mathbf{p}}{m_e}, \tag{13.77}$$

where the A^2 term, which is second order in A_0, has been neglected.

The perturbing Hamiltonian can be written

$$H_1 = -\frac{e\,A_0\,\boldsymbol{\epsilon}\cdot\mathbf{p}}{2\,m_e}\left[\exp(\,i\,\mathbf{k}\cdot\mathbf{r} - i\,\omega t) + \exp(-i\,\mathbf{k}\cdot\mathbf{r} + i\,\omega t)\right]. \tag{13.78}$$

This has the same form as Eq. (13.51), provided that

$$V^\dagger = -\frac{e\,A_0\,\boldsymbol{\epsilon}\cdot\mathbf{p}}{2\,m_e}\,\exp(\,i\,\mathbf{k}\cdot\mathbf{r}\,). \tag{13.79}$$

It follows from Eqs. (13.53), (13.63), and (13.79) that the transition probability for radiation induced absorption is

$$P^{abs}_{i\rightarrow f}(t) = \frac{t^2}{\hbar^2}\,\frac{e^2\,|A_0|^2}{4\,m_e^2}\,|\langle f|\boldsymbol{\epsilon}\cdot\mathbf{p}\,\exp(\,i\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^2\,\text{sinc}^2[(\omega-\omega_{fi})\,t/2]. \tag{13.80}$$

Now, the mean energy density of an electromagnetic wave is

$$u = \frac{1}{2}\left(\frac{\epsilon_0\,|E_0|^2}{2}+\frac{|B_0|^2}{2\,\mu_0}\right) = \frac{1}{2}\,\epsilon_0\,|E_0|^2, \tag{13.81}$$

where $E_0 = A_0\,\omega$ and $B_0 = E_0/c$ are the peak electric and magnetic field-strengths, respectively. It thus follows that

$$P^{abs}_{i\rightarrow f}(t) = \frac{t^2\,e^2}{2\,\epsilon_0\,\hbar^2\,m_e^2\,\omega^2}\,|\langle f|\boldsymbol{\epsilon}\cdot\mathbf{p}\,\exp(\,i\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^2\,u\,\text{sinc}^2[(\omega-\omega_{fi})\,t/2]. \tag{13.82}$$

Thus, not surprisingly, the transition probability for radiation induced absorption (or stimulated emission) is directly proportional to the *energy density* of the incident radiation.

Suppose that the incident radiation is not monochromatic, but instead extends over a range of frequencies. We can write

$$u = \int_{-\infty}^{\infty}\rho(\omega)\,d\omega, \tag{13.83}$$

where $\rho(\omega)\,d\omega$ is the energy density of radiation whose frequencies lie between ω and $\omega + d\omega$. Equation (13.82) generalizes to

$$P^{abs}_{i\rightarrow f}(t) = \int_{-\infty}^{\infty}\frac{t^2\,e^2}{2\,\epsilon_0\,\hbar^2\,m_e^2\,\omega^2}\,|\langle f|\boldsymbol{\epsilon}\cdot\mathbf{p}\,\exp(\,i\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^2\,\rho(\omega)\,\text{sinc}^2[(\omega-\omega_{fi})\,t/2]\,d\omega. \tag{13.84}$$

Note, however, that the above expression is only valid provided the radiation in question is *incoherent*: *i.e.*, there are no phase correlations between waves of different frequencies. This follows because it is permissible to add the *intensities* of incoherent radiation, whereas we must always add the *amplitudes* of coherent radiation. Given that the function $\text{sinc}^2[(\omega-\omega_{fi})\,t/2]$ is very strongly peaked (see Fig. 13.1) about $\omega = \omega_{fi}$ (assuming that $t \gg 2\pi/\omega_{fi}$), and

$$\int_{-\infty}^{\infty}\text{sinc}^2(x)\,dx = \pi, \tag{13.85}$$

the above equation reduces to

$$P^{abs}_{i\rightarrow f}(t) = \frac{\pi\,e^2\,\rho(\omega_{fi})}{\epsilon_0\,\hbar^2\,m_e^2\,\omega_{fi}^2}\,|\langle f|\boldsymbol{\epsilon}\cdot\mathbf{p}\,\exp(\,i\,\mathbf{k}\cdot\mathbf{r})|i\rangle|^2\,t. \tag{13.86}$$

where $d\Omega = \sin\theta\, d\theta\, d\phi$, and the integral is taken over all solid angle. It is easily demonstrated that

$$\left\langle |\boldsymbol{\epsilon}\cdot\mathbf{d}_{if}|^2\right\rangle_{av} = \frac{d_{if}^2}{3}. \tag{13.105}$$

Here, d_{if}^2 stands for

$$d_{if}^2 = |\langle f|e\,x|i\rangle|^2 + |\langle f|e\,y|i\rangle|^2 + |\langle f|e\,z|i\rangle|^2. \tag{13.106}$$

Hence, the transition rates for absorption and stimulated emission induced by unpolarized isotropic radiation are

$$w_{i\to f}^{abs} = \frac{\pi}{3\,\epsilon_0\,\hbar^2}\, d_{if}^2\, \rho(\omega_{fi}), \tag{13.107}$$

$$w_{i\to f}^{stm} = \frac{\pi}{3\,\epsilon_0\,\hbar^2}\, d_{if}^2\, \rho(\omega_{if}), \tag{13.108}$$

respectively.

13.9 Spontaneous Emission

So far, we have calculated the rates of *radiation induced* transitions between two atomic states. This process is known as *absorption* when the energy of the final state exceeds that of the initial state, and *stimulated emission* when the energy of the final state is less than that of the initial state. Now, in the absence of any external radiation, we would not expect an atom in a given state to spontaneously jump into an state with a higher energy. On the other hand, it should be possible for such an atom to spontaneously jump into an state with a lower energy via the emission of a photon whose energy is equal to the difference between the energies of the initial and final states. This process is known as *spontaneous emission*.

It is possible to derive the rate of spontaneous emission between two atomic states from a knowledge of the corresponding absorption and stimulated emission rates using a famous thermodynamic argument due to Einstein. Consider a very large ensemble of similar atoms placed inside a closed cavity whose walls (which are assumed to be perfect emitters and absorbers of radiation) are held at the constant temperature T. Let the system have attained thermal equilibrium. According to statistical thermodynamics, the cavity is filled with so-called "black-body" electromagnetic radiation whose energy spectrum is

$$\rho(\omega) = \frac{\hbar}{\pi^2\,c^3}\,\frac{\omega^3}{\exp(\hbar\,\omega/k_B\,T) - 1}, \tag{13.109}$$

where k_B is the Boltzmann constant. This well-known result was first obtained by Max Planck in 1900.

Consider two atomic states, labeled i and f, with $E_i > E_f$. One of the tenants of statistical thermodynamics is that in thermal equilibrium we have so-called *detailed balance*. This where the radial functions $R_{n,l}$ are given in Sect. 9.4, and the spherical harmonics $Y_{l,m}$ are given in Sect. 8.7. Some straight-forward, but tedious, integration reveals that

$$\langle 1,0,0|x|2,1,\pm 1\rangle = \pm\frac{2^7}{3^5}\,a_0, \tag{13.136}$$

$$\langle 1,0,0|y|2,1,\pm 1\rangle = i\,\frac{2^7}{3^5}\,a_0, \tag{13.137}$$

$$\langle 1,0,0|z|2,1,0\rangle = \sqrt{2}\,\frac{2^7}{3^5}\,a_0, \tag{13.138}$$

where a_0 is the Bohr radius specified in Eq. (9.58). All of the other possible $2P \rightarrow 1S$ matrix elements are zero because of the selection rules. If follows from Eq. (13.128) that the modulus squared of the dipole moment for the $2P \rightarrow 1S$ transition takes the same value

$$d^2 = \frac{2^{15}}{3^{10}}\,(e\,a_0)^2 \tag{13.139}$$

for $m = 0$, 1, or -1. Clearly, the transition rate is independent of the quantum number m. It turns out that this is a general result.

Now, the energy of the eigenstate of the hydrogen atom characterized by the quantum numbers n, l, m is $E = E_0/n^2$, where the ground-state energy E_0 is specified in Eq. (9.57). Hence, the energy of the photon emitted during a $2P \rightarrow 1S$ transition is

$$\hbar\,\omega = E_0/4 - E_0 = -\frac{3}{4}\,E_0 = 10.2\,\text{eV}. \tag{13.140}$$

This corresponds to a wavelength of 1.215×10^{-7} m.

Finally, according to Eq. (13.115), the $2P \rightarrow 1S$ transition rate is written

$$w_{2P\rightarrow 1S} = \frac{\omega^3\,d^2}{3\pi\,\epsilon_0\,\hbar\,c^3}, \tag{13.141}$$

which reduces to

$$w_{2P\rightarrow 1S} = \left(\frac{2}{3}\right)^8 \alpha^5\,\frac{m_e\,c^2}{\hbar} = 6.27 \times 10^8\,\text{s}^{-1} \tag{13.142}$$

with the aid of Eqs. (13.139) and (13.140). Here, $\alpha = 1/137$ is the fine-structure constant. Hence, the mean life-time of a hydrogen 2P state is

$$\tau_{2P} = (w_{2P\rightarrow 1S})^{-1} = 1.6\,\text{ns}. \tag{13.143}$$

Incidentally, since the 2P state only has a finite life-time, it follows from the energy-time uncertainty relation that the energy of this state is uncertain by an amount

$$\Delta E_{2P} \sim \frac{\hbar}{\tau_{2P}} \sim 4 \times 10^{-7}\,\text{eV}. \tag{13.144}$$

This uncertainty gives rise to a *finite width* of the spectral line associated with the $2P \rightarrow 1S$ transition. This natural line-width is of order

$$\frac{\Delta\lambda}{\lambda} \sim \frac{\Delta E_{2P}}{\hbar\,\omega} \sim 4 \times 10^{-8}. \tag{13.145}$$

13.13 Intensity Rules

Now, we know, from Sect. 12.8, that when we take electron spin and spin-orbit coupling into account the degeneracy of the six 2P states of the hydrogen atom is broken. In fact, these states are divided into two groups with slightly different energies. There are four states characterized by the overall angular momentum quantum number $j = 3/2$—these are called the $2P_{3/2}$ states. The remaining two states are characterized by $j = 1/2$, and are thus called the $2P_{1/2}$ states. The energy of the $2P_{3/2}$ states is slightly higher than that of the $2P_{1/2}$ states. In fact, the energy difference is

$$\Delta E = -\frac{\alpha^2}{16}\,E_0 = 4.53\times 10^{-5}\,\text{eV}. \tag{13.146}$$

Thus, the wavelength of the spectral line associated with the $2P \rightarrow 1S$ transition in hydrogen is split by a relative amount

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta E}{\hbar\,\omega} = 4.4\times 10^{-6}. \tag{13.147}$$

Note that this splitting is much greater than the natural line-width estimated in Eq. (13.145), so there really are two spectral lines. How does all of this affect the rate of the $2P \rightarrow 1S$ transition?

Well, we have seen that the transition rate is independent of spin, and hence of the spin quantum number m_s, and is also independent of the quantum number m. It follows that the transition rate is independent of the z-component of total angular momentum quantum number $m_j = m + m_s$. However, if this is the case, then the transition rate is plainly also independent of the total angular momentum quantum number j. Hence, we expect the $2P_{3/2} \rightarrow 1S$ and $2P_{1/2} \rightarrow 1S$ transition rates to be the *same*. However, there are *four* $2P_{3/2}$ states and only *two* $2P_{1/2}$ states. If these states are equally populated—which we would certainly expect to be the case in thermal equilibrium, since they have almost the same energies—and since they decay to the 1S state at the same rate, it stands to reason that the spectral line associated with the $2P_{3/2} \rightarrow 1S$ transition is *twice* as bright as that associated with the $2P_{1/2} \rightarrow 1S$ transition.

13.14 Forbidden Transitions

Atomic transitions which are forbidden by the electric dipole selection rules (13.133) and (13.134) are unsurprisingly known as *forbidden transitions*. It is clear from the analysis in Sect. 13.8 that a forbidden transition is one for which the matrix element $\langle f|\boldsymbol{\epsilon}\cdot\mathbf{p}|i\rangle$ is zero. However, this matrix element is only an approximation to the true matrix element for radiative transitions, which takes the form $\langle f|\boldsymbol{\epsilon}\cdot\mathbf{p}\,\exp(\,i\,\mathbf{k}\cdot\mathbf{r})|i\rangle$. Expanding $\exp(\,i\,\mathbf{k}\cdot\mathbf{r})$, and keeping the first two terms, the matrix element for a forbidden transition becomes

$$\langle f|\boldsymbol{\epsilon}\cdot\mathbf{p}\,\exp(\,i\,\mathbf{k}\cdot\mathbf{r})|i\rangle \simeq i\,\langle f|(\boldsymbol{\epsilon}\cdot\mathbf{p})\,(\mathbf{k}\cdot\mathbf{r})|i\rangle. \tag{13.148}$$

14 Variational Methods

14.1 Introduction

We have seen, in Sect. 9.4, that we can solve Schrödinger's equation *exactly* to find the stationary eigenstates of a hydrogen atom. Unfortunately, it is not possible to find exact solutions of Schrödinger's equation for atoms more complicated than hydrogen, or for molecules. In such systems, the best that we can do is to find *approximate* solutions. Most of the methods which have been developed for finding such solutions employ the so-called *variational principle* discussed below.

14.2 Variational Principle

Suppose that we wish to solve the time-independent Schrödinger equation

$$H\,\psi = E\,\psi, \tag{14.1}$$

where H is a known (presumably complicated) time-independent Hamiltonian. Let ψ be a *normalized* trial solution to the above equation. The variational principle states, quite simply, that the ground-state energy, E_0, is always less than or equal to the expectation value of H calculated with the trial wavefunction: *i.e.*,

$$E_0 \leq \langle\psi|H|\psi\rangle. \tag{14.2}$$

Thus, by varying ψ until the expectation value of H is *minimized*, we can obtain an approximation to the wavefunction and energy of the ground-state.

Let us prove the variational principle. Suppose that the ψ_n and the E_n are the true eigenstates and eigenvalues of H: *i.e.*,

$$H\,\psi_n = E_n\,\psi_n. \tag{14.3}$$

Furthermore, let

$$E_0 < E_1 < E_2 < \cdots, \tag{14.4}$$

so that ψ_0 is the ground-state, ψ_1 the first excited state, *etc*. The ψ_n are assumed to be orthonormal: *i.e.*,

$$\langle\psi_n|\psi_m\rangle = \delta_{nm}. \tag{14.5}$$

If our trial wavefunction ψ is properly normalized then we can write

$$\psi = \sum_n c_n\,\psi_n, \tag{14.6}$$

as our trial wavefunction, where

$$\psi_0(\mathbf{r}) = \frac{1}{\sqrt{\pi}\, a_0^{3/2}}\, e^{-r/a_0} \tag{14.58}$$

is a normalized hydrogen ground-state wavefunction centered on the origin, and $\mathbf{r}_{1,2}$ are the position vectors of the electron with respect to each of the protons (see Fig. 14.1). Obviously, this is a very simplistic wavefunction, since it is just a linear combination of hydrogen ground-state wavefunctions centered on each proton. Note, however, that the wavefunction respects the obvious symmetries in the problem.

Our first task is to normalize our trial wavefunction. We require that

$$\int |\psi_\pm|^2\, d^3\mathbf{r} = 1. \tag{14.59}$$

Hence, from (14.57), $A = I^{-1/2}$, where

$$I = \int \left[|\psi_0(\mathbf{r}_1)|^2 + |\psi_0(\mathbf{r}_2)|^2 \pm 2\, \psi_0(\mathbf{r}_1)\, \psi_0(\mathbf{r}_2)\right] d^3\mathbf{r}. \tag{14.60}$$

It follows that

$$I = 2\,(1 \pm J), \tag{14.61}$$

with

$$J = \int \psi_0(\mathbf{r}_1)\, \psi_0(\mathbf{r}_2)\, d^3\mathbf{r}. \tag{14.62}$$

Let us employ the standard spherical polar coordinates $(r,\, \theta,\, \phi)$. Now, it is easily seen that $r_1 = r$ and $r_2 = (r^2 + R^2 - 2\, r\, R\, \cos\theta)^{1/2}$. Hence,

$$J = 2 \int_0^\infty \int_0^\pi \exp\left[-x - (x^2 + X^2 - 2\, x\, X\, \cos\theta)^{1/2}\right]\, x^2\, dx\, \sin\theta\, d\theta, \tag{14.63}$$

where $X = R/a_0$. Here, we have already performed the trivial ϕ integral. Let $y = (x^2 + X^2 - 2\, x\, X\, \cos\theta)^{1/2}$. It follows that $d(y^2) = 2\, y\, dy = 2\, x\, X\, \sin\theta\, d\theta$, giving

$$\begin{aligned} \int_0^\pi e^{\,(x^2+X^2-2\,x\,X\,\cos\theta)^{1/2}}\, \sin\theta\, d\theta &= \frac{1}{x\,X} \int_{|x-X|}^{x+X} e^{-y}\, y\, dy \\ &= -\frac{1}{x\,X}\left[e^{-(x+X)}\,(1 + x + X) - e^{-|x-X|}\,(1 + |x - X|)\right]. \end{aligned} \tag{14.64}$$

Thus,

$$\begin{aligned} J &= -\frac{2}{X}\, e^{-X} \int_0^X \left[e^{-2\,x}\,(1 + X + x) - (1 + X - x)\right] x\, dx \\ &\quad -\frac{2}{X} \int_X^\infty e^{-2\,x}\left[e^{-X}\,(1 + X + x) - e^{X}\,(1 - X + x)\right] x\, dx, \end{aligned} \tag{14.65}$$

Note that the $j_l(z)$ are well-behaved in the limit $z \to 0$, whereas the $y_l(z)$ become singular. The asymptotic behaviour of these functions in the limit $z \to \infty$ is

$$j_l(z) \;\to\; \frac{\sin(z - l\,\pi/2)}{z}, \tag{15.42}$$

$$y_l(z) \;\to\; -\frac{\cos(z - l\,\pi/2)}{z}. \tag{15.43}$$

We can write

$$\exp(\,i\,k\,r\cos\theta) = \sum_l a_l\, j_l(k\,r)\, P_l(\cos\theta), \tag{15.44}$$

where the a_l are constants. Note there are no $y_l(k\,r)$ functions in this expression, because they are not well-behaved as $r \to 0$. The Legendre functions are orthonormal,

$$\int_{-1}^{1} P_n(\mu)\, P_m(\mu)\, d\mu = \frac{\delta_{nm}}{n + 1/2}, \tag{15.45}$$

so we can invert the above expansion to give

$$a_l\, j_l(k\,r) = (l + 1/2) \int_{-1}^{1} \exp(\,i\,k\,r\,\mu)\, P_l(\mu)\, d\mu. \tag{15.46}$$

It is well-known that

$$j_l(y) = \frac{(-i)^l}{2} \int_{-1}^{1} \exp(\,i\,y\,\mu)\, P_l(\mu)\, d\mu, \tag{15.47}$$

where $l = 0, 1, 2, \cdots$ [see M. Abramowitz and I.A. Stegun, *Handbook of mathematical functions*, (Dover, New York NY, 1965), Eq. 10.1.14]. Thus,

$$a_l = i^{\,l}\,(2\,l + 1), \tag{15.48}$$

giving

$$\psi_0(\mathbf{r}) = \sqrt{n}\,\exp(\,i\,k\,r\cos\theta) = \sqrt{n}\sum_l i^{\,l}\,(2\,l+1)\, j_l(k\,r)\, P_l(\cos\theta). \tag{15.49}$$

The above expression tells us how to decompose the incident plane-wave into a series of spherical waves. These waves are usually termed “partial waves”.

The most general expression for the total wavefunction outside the scattering region is

$$\psi(\mathbf{r}) = \sqrt{n}\sum_l \left[A_l\, j_l(k\,r) + B_l\, y_l(k\,r)\right] P_l(\cos\theta), \tag{15.50}$$

where the A_l and B_l are constants. Note that the $y_l(k\,r)$ functions are allowed to appear in this expansion, because its region of validity does not include the origin. In the large-r limit, the total wavefunction reduces to

$$\psi(\mathbf{r}) \simeq \sqrt{n}\sum_l \left[A_l\,\frac{\sin(k\,r - l\,\pi/2)}{k\,r} - B_l\,\frac{\cos(k\,r - l\,\pi/2)}{k\,r}\right] P_l(\cos\theta), \tag{15.51}$$

The boundary condition

$$u_l(0) = 0 \tag{15.67}$$

ensures that the radial wavefunction is well-behaved at the origin. We can launch a well-behaved solution of the above equation from $r = 0$, integrate out to $r = a$, and form the logarithmic derivative

$$\beta_{l-} = \left.\frac{1}{(u_l/r)}\frac{d(u_l/r)}{dr}\right|_{r=a}. \tag{15.68}$$

Since $\psi(\mathbf{r})$ and its first derivatives are necessarily continuous for physically acceptible wavefunctions, it follows that

$$\beta_{l+} = \beta_{l-}. \tag{15.69}$$

The phase-shift δ_l is then obtainable from Eq. (15.63).

15.6 Hard Sphere Scattering

Let us test out this scheme using a particularly simple example. Consider scattering by a *hard sphere*, for which the potential is infinite for $r < a$, and zero for $r > a$. It follows that $\psi(\mathbf{r})$ is zero in the region $r < a$, which implies that $u_l = 0$ for all l. Thus,

$$\beta_{l-} = \beta_{l+} = \infty, \tag{15.70}$$

for all l. Equation (15.63) thus gives

$$\tan\delta_l = \frac{j_l(k\,a)}{y_l(k\,a)}. \tag{15.71}$$

Consider the $l = 0$ partial wave, which is usually referred to as the S-wave. Equation (15.71) yields

$$\tan\delta_0 = \frac{\sin(k\,a)/k\,a}{-\cos(k\,a)/ka} = -\tan(k\,a), \tag{15.72}$$

where use has been made of Eqs. (15.40) and (15.41). It follows that

$$\delta_0 = -k\,a. \tag{15.73}$$

The S-wave radial wave function is [see Eq. (15.61)]

$$\begin{aligned}\mathcal{R}_0(r) &= \exp(-i\,k\,a)\frac{[\cos(k\,a)\,\sin(k\,r) - \sin(k\,a)\,\cos(k\,r)]}{k\,r}\\ &= \exp(-i\,k\,a)\,\frac{\sin[k\,(r-a)]}{k\,r}.\end{aligned} \tag{15.74}$$

The corresponding radial wavefunction for the incident wave takes the form [see Eq. (15.49)]

$$\tilde{\mathcal{R}}_0(r) = \frac{\sin(k\,r)}{k\,r}. \tag{15.75}$$

Thus, the actual $l = 0$ radial wavefunction is similar to the incident $l = 0$ wavefunction, except that it is phase-shifted by $k\,a$.

Let us examine the low and high energy asymptotic limits of $\tan\delta_l$. Low energy implies that $k\,a \ll 1$. In this regime, the spherical Bessel functions reduce to:

$$j_l(k\,r) \simeq \frac{(k\,r)^l}{(2\,l+1)!!}, \tag{15.76}$$

$$y_l(k\,r) \simeq -\frac{(2\,l-1)!!}{(k\,r)^{l+1}}, \tag{15.77}$$

where $n!! = n\,(n-2)\,(n-4)\cdots 1$. It follows that

$$\tan\delta_l = \frac{-(k\,a)^{2\,l+1}}{(2\,l+1)\,[(2\,l-1)!!]^2}. \tag{15.78}$$

It is clear that we can neglect δ_l, with $l > 0$, with respect to δ_0. In other words, at low energy only S-wave scattering (*i.e.*, spherically symmetric scattering) is important. It follows from Eqs. (15.17), (15.57), and (15.73) that

$$\frac{d\sigma}{d\Omega} = \frac{\sin^2 k\,a}{k^2} \simeq a^2 \tag{15.79}$$

for $k\,a \ll 1$. Note that the total cross-section

$$\sigma_{\rm total} = \int \frac{d\sigma}{d\Omega}\,d\Omega = 4\pi\,a^2 \tag{15.80}$$

is *four times* the *geometric cross-section* $\pi\,a^2$ (*i.e.*, the cross-section for classical particles bouncing off a hard sphere of radius a). However, low energy scattering implies relatively long wavelengths, so we would not expect to obtain the classical result in this limit.

Consider the high energy limit $k\,a \gg 1$. At high energies, all partial waves up to $l_{\rm max} = k\,a$ contribute significantly to the scattering cross-section. It follows from Eq. (15.59) that

$$\sigma_{\rm total} \simeq \frac{4\pi}{k^2}\sum_{l=0}^{l_{\rm max}}(2\,l+1)\,\sin^2\delta_l. \tag{15.81}$$

With so many l values contributing, it is legitimate to replace $\sin^2\delta_l$ by its average value $1/2$. Thus,

$$\sigma_{\rm total} \simeq \sum_{l=0}^{k\,a}\frac{2\pi}{k^2}\,(2\,l+1) \simeq 2\pi\,a^2. \tag{15.82}$$

This is *twice* the classical result, which is somewhat surprizing, since we might expect to obtain the classical result in the short wavelength limit. For hard sphere scattering, incident waves with impact parameters less than a must be deflected. However, in order to produce a "shadow" behind the sphere, there must also be some scattering in the forward