12 Central Potentials. The Hydrogen Atom

Central symmetry plays an important role in many physical systems, such as the rotor, the isotropic harmonic oscillator, the van der Waals potential, the diatomic molecule or the hydrogen atom. In these cases, the system typically consists of two particles interacting via a central potential. It is therefore convenient to begin this chapter by transforming the Hamiltonian of the two-particle system into one that separates the center-of-mass motion from the relative motion. When the potential is spherically symmetric, the relative motion is conveniently described in spherical coordinates to take advantage of the conservation of angular momentum and the solution of the corresponding eigenvalue problem as discussed in the previous chapter. We therefore begin this chapter by reducing the 6D two-body problem to the 3D problem of relative motion under a central potential.

12.1 Reduction of the Two-Body Problem

Consider a physical system consisting of two interacting parts that can be thought of as a pair of particles. The Hamiltonian consists of the Hamiltonians of the two particles plus the interaction potential. When the interaction depends only on the relative position of the particles, we write

$$\widehat{H}(\widehat{\boldsymbol{p}}_1, \widehat{\boldsymbol{p}}_2, \boldsymbol{r}_1, \boldsymbol{r}_2) = \widehat{H}_1(\widehat{\boldsymbol{p}}_1, \boldsymbol{r}_1) + \widehat{H}_2(\widehat{\boldsymbol{p}}_2, \boldsymbol{r}_2) + V(\boldsymbol{r}_1 - \boldsymbol{r}_2), \tag{12.1}$$

with the single-particle Hamiltonians given by

$$\widehat{H}_i = \frac{\widehat{\boldsymbol{p}}_i^2}{2m_i} + V_i(\boldsymbol{r}_i) = -\frac{\hbar^2}{2m_i}\nabla_i^2 + V_i(\boldsymbol{r}_i), \quad i = 1, 2. \tag{12.2}$$

The Schrödinger equation is then (here we will analyze only the stationary case)

$$E\Psi = \widehat{H}\Psi = \left[-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V_1(\boldsymbol{r}_1) + V_2(\boldsymbol{r}_2) + V(\boldsymbol{r}_1 - \boldsymbol{r}_2)\right]\Psi. \tag{12.3}$$

Before proceeding, it is worth noting the following. In the preceding equation, $\Psi = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is a function of six variables, three for each of the particles; more generally, the wave function will be a function of $3N$ variables, where N is the number of (point-like) particles. This means that it is not possible to interpret Ψ as a physical wave in the conventional sense of the term, because if it were, we could only describe it in terms of the three variables that specify the point of physical space in which it is being considered. An electromagnetic wave, in contrast, satisfies the wave equation

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

in 3D space (apart from time), regardless of the number of sources that produce it. Nevertheless, $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ can still be interpreted as a probability (density) amplitude, since a probability density can depend on any number of variables.

For simplicity, we restrict ourselves to the case of an isolated system, where the potentials V_1 and V_2 produced by external fields are zero, and only the (internal) interaction between the particles remains. Under this condition, Eq. (12.3) takes the form

$$E\Psi = \left[-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\boldsymbol{r}_1 - \boldsymbol{r}_2)\right]\Psi. \tag{12.4}$$

The structure of this equation suggests going from the variables $\boldsymbol{r}_1, \boldsymbol{r}_2$ to the relative and CM variables,[1]

$$\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \ \boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{M}, \tag{12.5}$$

where $M = m_1 + m_2$. From (12.5) it follows that

$$\nabla_1 = \nabla_r + \frac{m_1}{M}\nabla_R, \tag{12.6}$$

$$\nabla_2 = -\nabla_r + \frac{m_2}{M}\nabla_R. \tag{12.7}$$

Taking the square of these operators we get

$$\frac{\nabla_1^2}{m_1} + \frac{\nabla_2^2}{m_2} = \frac{\nabla_r^2}{m} + \frac{\nabla_R^2}{M}, \tag{12.8}$$

where m is the reduced mass of the system (smaller than m_1, m_2),

$$m = \frac{m_1 m_2}{m_1 + m_2} = m_1\frac{1}{1 + \frac{m_1}{m_2}} = m_2\frac{1}{1 + \frac{m_2}{m_1}}. \tag{12.9}$$

Substituting this result into (12.4), we get

$$E\Psi = \left[-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 + V(\boldsymbol{r})\right]\Psi. \tag{12.10}$$

This equation is solved using the method of separation of variables. We write Ψ in the form

$$\Psi(\boldsymbol{R}, \boldsymbol{r}) = \Phi(\boldsymbol{R})\psi(\boldsymbol{r}) \tag{12.11}$$

and split the energy into two parts,

$$E = E_R + E_r, \tag{12.12}$$

so that we can write

$$(E_R + E_r)\Phi\psi = -\frac{\hbar^2}{2M}\psi\nabla_R^2\Phi + \Phi\left[-\frac{\hbar^2}{2m}\nabla_r^2 + V(\boldsymbol{r})\right]\psi. \tag{12.13}$$

which can be broken down into the pair of equations

$$E_R\Phi(\boldsymbol{R}) = -\frac{\hbar^2}{2M}\nabla_R^2\Phi(\boldsymbol{R}), \tag{12.14}$$

[1] Section 18.1 deals with the problem of removing CM coordinates in a slightly more general way.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

$$E_r\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla_r^2\psi(\boldsymbol{r}) + V\psi(\boldsymbol{r}). \tag{12.15}$$

Equation (12.14) describes the free motion of a particle of total mass M (such purely formal "particles" without a real counterpart are called *quasiparticles*); it is the equation for the CM moving freely with energy E_R. This motion is irrelevant for our purposes and it is better to switch to a coordinate system in which the CM is at rest (CM system), so that we can take the trivial solution $E_R = 0$ and $\Phi = \text{const}$.

Equation (12.15), on the other hand, describes the relative motion of a quasiparticle of reduced mass m acted upon by the interaction potential $V(\boldsymbol{r})$. This is the Schrödinger equation for the two-particle central problem, reduced to a one-quasiparticle problem, the equation of real interest for us. It must be remembered that in (12.15) $\boldsymbol{r}$ is not the coordinate of one of the two particles and m is the reduced mass of the system. In the case of the H atom, for example, the reduced mass of the electron-proton system differs very little from the mass of the electron, because the mass of the proton is almost 2,000 times that of the electron, but the difference is noticeable to spectroscopists. The proton itself, due to its large relative mass, remains almost motionless very close to the origin of the coordinates.

12.1.1 Canonical variables for the central problem

From the Heisenberg equations of motion applied to the variables $\boldsymbol{r}$ and $\boldsymbol{R}$ it follows that the relative and CM momenta are given by

$$\widehat{\boldsymbol{p}} = m\left(\frac{\widehat{\boldsymbol{p}}_1}{m_1} - \frac{\widehat{\boldsymbol{p}}_2}{m_2}\right), \quad \widehat{\boldsymbol{P}} = \widehat{\boldsymbol{p}}_1 + \widehat{\boldsymbol{p}}_2. \tag{12.16}$$

These variables obey the quantum laws of independent particles, since their commutation relations are

$$[\widehat{r}_i, \widehat{p}_j] = i\hbar\delta_{ij}, \quad [\widehat{R}_i, \widehat{P}_j] = i\hbar\delta_{ij}, \quad [\widehat{r}_i, \widehat{P}_j] = [\widehat{R}_i, \widehat{p}_j] = 0, \tag{12.17}$$

which shows that the change of variables from $\boldsymbol{r}_1, \boldsymbol{r}_2$ to $\boldsymbol{R}, \boldsymbol{r}$ and from $\widehat{\boldsymbol{p}}_1, \widehat{\boldsymbol{p}}_2$ to $\widehat{\boldsymbol{P}}, \widehat{\boldsymbol{p}}$ is a canonical transformation; this observation could have been used to perform the separation of variables. It can also be shown that

$$\boldsymbol{L}_1 + \boldsymbol{L}_2 = \boldsymbol{l} + \boldsymbol{L}, \tag{12.18}$$

where

$$\widehat{\boldsymbol{L}}_{1,2} = \boldsymbol{r}_{1,2} \times \widehat{\boldsymbol{p}}_{1,2}, \quad \widehat{\boldsymbol{l}} = \boldsymbol{r} \times \widehat{\boldsymbol{p}}, \quad \widehat{\boldsymbol{L}} = \boldsymbol{R} \times \widehat{\boldsymbol{P}}, \tag{12.19}$$

where $\widehat{\boldsymbol{L}}_1$ and $\hat{\boldsymbol{L}}_2$ the angular momenta of particles 1 and 2, respectively, $\widehat{\boldsymbol{l}}$ is the angular momentum of the relative motion and $\hat{\boldsymbol{L}}$ is that of the CM.

Equation (12.15) can be solved using the techniques of Chapter 11; in particular, we concluded there that the solution of the Schrödinger equation for a central problem is the product of a spherical harmonic $Y_l^m(\theta, \varphi)$ and the solution of the radial equation, that is,

$$\psi_{nlm} = R_{nl}(r)Y_l^m(\theta, \varphi). \tag{12.20}$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

The radial equation for $R(r)$ is given by Eq. (11.82),

$$\left[\frac{\widehat{p}_r^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right] R(r) = E R(r), \tag{12.21}$$

where the index r has been omitted from the energy eigenvalue, $E = E_r$. The operator

$$\widehat{p}_r = -i\hbar \frac{1}{r}\frac{\partial}{\partial r} r = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \tag{12.22}$$

is the canonical conjugate momentum of r, and $\widehat{p}_r^2$ is

$$\widehat{p}_r^2 = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = -\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2} r. \tag{12.23}$$

Due to the form of $\widehat{p}_r^2$, (12.21) is not strictly a 1D Schrödinger equation; but by introducing a new radial function $u(r)$ defined as

$$u = rR, \tag{12.24}$$

it becomes one,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V\right] u = E u. \tag{12.25}$$

Thus the 6D central two-body problem has been formally reduced to a 1D problem for a quasiparticle associated with the relative radial motion and driven by the effective potential $V + \hbar^2 l\,(l+1)\,/2mr^2$ in the region $r \geq 0$.

Due to the factors $1/r$, both $\widehat{p}_r$ and Eq. (12.25) remain undefined for $r = 0$; therefore it is necessary to specify the boundary condition that must be satisfied at the origin. To this aim, we observe that if $\widehat{p}_r$ is Hermitian with respect to the (square-integrable) eigenfunctions of the Hamiltonian, then the Hamiltonian will also be Hermitian with respect to its eigenfunctions. From an integration by parts it follows that

$$\int_0^\infty R_2^*(\widehat{p}_r R_1) r^2\, dr = -i\hbar r^2 R_2^* R_1\Big|_0^\infty + \int_0^\infty R_1(\widehat{p}_r^* R_2^*) r^2\, dr, \tag{12.26}$$

where R_1 and R_2 are two arbitrary radial functions. Therefore we see that if $\lim_{r\to\infty}(rR_1) = 0$ (and an analogous behavior for R_2), $\widehat{p}_r$ is Hermitian if $\lim_{r\to 0} r^2 R_1 R_2^* = 0$. This is true in particular when the condition

$$u(0) = 0 \tag{12.27}$$

is imposed. For all nonrelativistic problems, this boundary condition is sufficient to select the acceptable radial solutions at the origin; it is equivalent to requiring that the radial function $R(r) = u(r)/r$ remains finite at the origin, or, alternatively, to considering that in (12.25) the potential V is infinite for $r < 0$. In other words, the acceptable solutions are the *odd* solutions (which vanish at the origin) of the 1D Schrödinger problem with potential $V(|x|) + \hbar^2 l(l+1)/2mx^2$.

Two additional remarks are useful here, both arising from the fact that the differential equation for u is precisely a 1D Schrödinger equation. The first is that the u's obtained for any potential form a complete set in $[0, \infty)$. The second is that the WKB method can be applied directly to the radial equation for u; for example, this method has been used successfully to investigate positive-energy solutions for the Coulomb potential.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

Exercise E12.1. Central problem in two and three dimensions
Show that the discrete energy spectrum of a central problem is different when the system is treated in two or three dimensions.

Solution. That this must be the case in general can be seen by referring to the example of the isotropic harmonic oscillator. Treating the problem in a Cartesian coordinate system we obtain for the eigenvalues of the Hamiltonian the formula $E_n = \hbar\omega \sum_{i=1}^{2} (n_i + \frac{1}{2}) = \hbar\omega(n+1)$ where n is an integer in the 2D case, while in the 3D case we get $E_n = \hbar\omega \sum_{i=1}^{3} (n_i + \frac{1}{2}) = \hbar\omega(n + \frac{3}{2})$ with n integer.

In the general 3D case, the radial Schrödinger equation is (12.25),

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + l(l+1)\frac{\hbar^2}{2mr^2} + V(r)\right]u(r) = Eu(r). \tag{12.28}$$

To treat the 2D case we use a polar plane coordinate system and write the wave function in the form

$$\psi = \frac{u(r)}{\sqrt{r}} e^{ik\phi}. \tag{12.29}$$

The usual requirement that ψ be single-valued demands that $|k|$ be an integer. Proceeding as in the derivation of Eq. (12.28), we get

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \left(k - \tfrac{1}{2}\right)\left(k + \tfrac{1}{2}\right)\frac{\hbar^2}{2mr^2} + V(r)\right]u(r) = Eu(r). \tag{12.30}$$

The comparison of Eqs. (12.28) and (12.30) shows that the eigenvalues of H of the 2D case are obtained from the 3D case by substituting the integer l for the half-integer $k - 1/2$ (obviously E does not depend on the sign of k).

Exercise E12.2. Recurrence relation between expectation values of powers of r
Use the formula for the canonical momentum operator $\hat{p}_r$ to obtain a recurrence relation between the expectation values of powers of r, both for the hydrogen-like atom and for the isotropic 3D harmonic oscillator.

Solution. In a bound stationary system, the virial theorem states that $\langle\dot{\widehat{A}}\rangle = 0$ for any $\widehat{A}$, $\langle[\widehat{A}, \widehat{H}]\rangle = 0$. Let us apply this result to the operator $\widehat{A} = \widehat{p}_r r^{s+1} = (\hat{\boldsymbol{p}} \cdot \boldsymbol{r})r^s$; it is obvious that for s = 0, the usual virial theorem holds. By taking the time derivative of $\hat{A}$ we get

$$\frac{d}{dt}\langle\widehat{p}_r r^{s+1}\rangle = \langle\dot{\widehat{p}}_r r^{s+1}\rangle + \langle\widehat{p}_r\dot{\widehat{r}}r^s\rangle + \cdots + \langle\widehat{p}_r r^s\dot{r}\rangle = 0. \tag{12.31}$$

To simplify this expression we write $\dot{r} = \hat{p}_r/m$ and pass all the $\widehat{p}_r$'s to the left using the commutation relation

$$[r^n, \widehat{p}_r] = i\hbar n r^{n-1}. \tag{12.32}$$

The result is

$$\langle\dot{\widehat{p}}_r r^{s+1}\rangle + \frac{s+1}{m}\langle\widehat{p}_r^2 r^s\rangle + \frac{is(s+1)}{2}\frac{\hbar}{m}\langle\widehat{p}_r r^{s-1}\rangle = 0. \tag{12.33}$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

We now simplify each term separately. The last term can be simplified by noting that the generalized virial theorem itself implies that $\frac{d}{dt}\langle r^s\rangle = 0$; proceeding with this expression as before, we get

$$\langle \widehat{p}_r r^{s-1}\rangle = -i(s-1)\frac{\hbar}{2}\langle r^{s-2}\rangle. \tag{12.34}$$

To simplify the first two terms, we must use the Hamiltonian of the system. We first take the case of the hydrogen-like atom, and write $\widehat{H}$ in the form

$$\widehat{H} = \frac{\widehat{p}_r^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{C}{r}. \tag{12.35}$$

This gives an expression for $\dot{p}_r$ in terms of r,

$$\dot{p}_r = \frac{-i}{\hbar}[\widehat{p}_r, \widehat{H}] = \frac{\hbar^2 l(l+1)}{mr^3} - \frac{C}{r^2}. \tag{12.36}$$

Substituting E for $\widehat{H}$, we get an expression for p_r^2 in terms of r,

$$\widehat{p}_r^2 = 2m\left[E - \frac{\hbar^2 l(l+1)}{2mr^2} + \frac{C}{r}\right]. \tag{12.37}$$

Substitution of the three previous results in (12.33) gives the following recurrence relation for the hydrogen-like atom, *known as the* Kramers formula,

$$2E(s+1)\langle r^s\rangle + C(2s+1)\langle r^{s-1}\rangle + \frac{\hbar^2}{m}s\left(\frac{s^2-1}{4} - l(l+1)\right)\langle r^{s-2}\rangle = 0. \tag{12.38}$$

Following the same procedure with the Hamiltonian of the isotropic oscillator with potential $V = \frac{1}{2}m\omega^2 r^2$, we obtain the recurrence relation

$$2E(s+1)\langle r^s\rangle - \tfrac{1}{2}m\omega^2(2s+4)\langle r^{s+2}\rangle + \frac{\hbar^2}{m}s\left(\frac{s^2-1}{4} - l(l+1)\right)\langle r^{s-2}\rangle = 0. \tag{12.39}$$

Note that by taking $\hbar = 0$, the generalization of the classical virial theorem is obtained in both cases.

An interesting exercise is to prove that for any central potential the following recurrence relation holds,

$$2E(s+1)\langle r^s\rangle - 2(s+1)\langle r^s V\rangle - \langle r^{s+1}V'\rangle + \frac{\hbar^2}{m}s\left(\frac{s^2-1}{4} - l(l+1)\right)\langle r^{s-2}\rangle = 0. \tag{12.40}$$

12.2 Angular Momentum Selection Rules for Dipole Transitions

The results obtained earlier can be applied to determine the angular-momentum dependence of the allowed radiative dipole transitions between quantum states for any central problem. For this purpose we recall from Section 9.3 that a dipole transition between two states $|nlm\rangle$ and $|n'l'm'\rangle$ can occur if the matrix element $\langle n'l'm'|\boldsymbol{r}|nlm\rangle$ is different from zero. We write $\boldsymbol{r} = \widehat{\mathbf{a}}_r r$ to factor out the angular and radial integrals as

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

follows, noting that the state vector $|nlm\rangle$ is a shorthand for the product vector $|nl\rangle|lm\rangle$. We can easily see this by writing the wave function (12.20) in Dirac notation:

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_l^m(\theta,\varphi) = \langle r,\theta,\varphi|nlm\rangle = \langle r|nl\rangle\langle\theta\varphi|lm\rangle. \tag{12.41}$$

Hence it follows by comparison that

$$R_{nl}(r) = \langle r|nl\rangle, \quad Y_l^m(\theta,\varphi) = \langle\theta\varphi|lm\rangle, \tag{12.42}$$

and we can write

$$\langle n'l'm'|\boldsymbol{r}|nlm\rangle = \langle n'l'|r|nl\rangle\langle l'm'|\widehat{\mathbf{a}}_r|lm\rangle, \tag{12.43}$$

where $\widehat{\mathbf{a}}_r$ is the unit vector

$$\begin{aligned}\widehat{\mathbf{a}}_r &= \widehat{\mathbf{a}}_x \sin\theta\cos\varphi + \widehat{\mathbf{a}}_y \sin\theta\sin\varphi + \widehat{\mathbf{a}}_z\cos\theta \\ &= \widehat{\mathbf{a}}_+ \sin\theta e^{i\varphi} + \widehat{\mathbf{a}}_- \sin\theta e^{-i\varphi} + \widehat{\mathbf{a}}_z\cos\theta \equiv \widehat{\mathbf{a}}_+\eta_+ + \widehat{\mathbf{a}}_-\eta_- + \widehat{\mathbf{a}}_z\eta_z,\end{aligned} \tag{12.44}$$

$$\begin{aligned}\widehat{\mathbf{a}}_\pm &= \tfrac{1}{2}(\widehat{\mathbf{a}}_x \mp i\,\widehat{\mathbf{a}}_y), \\ \eta_\pm &= \sin\theta e^{\pm i\varphi}, \quad \eta_z = \cos\theta.\end{aligned} \tag{12.45}$$

The change of $\widehat{\mathbf{a}}_r$ is described in terms of a clockwise or a counter-clockwise rotation around the z-axis plus an oscillation about the z-axis. The matrix elements of these components can be written in the form

$$\langle l'm'|\eta_+|lm\rangle = \int Y_{l'}^{m'*}\sin\theta e^{i\varphi}Y_l^m\,d\Omega = [A_{lm}^+\delta_{l',l+1} + B_{lm}^+\delta_{l',l-1}]\delta_{m',m+1}, \tag{12.46}$$

$$\langle l'm'|\eta_-|lm\rangle = \int Y_{l'}^{m'*}\sin\theta e^{-i\varphi}Y_l^m\,d\Omega = [A_{lm}^-\delta_{l',l+1} + B_{lm}^-\delta_{l',l-1}]\delta_{m',m-1}, \tag{12.47}$$

$$\langle l'm'|\eta_z|lm\rangle = \int Y_{l'}^{m'*}\cos\theta Y_l^m\,d\Omega = [A_{lm}\delta_{l',l+1} + B_{lm}\delta_{l',l-1}]\delta_{m',m}. \tag{12.48}$$

The value of the coefficients A_{lm} and B_{lm} in these expressions is obtained by using the recurrence relations of the spherical harmonics and their orthogonality properties; see Section A.1. Substituting Eqs. (12.46–12.48) into (12.43) we see that the selection rules for all three motions demand that l change by unity. The physical reason for this result is that the radiated or absorbed photon has spin 1 and the total angular momentum (atom + radiation) is conserved during the transition. The projection L_z can be preserved during the transition (for oscillations about the z-axis) or change by one (for rotations around the z-axis). In short, the angular-momentum selection rules for any central problem are

$$|\Delta l| = 1, \quad |\Delta m| = 0, 1. \tag{12.49}$$

12.3 The 3D Rigid Rotor

The simplest problem that we can treat with the previous results is that of the rotor, that is, the free movement of a particle on the surface of a sphere, or else, the rigid rotation of a diatomic molecule such as CO, HCl, etc., seen from the CM system. If we assume that the molecule rotates around its CM without changing the interatomic

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

distance a, the potential is reduced to a constant, which we can take to be zero (the reference level of the potential energy is arbitrary), so that the Schrödinger equation (12.25) becomes (m stands now for the reduced mass of the molecule)

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2 l(l+1)}{2ma^2}\right]u(r)=Eu(r),\quad r=a. \tag{12.50}$$

Since $u(a)$ is a constant, it immediately follows that the energy is given by

$$E_l=\frac{\hbar^2 l(l+1)}{2ma^2}=\frac{\hbar^2 l(l+1)}{2I}, \tag{12.51}$$

where $I=ma^2$ is the moment of inertia of the molecule. The wave functions $Y_l^m(\theta,\varphi)$ with $|m|\le l$ are associated with the eigenvalue E_l, so the level l has a degeneracy of order $2l+1$. The origin of this degeneracy lies in the spherical symmetry of the Hamiltonian, which implies that all directions are equivalent. In the s-state ($l=0$) the spatial probability density is

$$\rho_{00}=|Y_0^0|^2=\frac{1}{4\pi}, \tag{12.52}$$

which shows that the direction of the interatomic axis is uniformly distributed over the sphere. This solution therefore corresponds to the case where all orientations of the molecule are equally probable. In states with $l\neq 0$, favored molecular orientations appear on average; for example, for $l=1$ the probability densities depend on m, resulting in

$$\rho_{11}=\rho_{1\,-1}=|Y_1^1|^2=|Y_1^{-1}|^2=\frac{3}{8\pi}\sin^2\theta, \tag{12.53}$$

$$\rho_{10}=|Y_1^0|^2=\frac{3}{4\pi}\cos^2\theta. \tag{12.54}$$

These expressions show that for $m=\pm 1$, the most probable orbits are in the xy-plane, the direction of rotation being clockwise for $m=1$ and the opposite for $m=-1$. Conversely, for $m=0$, the most probable orbits are in planes containing the z-axis.

A word of caution is needed when interpreting the above results. If we interpret E_l as the energy of the rotor in state l minus the energy of the zero point (which we omit by arbitrarily taking $V(a)$ to be zero), we see that what Eq. (12.51) predicts is the separation between the rotor energy levels, not the absolute value of the energies.

To study the rigid rotation of bodies more complicated than the diatomic molecule, it is necessary to construct the eigenfunctions of the angular-momentum operator for any j (integer or half-integer), expressed in terms of the Euler angles; these eigenfunctions are the Wigner functions $D^{(j)}_{mm'}(\alpha,\beta,\gamma)$. The interested reader will find full discussions of such problems in texts on angular momentum.

The selection rules obtained in the previous section allow us to determine the rotational spectrum of diatomic molecules. In the case of the rigid rotor, $\boldsymbol{r}=a\hat{\mathbf{a}}_r$, the states are described by just the two angular-momentum quantum numbers l,m. The probability of transition per unit time between the states $|lm\rangle$ and $|l'm'\rangle$ is given by

$$A_{lm,l'm'}=\frac{4e^2a^2\omega_{ll'}^3}{3\hbar c^3}|\langle l'm'|\hat{\mathbf{a}}_r|lm\rangle|^2, \tag{12.55}$$

and the selection rules (12.49) apply. According to Eq. (12.51) the transition frequencies are

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

$$\omega_{l,l-1} = \frac{E_l - E_{l-1}}{\hbar} = \frac{\hbar}{2I}[l(l+1) - (l-1)l] = \frac{\hbar}{I}l = l\omega_{10}. \tag{12.56}$$

Consequently, the spectrum of a diatomic molecule is composed of a series of equidistant lines separated from each other by $\omega_{10} = \hbar/I$. The rotational spectrum of a diatomic molecule normally falls in the far infrared, with wavelengths of the order of 10^{-2} cm, and its study is extremely useful, as it provides information about the moment of inertia of the molecule and hence its dimensions.

Exercise E12.3. Time-dependent approach to the rigid rotor

Obtain the general solution of the time-dependent Schrödinger equation for a rigid rotor and check explicitly that the mean values of the operators $\widehat{H}$, $\widehat{L}_z$, and $\widehat{L}_x$ are conserved. What general conclusions can be drawn from these results?

Solution. The general solution for a rigid rotor can be written in the form

$$\psi(t) = \sum_{l,m} C_{lm} Y_l^m(\theta, \varphi) e^{-iE_l t/\hbar}. \tag{12.57}$$

The calculation of the required expectation values is immediate and gives

$$\langle \widehat{H} \rangle = \sum_{l,m} E_l |C_{lm}|^2, \qquad \langle \widehat{L}_z \rangle = \hbar \sum_{l,m} m |C_{lm}|^2, \tag{12.58}$$

$$\langle \widehat{L}_x \rangle = -\hbar \sum_{l,m} \sqrt{(l \pm m + 1)(l \mp m)} C^*_{l,m\pm1} C_{lm}. \tag{12.59}$$

Since $\widehat{H} = \widehat{L}^2/2I$ does not explicitly depend on time, the constancy of $\langle \widehat{H} \rangle$ is simply a result of energy conservation. Since $\widehat{L}_z$, $\widehat{L}_+$, and $\widehat{L}_-$ commute with $\widehat{H}$ (which is invariant against arbitrary rotations), they are constant, even though they do not commute with each other. The mean value of $\widehat{L}_z$ turns out to be constant simply because its eigenfunctions were used as the basis.

It is more interesting to analyze how the constancy of $\langle \widehat{L}_x \rangle$ is produced. In this case, the expectation value is not a sum of terms proportional to the squares of the modules of the coefficients $C_{lm} e^{-iE_l t/\hbar}$ of the expansion, as is the case with $\langle \widehat{H} \rangle$ and $\langle \widehat{L}_z \rangle$, but a sum of bilinear combinations of these coefficients, belonging to the same value of l and different values of m.

The temporal independence of these terms is due to the fact that the energy of the state $|lm\rangle$ depends only on l and not on m, $E_{lm} = E_l$. Consequently, we can conclude that if a system has two or more operators that commute with the Hamiltonian, but not with each other, degeneracy occurs.

12.4 The Free Particle in 3D

The solution of the free-particle problem can be expressed in terms of the common eigenfunction of $\widehat{\boldsymbol{p}}$ and $\widehat{H}$, which is $\psi = Ae^{i\boldsymbol{k}\cdot\boldsymbol{r}}$, where $\boldsymbol{k} = \boldsymbol{p}/\hbar$. This is the extension to

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

3D of the free-particle solution found in Section 7.1, and represents a plane wave traveling in the direction of the momentum. On the other hand, the free-particle problem is a special case of a central problem, so it should be possible to express the solution in terms of the angular-momentum eigenfunctions $Y_l^m(\theta, \varphi)$, multiplied by the solution R of the radial equation for the free particle, Eq. (12.21) with $V = 0$,

$$\left[\frac{\widehat{p}_r^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2}\right] R(r) = E R(r). \tag{12.60}$$

As shown in Section A.1 of the Mathematical Appendix, the solutions of this equation are the spherical Bessel functions $j_l(kr)$, which form a complete basis. Therefore we can use the functions

$$\psi_{klm} = A j_l(kr) Y_l^m(\theta, \varphi)$$

as a basis to represent the plane wave in three-dimensional space. This decomposition of a plane wave into spherical waves is very useful in dispersion theory, as will be seen in Chapter 18; we derive it here as a further exercise in dealing with orthogonal functions.

To begin the analysis, we note that the function $\psi = Ae^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ with $\boldsymbol{k}$ in any direction is not an eigenfunction of $\hat{L}_z$, that is, it has no well-defined angular momentum in the z-direction. Therefore, the required superposition must include all possible values of m; below (Eq. 12.70) we will see that this is the case. However, we can simplify things considerably by orienting the z-axis along $\boldsymbol{k}$; then the wave function is an eigenfunction of $\widehat{L}_z$, since $\boldsymbol{k} \cdot \boldsymbol{r} = kz = kr\cos\theta$, and

$$\widehat{L}_z e^{ikz} = -i\hbar \frac{\partial}{\partial \varphi} e^{ikr\cos\theta} = 0, \tag{12.61}$$

that is, the eigenvalue of $\widehat{L}_z$ is zero. This means that the expansion of a plane wave with momentum in the z-direction contains only spherical waves with $m = 0$. This result is obvious from the geometrical point of view, since if the z-axis is aligned with $\boldsymbol{p}$, then $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ lies in the xy-plane.

Since for $m = 0$ the spherical harmonics reduce to the Legendre polynomials $P_l(\cos\theta)$, we write

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} A_l j_l(kr) P_l(\cos\theta). \tag{12.62}$$

To determine the expansion coefficients A_l, we multiply by $P_{l'}(\cos\theta)$, integrate from 0 to π and use the orthogonality relations of the Legendre polynomials, which in terms of the variable $s = \cos\theta$ are (see Eq. (A.20)),

$$\int_{-1}^{1} P_l(s) P_{l'}(s)\, ds = \frac{2}{2l+1}\delta_{ll'}, \tag{12.63}$$

so we get

$$A_l j_l(kr) = \frac{2l+1}{2} \int_{-1}^{1} e^{ikrs} P_l(s)\, ds. \tag{12.64}$$

Using the Rodrigues formula, Eq. (A.19),

$$P_l(s) = \frac{1}{2^l l!} \frac{d^l}{ds^l}(s^2 - 1)^l \tag{12.65}$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

and integrating by parts l successive times, we obtain

$$A_l j_l(kr) = \frac{2l+1}{2}\frac{(-1)^l}{2^l l!}\int_{-1}^{1}(s^2-1)^l \frac{d^l}{ds^l}e^{ikrs}\,ds$$
$$= \frac{2l+1}{2}\frac{(ikr)^l}{2^l l!}\int_{-1}^{1}(1-s^2)^l e^{ikrs}ds. \tag{12.66}$$

On the other hand, from the theory of Bessel functions we have the following integral formula

$$\int_{-1}^{1}(1-x^2)^l e^{i\alpha x}\,dx = \sqrt{\frac{2\pi}{\alpha}}l!\left(\frac{2}{\alpha}\right)^l J_{l+1/2}(\alpha) = 2l!\left(\frac{2}{\alpha}\right)^l j_l(\alpha), \tag{12.67}$$

where the second equality follows from defining the spherical Bessel functions j_l in terms of the cylindrical Bessel functions $J_{l+1/2}$, Eq. (A.62),

$$j_l(\rho) = \sqrt{\frac{\pi}{2\rho}}J_{l+1/2}(\rho). \tag{12.68}$$

Substituting in the previous expression and canceling the common factor $j_l(kr)$, we obtain $A_l = i^l(2l+1)$. Using this result in Eq. (12.62), we obtain the desired expansion,

$$e^{ikz} = \sum_{l=0}^{\infty} i^l(2l+1)j_l(kr)P_l(\cos\theta). \tag{12.69}$$

The expression for any $\boldsymbol{k}$ can be obtained from here by interpreting θ as the angle between $\boldsymbol{k}$ and $\boldsymbol{r}$ and passing to an arbitrary coordinate system; since this is not of direct interest to us, we give only the final result:

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = 4\pi\sum_{l,m} i^l j_l(kr)Y_l^m(\theta,\varphi)Y_l^{m*}(\theta_k,\varphi_k), \tag{12.70}$$

where θ_k, φ_k correspond to the vector $\boldsymbol{k}$, and θ, φ correspond to the vector $\boldsymbol{r}$.

12.5 The Hydrogen-Like Atom

The ground is finally prepared for the study of the central problem of atomic physics: the hydrogen atom. The system simply consists of a single electron around the nucleus. More generally, we can consider a hydrogen-like atom consisting of an electron and a nucleus of arbitrary positive charge Ze, where Z is the number of protons in the nucleus (atomic number). The problem, as simple as it may sound, is not trivial, and a large number of results had to be accumulated before it was possible to approach it using Schrödinger's theory. The results are worth the effort because, as we shall see, the theory allows it to be studied in detail and gives satisfactory results in all cases.

We start by analyzing the asymptotic behavior of the radial function $u(r)$ when $r \to 0$ and when $r \to \infty$ for potentials $V(r)$ satisfying two conditions: (a) $\lim_{r\to 0} r^2V(r) = 0$, and (b) $\lim_{r\to\infty} V(r) = 0$. From Eq. (12.25) and condition (a) it follows that sufficiently close to the origin the equation for u reduces to

$$\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u = 0, \tag{12.71}$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

which has a solution of the form r^s if $s(s-1) - l(l+1) = 0$, that is, if

$$s = \tfrac{1}{2} \pm \left(l + \tfrac{1}{2}\right) = l + 1, -l. \tag{12.72}$$

The solution with s negative or zero, $s = -l$, is not acceptable, because it does not satisfy the condition (12.27), $u(0) = 0$. Hence the behavior of u near the origin is

$$u \sim r^{l+1}. \tag{12.73}$$

In the limit of very large r, the effective potential vanishes by property (b) and Eq. (12.25) reduces to

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} = Eu, \tag{12.74}$$

whose solution is (omitting the normalization factor)

$$u = e^{\beta r}, \tag{12.75}$$

with the constant β given by

$$\beta^2 = -\frac{2mE}{\hbar^2}. \tag{12.76}$$

We immediately see that there are two possible cases with completely different asymptotic behavior of u at infinity. If the energy E is negative, β is real, with a positive and a negative value of equal magnitude. In this case, the wave function increases or decreases exponentially at infinity; the integrability condition of the square of the wave function eliminates the solution with positive β, so that for negative energies we obtain

$$u \sim e^{-\beta r}, \quad \beta = \frac{\sqrt{2m|E|}}{\hbar} \quad (r \to \infty). \tag{12.77}$$

On the other hand, if the energy is positive, β takes on imaginary values, the wave function is oscillatory at infinity, and the required combination of the two solutions is determined by the demand that u correctly connects with the solution coming from the origin.[2]

Physically, these results are easy to understand. Bound states form when $E < 0$, as shown in Fig. 12.1; this case classically corresponds to the appearance of closed orbits (elliptical in the Coulomb case), and naturally the electron density must decrease rapidly as we move away from the center of attraction, giving rise to the exponential decrease in u. On the other hand, $E > 0$ if, for example, electrons are thrown against the center of attraction, which cannot capture them due to the excess energy but deflects them from their initial trajectory. This case classically corresponds to open orbits (hyperbolic in the Coulomb case); the electrons can escape to arbitrary distances from the scattering center, and the wave function remains finite as r increases. In line with the general discussion in Chapter 4, we conclude that the bound state corresponds to negative energies with a discrete spectrum, while the scattering states correspond to positive energies with a continuous spectrum.

Specifically for the hydrogen-like atom, the Coulomb potential is

$$V = -\frac{Ze^2}{r} \tag{12.78}$$

[2] Note that when $E > 0$, the wave function at infinity can be written as the superposition of an outgoing spherical wave (propagating from the center to the periphery) $R \sim e^{ikr}/r$, and an incoming wave $R \sim e^{-ikr}/r$, with $k = \sqrt{2mE}/\hbar$. This is the form we will have to take for the asymptotic wave function when we study the problem of particle scattering by potentials in Chapter 18.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

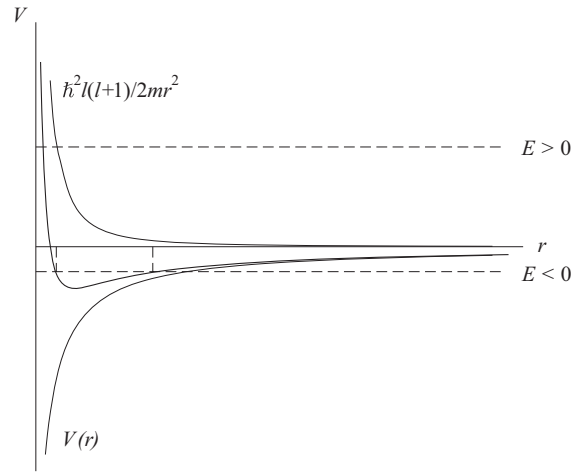


Figure 12.1 Effective potential, constructed as the sum of an attractive potential (a Coulomb potential in the case of the hydrogen-like atom) and the centrifugal barrier potential. Negative energies correspond to bound states, while positive energies correspond to Rutherford scattering.

and the radial equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left(\frac{\hbar^2 l(l+1)}{2mr^2}-\frac{Ze^2}{r}\right)u=Eu. \tag{12.79}$$

In this chapter we will mainly study the solutions corresponding to bound states. The scattering of particles by a uniform spherical potential is discussed in Chapter 18. It is convenient to rewrite Eq. (12.79) in dimensionless form, which we do by introducing the variable ρ defined as

$$\rho=2\beta r, \tag{12.80}$$

where β is given by (12.77) (the value 2 is chosen for convenience; other authors prefer 1). With this change of variable, we get ($u'=du/d\rho$)

$$u''+\left[-\tfrac{1}{4}+\frac{Z/\beta a_0}{\rho}-\frac{l(l+1)}{\rho^2}\right]u=0, \tag{12.81}$$

where

$$a_0=\frac{\hbar^2}{me^2}. \tag{12.82}$$

In order to guarantee the correct asymptotic behavior of u we use previous results to write the radial function in the form

$$u=\rho^{l+1}e^{-\rho/2}Q(\rho), \tag{12.83}$$

where $Q(\rho)$ is to be determined by solving the differential equation obtained by substituting (12.83) in (12.81), that is,

$$Q''+\left(\frac{2(l+1)}{\rho}-1\right)Q'+\frac{(Z/\beta a_0)-l-1}{\rho}Q=0. \tag{12.84}$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

To find out what boundary conditions we need to impose on $Q(\rho)$, we proceed as follows. At the origin, (12.73) is satisfied with $u \approx \rho^{l+1} Q(0)$. As $r \to \infty$, if Q is expressed as a power series of ρ, this series must reduce to a polynomial to grow slower than an exponential and be physically acceptable. In summary, the solutions of (12.84) that we are interested in are polynomials. A study of the differential equation shows that such solutions exist if and only if the numerical coefficient of the last term is a nonnegative integer, that is, if

$$\frac{Z}{\beta a_0} - l - 1 = k, \quad k = 0, 1, 2, \ldots \tag{12.85}$$

As shown in Section A.1 of the Appendix A, the polynomial solutions of Eq. (12.84) are the associated (or generalized) Laguerre polynomials,

$$Q = L_k^{2l+1}(\rho) = \frac{1}{k!} e^{\rho} \rho^{-(2l+1)} \frac{d^k}{d\rho^k} e^{-\rho} \rho^{k+2l+1}. \tag{12.86}$$

It is convenient to write the quantization condition of the energy, (12.85), in the form

$$\frac{Z}{\beta a_0} = k + l + 1 \equiv n, \tag{12.87}$$

introducing the *principal quantum number* n, which can take the values $1, 2, 3, \ldots$, while the angular momentum $l = n - 1 - k$ is restricted to integers satisfying the condition

$$l \leq n - 1. \tag{12.88}$$

Substituting the value of β given by Equation (12.87) into (12.76) and using (12.82), we obtain Bohr's formula for the energy (see Section 2.5),

$$E_n = -\frac{Z^2 e^2}{2a_0 n^2} = -\frac{Z^2 m e^4}{2\hbar^2 n^2}. \tag{12.89}$$

From this we see that the wavelength associated with an atomic transition with n and Δn of the order of unity is of the order of $2\pi\hbar c/E \sim a_0/\alpha \simeq 137 a_0$ ($\alpha = e^2/\hbar c \simeq 1/137$ is the fine structure constant[3] and $Z = 1$ has been set), that is, two orders of magnitude larger than the atomic radius (as we will see later, the radius of hydrogen in its ground state is of the order of a_0, *called Bohr radius*). The Rydberg constant predicted by QM coincides with that previously obtained by Bohr, since by substituting $E_n = -\hbar c R/n^2$ we obtain

$$R = \frac{m e^4}{2\hbar^3 c}. \tag{12.90}$$

We will have an opportunity to comment on these formulas in Section 12.6.

This seems a suitable place for an important observation. Quantum formalism says that the angular momentum for the s-states of a central problem (including the H atom) is zero. However, to interpret this to mean that the electron is at rest would contradict basic laws of physics; in fact, the electron would collide with the nucleus under the

[3] The (dimensionless) fine-structure constant α was introduced into physics in 1916 by Arnold Sommerfeld to account for the relativistic splitting of atomic spectral lines, hence its name. It was later found to be a fairly ubiquitous constant, appearing frequently in the physics of atomic-scale systems and QED as the measure of the strength of the electromagnetic force. Its currently accepted value is 1/137.035999206, to an accuracy of 11 digits.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

action of the Coulomb force. In seeking a way out of this difficulty, it will be important to remember that the preceding formulas do not refer to individual electrons but only provide statistical information.

12.5.1 Energy eigenfunctions

The radial functions of the H atom are obtained by inserting Eq. (12.86) into (12.83) and remembering that $R = u/r$. This gives[4]

$$R_{nl}(\rho) = c_{nl}\rho^l e^{-\rho/2} L_{n-l-1}^{2l+1}(\rho). \tag{12.91}$$

The normalization coefficient is obtained from the condition $\int_0^\infty r^2 R_{nl}^2(r)dr = 1$ and gives (see Problem 12.3)

$$c_{nl} = \frac{2}{n^2}\sqrt{\frac{Z^3}{a_0^3}\frac{(n-l-1)!}{(n+l)!}}. \tag{12.92}$$

Using (12.20), the complete energy eigenfunctions for the hydrogen-like atom are therefore given by

$$\psi_{nlm} = R_{nl}(\rho)Y_l^m(\theta,\varphi), \tag{12.93}$$

where $R_{nl}(\rho)$ is given by (12.91) in terms of the associated Laguerre polynomials (12.86), and $\rho = (2\sqrt{2m|E|}/\hbar)r$.

Since the energy depends only on the principal quantum number, for $n > 1$ there are several wave functions associated with the same energy, that is, the states are generally degenerate. The order of degeneracy is determined by considering that for each value of l there are $2l+1$ values of m and for each n there are n possible values of l $(0, 1, 2, \ldots, n-1)$; then the total number of linearly independent wave functions for a given n is

$$\sum_{l=0}^{n-1}(2l+1) = n^2. \tag{12.94}$$

This degeneracy has two causes. On the one hand, the absence of a preferred spatial direction introduces the degeneracy with respect to m (by adding an external field that fixes a spatial direction, this degeneracy is broken, as we will see in Section 12.6). On the other hand, the shape of the Coulomb potential $\sim r^{-1}$ determines the degeneracy with respect to l (it is enough to introduce any additional potential, even a central one, that changes this shape to make this degeneracy disappear, as shown in Problem P12.9).

The energy of the ground state, corresponding to $n = 1$, $l = 0$, is

$$E_1 = -\frac{Z^2e^2}{2a_0} \simeq -13.6Z^2 \text{ eV}. \tag{12.95}$$

This means that in order to extract the orbital electron from an H atom ($Z = 1$) in its ground state, at least 13.6 eV of work needs to be invested; this is the theoretical

[4] The notation and normalization of the associated Laguerre polynomials varies widely in the literature. For example, what we call L_{n-l-1}^{2l+1} is called L_{n+l}^{2l+1} by other authors. This follows from the fact that we have defined the associated Laguerre polynomials $L_n^k(x)$ in terms of the Laguerre polynomials $L_n^0(x) = L_n(x)$ by the expression $L_{q-p}^p(x) = (-1)^p\left(d^p/dx^p\right)L_q(x)$. This is a common convention, but not the only one; other authors prefer to write $L_q^p(x) = (-1)^p\left(d^p/dx^p\right)L_q(x)$, which is equivalent to L_{q-p}^p.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

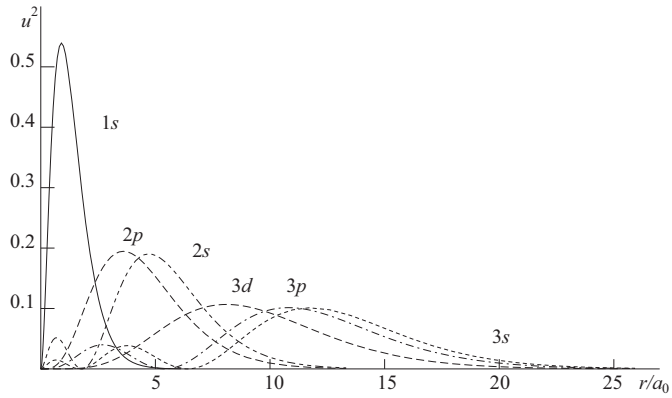


Figure 12.2 Behavior of the radial probability density $u^2(r) = r^2R^2(r)$ for the H atom, for small quantum numbers. Note that for $l = n - 1$, $u^2(r)$ has no nodes.

value of the ionization energy of H, which agrees well with the experimental value. The first excited state corresponds to $n = 2$ and has a degeneracy of 4, with one state corresponding to $l = 0$ and the other three to $l = 1$, and so on.

From (12.91) it is clear that the radial function $R(r)$ varies in general in a complicated way with r, and can have several maxima and nodes; but in the particular case where l reaches its maximum value $n - 1$, the associated Laguerre polynomial reduces to $L^{2l+1}_{n-l-1}(\rho) = L^{2l+1}_0 = 1$, and the function $r^2R^2_{n,n-1}$ then has a single maximum, located at

$$r_{\max} = \frac{a_0}{Z}n^2. \tag{12.96}$$

In the ground state ($n = 1$), $r_{\max} = a_0 = \hbar^2/me^2$; this is the so-called *Bohr radius* of H and has a value of 0.53×10^{-8} cm, just over half an angstrom. For $l < n-1$, the function r^2R^2 has more than one maximum. If the case $l = n-1$ is considered as a circular orbit, in analogy to the classical case, the lower values of l correspond to elliptical orbits. It follows that the quantum number $k = n - l - 1$ measures the eccentricity of the orbit, although it is an indirect measure. Fig. 12.2 shows the behavior of $u^2 = r^2R^2(r)$ for some small values of nl.

12.6 The Hydrogen Spectrum

To determine the transition (selection) rules for the H atom we write again $\boldsymbol{r} = \hat{\mathbf{a}}_r r$ and factor out the angular and radial integrals, $\langle n'l'm'|\boldsymbol{r}|nlm\rangle = \langle n'l'|r|nl\rangle\langle l'm'|\hat{\mathbf{a}}_r|lm\rangle$. Direct calculation shows that the integral $\langle n'l'|r|nl\rangle = \int R_{n'l'}(r)R_{nl}(r)r^3dr$ is not zero for any combination nn'. Thus the selection rules for H are those given previously for the general central problem, $\Delta l = \pm1, \Delta m = 0, \pm1$, to which we add the radial rule, namely arbitrary integer.

Spontaneous transitions to the n' level occur from states with $n > n'$ and produce photons of frequency

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

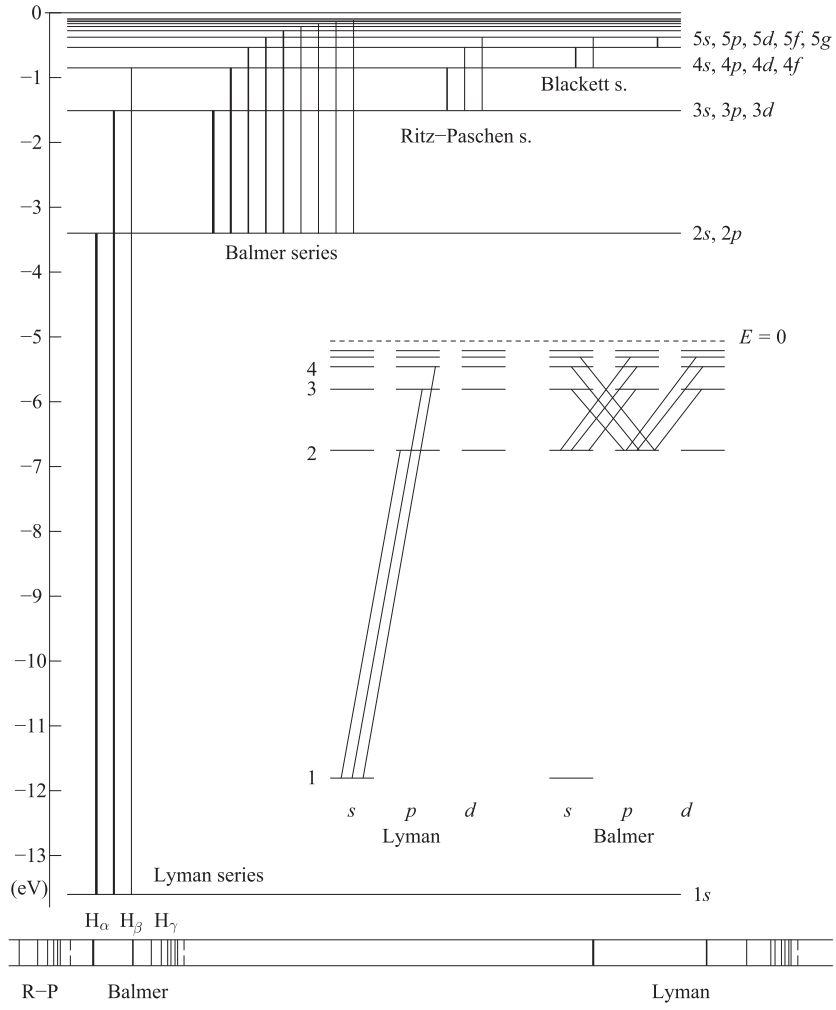


Figure 12.3 Diagram of the energy levels of the H atom, showing the allowed transitions and the corresponding frequency spectrum. The insets show the transitions that give rise to the Lyman and Balmer series.

$$\omega_{nn'} = \frac{E_n - E_{n'}}{\hbar} = Z^2 Rc \left(\frac{1}{n'^2} - \frac{1}{n^2} \right). \tag{12.97}$$

In the following we will restrict ourselves to the case of the H atom, $Z = 1$. Formula (12.97) predicts the existence of several spectral series, each characterized by a fixed value of n' and a variable value of n, with the only restriction being $n > n'$. Transitions to the ground state $1s$ ($l = 0$) occur from all np states ($l = 1$) with $n > 1$, giving rise to the Lyman series (see Fig. 12.3), whose lines have the frequencies

$$\omega = Rc \left(\frac{1}{1^2} - \frac{1}{n^2} \right), \quad n = 2, 3, 4, \ldots \quad \text{(Lyman series)}.$$

The large energy difference between the ground state and the excited states causes all lines in this series to fall in the ultraviolet.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

A second series is generated with the transitions to the first excited level consisting of the states $2s$ and $2p$; to the state $2s$ there can be transitions from states $np, n > 2$, while to $2p$ ($l = 1$) there are transitions from states ns ($l = 0$) and nd ($l = 2$) with $n > 2$ (see Fig. 12.3). Since the energy does not depend on l, these spectral lines coincide and their frequencies are

$$\omega = Rc\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \quad n = 3, 4, 5, \ldots \quad \text{(Balmer series)}. \tag{12.98}$$

This is the well-known Balmer series, whose lines H_α, H_β, H_γ, H_δ, ... correspond to the visible part of the H spectrum.

The Ritz–Paschen series follows, with frequencies

$$\omega = Rc\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \quad n = 4, 5, 6, \ldots \quad \text{(Ritz–Paschen series)}, \tag{12.99}$$

followed by the Blackett[5] series, and so on, all of them in the infrared. Note that each series has a minimum and maximum frequency, that is, it occupies a well-defined region of the spectrum. For example, the Balmer series lies between the frequencies $\omega^B_{\min} = (5/36)Rc$ and $\omega^B_{\max} = Rc/4$; this interval contains an infinite number of lines, which become more and more concentrated as they approach the higher frequency extreme, while their intensity decreases; the variable thickness of the lines in the lower part of Fig. 12.3 is intended to show this phenomenon. The formulas for the frequencies of the different spectral series are in perfect agreement with those obtained using Bohr's atomic model, but such a simple model was not able to predict the relative intensity of the spectral lines. This will be the subject of the next section.

12.6.1 Lifetimes of the excited H states

As mentioned in Chapter 10, in the presence of an external radiation field, transitions between the stationary states can take place. In the absence of external radiation, the spectral lines are due only to spontaneous emission from higher excited states to lower excited states or to the ground state. The relative intensity of the spectral lines, such as those shown in Fig. 12.3 for the H atom, is determined by the respective probability per unit time of spontaneous emission, which is inversely proportional to the average time the atom remains in the excited state before making the transition. To calculate the transition probability we use Einstein's formula for the spontaneous transition coefficient, Eq. (17.134) and proceed as follows.

First we consider only those transitions where the angular momentum increases by one, that is, $(nlm) \to (n', l+1, m')$. From Eqs. (12.44)–(12.48) it follows that

$$\langle l+1, m'|\widehat{\mathbf{a}}_r|lm\rangle = \widehat{\mathbf{a}}_+ A^+_{lm}\delta_{m',m+1} + \widehat{\mathbf{a}}_- A^-_{lm}\delta_{m',m-1} + \widehat{\mathbf{a}}_z A_{lm}\delta_{m',m}. \tag{12.100}$$

[5] Patrick Maynart Stuart Blackett (Lord Blackett) (1897–1974) FRS was a British experimental physicist known for his work on cloud chambers and cosmic rays; he was awarded the 1948 Nobel Prize for his investigations on cosmic rays; Blackett was the first person that intentionally produced and demonstrated the transmutation of an element into another ($N + \alpha \to$F).

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

Each of the three components of this result contributes to transitions with different m'; therefore,

$$|\langle l+1, m+1|\widehat{\mathbf{a}}_r|lm\rangle + \langle l+1, m-1|\widehat{\mathbf{a}}_r|lm\rangle + \langle l+1, m|\widehat{\mathbf{a}}_r|lm\rangle|^2$$
$$= \tfrac{1}{2}(A^+_{lm})^2 + \tfrac{1}{2}(A^-_{lm})^2 + A^2_{lm} = \frac{l+1}{2l+1}. \tag{12.101}$$

The final result was obtained by calculating the different coefficients A_{nl} using the recurrence relations of the spherical harmonics. Therefore, the probability of emission from state n, l, m, to state $n', l+1$, all allowed m' taken together, is

$$A_{nlm\to n',l+1,\text{all } m'} = \frac{4e^2\omega^3_{nn'}}{3\hbar c^3}\frac{l+1}{2l+1}|\langle n'l+1|r|nl\rangle|^2. \tag{12.102}$$

Similarly, for transitions where the orbital momentum decreases by one we obtain

$$A_{nlm\to n',l-1,\text{all } m'} = \frac{4e^2\omega^3_{nn'}}{3\hbar c^3}\frac{l}{2l-1}|\langle n'l-1|r|nl\rangle|^2. \tag{12.103}$$

Exercise E12.4. Lifetime of the lowest excited state

Use the preceding results to calculate the lifetime of the lowest excited state, the $2p$ state of H.

Solution. From this state the atom can only decay to the $1s$ state – producing the so-called Lyman α line, L_α – so this single transition determines the lifetime of the $2p$ state. Using Eq. (12.103), we get

$$\frac{1}{\tau_{2p}} = A_{2p\to 1s} = \frac{4e^2\omega^3_{21}}{3\hbar c^3}|\langle 10|r|21\rangle|^2. \tag{12.104}$$

The radial functions needed are ($\rho = 2r/a_0 n$)

$$R_{10} = \frac{2}{a_0^{3/2}}e^{-r/a_0}, \quad R_{21} = \frac{1}{\sqrt{24}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}, \tag{12.105}$$

and the required integral gives

$$\int_0^\infty R_{10}(r)R_{21}(r)r^3\,dr = 4(2/3)^5\sqrt{6}a_0. \tag{12.106}$$

On the other hand, we have from (12.97) that $\omega_{21} = 3Rc/4$ and $a_0 R = \alpha/2$, where $\alpha = e^2/\hbar c \approx 1/137$, so that

$$\frac{e^2\omega^3_{21}}{\hbar c^3}a_0^2 = 2(3\alpha/8)^3 Rc. \tag{12.107}$$

Substituting these results in (12.104), we get

$$\frac{1}{\tau_{2p}} = \tfrac{1}{3}(8/9)^3\alpha^3 Rc. \tag{12.108}$$

Given the approximate value for the Rydberg constant, $Rc \approx 3.3\times 10^{15}\ \text{s}^{-1}$, the result obtained for the lifetime of the $2p$ state is

$$\tau_{2p} \approx 2.1\times 10^{-9}\ \text{s}, \tag{12.109}$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

which seems a very short time indeed. However, a semiclassical estimate of the orbital period of the $2p$ state (equating the mean kinetic energy written as $\frac{1}{2}ma_0^2\Omega^2$ with $-E_2$) gives $T_{2p} = 2\pi/\Omega \approx 2\pi/Rc$, from which $\tau_{2p}/T_{2p} \approx \alpha^{-3} \simeq 2.5 \times 10^6$; this means that the electron has time to complete its orbit several million times before it decays. We can therefore justifiably speak of a quasi-stationary state.

12.6.2 Significance of the reduced mass

A few remarks on the scope of quantum analysis are in order. In the preceding formulas, m represents the reduced mass of the orbital electron; therefore, if M is the mass of the atomic nucleus and m_e that of the electron, the reduced mass is approximately given by

$$m = \frac{m_e M}{m_e + M} \approx m_e \left(1 - \frac{m_e}{M}\right). \tag{12.110}$$

This result shows that the spectrum depends slightly on the mass of the nucleus through the Rydberg constant $R \propto m$ (see (12.90)). The dependence of R on m, due to the motion of the nucleus with respect to the CM, produces important and interesting effects. If we call R_∞ the Rydberg constant for a nucleus of infinite mass, we have that the Balmer formula for a nucleus of mass M is given by

$$\omega_{nn'} = Z^2 R_\infty c \left(1 - \frac{m_e}{M}\right)\left(\frac{1}{n'^2} - \frac{1}{n^2}\right). \tag{12.111}$$

The different isotopes of H (protium, deuterium, and tritium) have different values of nuclear mass.[6] The emission spectrum of natural H is therefore the superposition of three similar spectra, slightly shifted on the frequency axis and with relative intensities essentially proportional to the concentration of each isotope.

On the other hand, if we apply Eq. (12.111) to He^+ for which $Z = 2$, we obtain

$$\omega_{nn'} = 4R_\infty c \left(1 - \frac{m_e}{M_{He}}\right)\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) = R_\infty c \left(1 - \frac{m_e}{M_{He}}\right)\left(\frac{1}{(n'/2)^2} - \frac{1}{(n/2)^2}\right). \tag{12.112}$$

In particular, for $n' = 4$ and $n = 5, 6, 7, 8, \ldots$, we get

$$\omega_{n4} = R_\infty c \left(1 - \frac{m_e}{m_{He}}\right)\left(\frac{1}{2^2} - \frac{1}{(n/2)^2}\right); \quad \frac{n}{2} = \frac{5}{2}, 3, \frac{7}{2}, 4, \ldots \tag{12.113}$$

If we ignore the correction due to nuclear motion, this looks like the Balmer series of H $\left(\frac{n}{2} = 3, 4, 5, \ldots\right)$ plus an anomalous series of intermediate lines corresponding to half-integer "quantum numbers" $\left(\frac{n}{2} = \frac{5}{2}, \frac{7}{2} \ldots\right)$. The phenomenon was effectively observed in stellar spectra by Pickering and theoretically explained by Bohr as a regular spectrum, with integer quantum numbers, but due to He. This was confirmed by a careful analysis of the position of the spectral lines, which showed that the corresponding Rydberg constant was indeed $R_{He} = R_\infty \left(1 - \frac{m_e}{M_{He}}\right)$ and not $R_H = R_\infty \left(1 - \frac{m_e}{M_H}\right)$.

[6] The nucleus of protium has no neutrons, that of D has one neutron, and that of T, has two. The mass of a neutron is essentially the same as that of a proton.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

The results thus validate Schrödinger's description of the two-body problem, although at the time they were "smoking guns" in favor of half-integer quantum numbers.

12.7 The Atom in an Electromagnetic Field. The Zeeman Effect

In 1896, after several decades of research initiated by Faraday and long before the advent of QM, Pieter Zeeman[7] – following a suggestion by Lorentz – demonstrated that the spectral lines of sodium are modified by the action of an external magnetic field. In the course of a few years, it became clear that the modification essentially consisted of a splitting of the emission lines into multiplets (doublets, triplets, etc.) characteristic of the element and dependent on the intensity of the external field. This phenomenon, now known as the Zeeman effect, played a key role in the study of the magnetic properties of the atom, and, in particular, contributed to the discovery of the spin of the electron and its associated magnetic moment.

If the atom has a nonzero electronic spin, the spectral lines decompose in a very complicated way, giving rise to the so-called *anomalous Zeeman effect*, a problem that will be treated in Section 14.3, based on the Pauli electron spin theory. Since we will not consider the effects due to electronic spin here, the results will only apply to atoms whose total electronic spin is zero (this automatically excludes H). This case is known as the *normal Zeeman effect* or the *Paschen–Back effect.*

12.7.1 The minimal coupling

To study the normal Zeeman effect, we need to write the Schrödinger equation for a (spinless) atom immersed in a magnetic field. In general, a body with electromagnetic properties can have an electric charge and a range of electric and magnetic moments, either intrinsic or induced by external fields. When interacting with the field, the charge is coupled to the potentials Φ and $\boldsymbol{A}$ of the electromagnetic field, while the higher moments are coupled to the field through the derivatives of the potentials.

The interaction energy of a charge distribution with the external field Φ can be expressed in terms of electric multipoles by means of a Taylor expansion of the potential around the origin of the charge distribution $\rho(\boldsymbol{r})$,

$$\int \rho(\boldsymbol{r})\Phi(\boldsymbol{r})d^3x = \int \rho(\boldsymbol{r})\left[\Phi(0) + \sum x_i\,\partial_i\phi(0) + 1/2\sum x_i x_j\,\partial_i\partial_j\Phi(0) + \dots\right]d^3x. \tag{12.114}$$

Identifying $\int \rho(\boldsymbol{r})d^3x$ with the total charge q, $\int x_i\rho(\boldsymbol{r})d^3x$ with the i-component of the electric dipole moment $\boldsymbol{d}$, $\int x_i x_j\rho(\boldsymbol{r})d^3x$ with the ij-component of the electric quadrupole moment $\overleftrightarrow{\mathbf{Q}}$, and so on, the interaction energy can be written as

$$\int \rho(\boldsymbol{r})\Phi(\boldsymbol{r})d^3x = q\,\Phi(0) + \sum d_i\,\partial_i\Phi(0) + 1/2\sum Q_{ij}\,\partial_i\partial_j\Phi(0) + \dots \tag{12.115}$$

[7] Pieter Zeeman (1865–1943) was a Dutch physicist who shared the 1902 Nobel Prize with his mentor H. A. Lorentz for their discovery of the Zeeman effect.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

This expression shows that while q is directly coupled to the potential Φ, the higher moments d_i, Q_{ij}, etc., are coupled to the electromagnetic field through the derivatives of the potential. When the coupling between the particle and the field is *only* through the potentials, it is said to be *minimal*.[8] It is an empirical fact, usually raised to the status of a principle (there is no conclusive theoretical reason why this should be so), that elementary particles (in particular, the electron) are minimally coupled to the field. Once this principle is applied, no additional couplings are required. We will use this principle to extend the Schrödinger equation to the electromagnetic case.

As in classical theory, when there is an interaction with the field $\boldsymbol{A}$, the canonical momentum of the quantum particle is

$$\boldsymbol{p} = m\boldsymbol{v} + \frac{e}{c}\boldsymbol{A}. \tag{12.116}$$

By eliminating the *mechanical* or *kinetic momentum* $m\boldsymbol{v}$, the Hamiltonian is properly expressed in terms of the canonical momentum $\boldsymbol{p}$,[9]

$$H = \frac{1}{2m}\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 + e\Phi, \tag{12.117}$$

and the stationary Schrödinger equation becomes

$$E\psi = \frac{1}{2m}\left(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A}\right)^2 \psi + e\Phi\psi. \tag{12.118}$$

The minimal-coupling principle allows us to postulate this as the Schrödinger equation when there is an external electromagnetic field. The validity of this hypothesis is confirmed by the predictions of the theory so constructed, as we shall have opportunity to see.

Expanding the term in parentheses in (12.118) gives the term

$$\hat{\boldsymbol{p}} \cdot \boldsymbol{A}\psi = \boldsymbol{A} \cdot \hat{\boldsymbol{p}}\psi - i\hbar(\nabla \cdot \boldsymbol{A})\psi. \tag{12.119}$$

In the Coulomb gauge, for which $\nabla \cdot \boldsymbol{A} = 0$, the operators $\hat{\boldsymbol{p}}$ and $\widehat{\boldsymbol{A}}$ commute and (12.118) reduces to

$$E\psi = \frac{\hat{\boldsymbol{p}}^2}{2m}\psi + e\Phi\psi - \frac{e}{mc}\boldsymbol{A} \cdot \hat{\boldsymbol{p}}\psi + \frac{e^2}{2mc^2}\boldsymbol{A}^2\psi. \tag{12.120}$$

With $\widehat{H}_0$ being the Hamiltonian of the problem in the absence of a magnetic field,

$$\widehat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m} + e\Phi, \tag{12.121}$$

we have

$$E\psi = \widehat{H}_0\psi + \left[-\frac{e}{mc}\boldsymbol{A} \cdot \hat{\boldsymbol{p}} + \frac{e^2}{2mc^2}\boldsymbol{A}^2\right]\psi. \tag{12.122}$$

Thus the interaction Hamiltonian consists of a linear term, proportional to $\boldsymbol{A} \cdot \hat{\boldsymbol{p}}$, and a quadratic term, proportional to $\boldsymbol{A}^2$, which depends only on the field. If in this equation we make the substitution $E\psi \to i\hbar\frac{\partial\psi}{\partial t}$ to go to the time-dependent case and apply to

[8] We prefer to use the term *minimal*, since minimalist refers to a theory built with a minimum of elements, i.e. *structurally minimal*.

[9] Compare with the Hamiltonian used in Section 10.4.1 for the SED derivation of the operator formalism; here we omit the Hamiltonian of the radiation field because it is irrelevant to the present calculation.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

the resulting equation a procedure analogous to that used in Section 7.2, we obtain for the flow density

$$\hat{\boldsymbol{j}} = \frac{1}{2m}\left[\psi^*(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A})\psi - \psi(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A})\psi^*\right]. \tag{12.123}$$

12.7.2 The normal Zeeman effect

Except when the external field is extraordinarily strong, the quadratic Zeeman effect is very weak compared to the linear one, so we can limit ourselves to studying the linear effect. We will assume that the magnetic field, with intensity B, is constant and homogeneous. Since $\boldsymbol{B} = \nabla \times \boldsymbol{A}$, for a homogeneous field we can write

$$\boldsymbol{A} = \tfrac{1}{2}\boldsymbol{B} \times \boldsymbol{r}, \tag{12.124}$$

as follows from

$$\begin{aligned} \nabla \times \boldsymbol{A} &= \tfrac{1}{2}\nabla \times (\boldsymbol{B} \times \boldsymbol{r}) = \tfrac{1}{2}[(\nabla \cdot \boldsymbol{r})\boldsymbol{B} - (\boldsymbol{B} \cdot \nabla)\boldsymbol{r}] = \boldsymbol{B}, \\ \nabla \cdot \boldsymbol{A} &= \tfrac{1}{2}\nabla \cdot (\boldsymbol{B} \times \boldsymbol{r}) = \tfrac{1}{2}[\boldsymbol{r} \cdot \nabla \times \boldsymbol{B} - \boldsymbol{B} \cdot \nabla \times \boldsymbol{r}] = 0. \end{aligned} \tag{12.125}$$

Therefore,

$$\boldsymbol{A} \cdot \hat{\boldsymbol{p}} = \tfrac{1}{2}(\boldsymbol{B} \times \boldsymbol{r}) \cdot \hat{\boldsymbol{p}} = \tfrac{1}{2}\boldsymbol{B} \cdot (\boldsymbol{r} \times \hat{\boldsymbol{p}}) = \tfrac{1}{2}\boldsymbol{B} \cdot \widehat{\boldsymbol{L}}, \tag{12.126}$$

where $\widehat{\boldsymbol{L}}$ is the orbital angular momentum operator, and the Schrödinger equation is written, in the linear approximation, as

$$E\psi = \widehat{H}_0\psi - \frac{e}{2mc}\boldsymbol{B} \cdot \widehat{\boldsymbol{L}}\psi. \tag{12.127}$$

The last term in this equation can be interpreted as due to an orbital magnetic moment $\hat{\boldsymbol{\mu}}$ associated with the orbital angular momentum $\widehat{\boldsymbol{L}}$ which, when coupled to the magnetic field $\boldsymbol{B}$, produces the mutual energy

$$\hat{H}_{\text{mag}} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{B}. \tag{12.128}$$

Comparing this expression with (12.127), we see that the orbital magnetic moment operator is

$$\hat{\mu} = \frac{e}{2mc}\widehat{\boldsymbol{L}}. \tag{12.129}$$

The coefficient of proportionality between the magnetic moment of a charge and the angular momentum that generates it is known as the *gyromagnetic ratio*; in the present case its value (omitting the sign) is $e_0/2mc$. The z-component of this magnetic moment has the eigenvalues (to avoid confusion, we write the mass of the electron as m_e)

$$\mu_z = \frac{e\hbar}{2m_e c}m, \tag{12.130}$$

where m is the projection of the orbital angular momentum on the z-axis. This result, among others, justifies the name *magnetic quantum number* given to m by Sommerfeld. To simplify the writing, it is customary to introduce the *Bohr magneton* μ_0, defined as

$$\mu_0 = \frac{e_0\hbar}{2m_e c} = 9.27 \times 10^{-21}\ \text{erg gauss}^{-1}, \tag{12.131}$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

where e_0 is the absolute value of the charge of the electron. Then $\mu_z = -\mu_0 m$, and the Schrödinger equation becomes

$$E\psi = \widehat{H}_0\psi + \frac{\mu_0}{\hbar}\boldsymbol{B}\cdot\widehat{\boldsymbol{L}}\psi. \tag{12.132}$$

The simplest way to solve this equation is to choose the z-axis in the direction of the magnetic field, so that

$$E\psi = \widehat{H}_0\psi + \frac{\mu_0}{\hbar}B\widehat{L}_z\psi \equiv \widehat{H}\psi. \tag{12.133}$$

When $\widehat{H}_0$ corresponds to a central potential (not necessarily that of the H atom), $[\widehat{L}_z, \widehat{H}] = 0$ and the wave functions ψ can be taken as simultaneous eigenfunctions of $\widehat{H}$ with eigenvalue E and of $\widehat{L}_z$ with eigenvalue $\hbar m$. In this subspace the preceding equation reduces to

$$E\psi = \widehat{H}_0\psi + \mu_0 Bm\psi = \left(\widehat{H}_0 + \mu_0 Bm\right)\psi, \tag{12.134}$$

from which it follows that the eigenfunctions of $\widehat{H}$ and $\widehat{H}_0$ coincide, but not their eigenvalues, which are related by the equation

$$E = E_0 + \mu_0 Bm, \tag{12.135}$$

where E_0 is an eigenvalue of $\widehat{H}_0$.

Equation (12.135) allows us to derive the frequencies of the emission lines in the presence of the magnetic field **B**. For the transitions between two levels 1 and 2, we get

$$\omega = \frac{E_1 - E_2}{\hbar} = \frac{E_{01} - E_{02}}{\hbar} + \frac{\mu_0 B}{\hbar}(m_1 - m_2). \tag{12.136}$$

If we call ω_0 the frequency of the corresponding spectral line in the absence of field B, we finally get

$$\omega = \omega_0 + \frac{\mu_0 B}{\hbar}\Delta m. \tag{12.137}$$

From the selection rules for the central problem we know that $\Delta m = 0, \pm 1$; therefore, the field transforms each line of the original spectrum into a triplet with frequencies ω_0, $\omega_0 \pm (\mu_0 B/\hbar)$, that is, the original frequency plus a pair of lines symmetrically shifted with respect to the first one by the amount $\mu_0 B/\hbar$. It is precisely the m selection rule that ensures that, although each level is split into $2l + 1$ contiguous levels, only triplets appear in the spectrum, as shown in Fig. 12.4. These results confirm that it is sufficient to break the spherical symmetry of the Hamiltonian for the degeneracy in the magnetic quantum number m to disappear.

We can express the preceding result in another interesting way, by noting from the definition of the Bohr magneton that $\mu_0 B/\hbar$ does not depend on $\hbar$; this is in fact the Larmor frequency Ω_L, that is, the precession frequency of a magnetic moment in an external field,

$$\Omega_L = \frac{e_0 B}{2mc} = \frac{\mu_0 B}{\hbar}. \tag{12.138}$$

Consequently, Eq. (12.137) says that the triplet of frequencies are the original and the original plus or minus the Larmor frequency. Since this frequency does not depend on

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

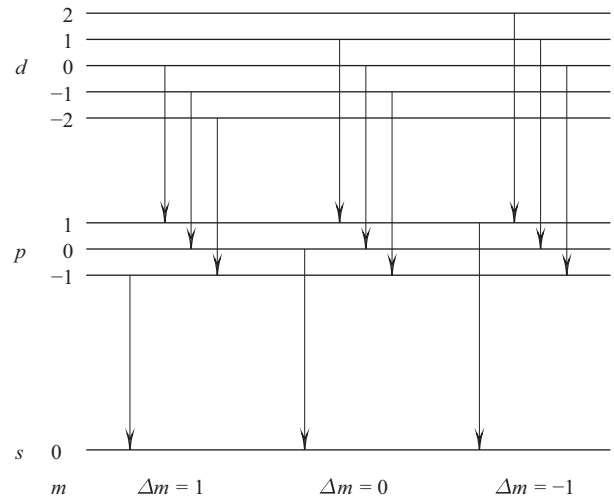


Figure 12.4 Transitions allowed by the selection rule $\Delta m = 0, \pm 1$, between atomic states s, p, and d. Due to the equidistance between levels with successive values of m, the three transitions between states p and d with a fixed value of Δm produce the same spectral line, so the spectrum consists of a series of triplets.

$\hbar$, it was possible to derive it from the classical Lorentz model of the atom. In fact, we have seen that Eq. (12.130) predicts for the orbital motion the gyromagnetic ratio

$$\frac{\mu_z}{L_z} = -\frac{\mu_0}{\hbar} = -\frac{e_0}{2mc}. \tag{12.139}$$

The agreement of this expression with the corresponding classical one led to qualifying this part of the Zeeman effect as "normal."

12.7.3 Gauge transformations of the electromagnetic field

From electrodynamics we know that an electromagnetic field, described by its electric and magnetic components $\boldsymbol{E}$ and $\boldsymbol{B}$, is invariant under a local transformation

$$\boldsymbol{A} \to \boldsymbol{A}' = \boldsymbol{A} + \nabla\chi, \quad \Phi \to \Phi' = \Phi - \frac{1}{c}\frac{\partial\chi}{\partial t}, \tag{12.140}$$

where $\chi = \chi(\boldsymbol{x}, t)$ is an arbitrary scalar function. This *gauge transformation* in no way affects the physical results in classical physics, which allows us to conclude that the potentials $\boldsymbol{A}, \Phi$ are mathematical entities with no direct correspondence to the elements of the physical system being described. We will now see that something similar occurs in Schrödinger's theory, which manifests itself in the fact that, under a gauge transformation, the wave function is transformed into another physically equivalent one that differs from the first one by a local phase.

Using the appropriate Hamiltonian in the presence of an electromagnetic field, Eq. (12.117), the Schrödinger equation reads

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}\right)^2\psi + (V + e\Phi)\,\psi. \tag{12.141}$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

The field gauge transformation modifies this equation, and hence the wave function. Since the density $\rho(\boldsymbol{x},t)=|\psi(\boldsymbol{x},t)|^2$ must not be changed by this transformation, the only possibility is a phase shift in ψ. Therefore, the *quantum gauge transformation* must be defined as in (12.140), with

$$\psi \to \psi' = \psi e^{i(e/\hbar c)\chi}. \tag{12.142}$$

The transformed Schrödinger equation is

$$i\hbar\frac{\partial\psi'}{\partial t} = \frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}'\right)^2\psi' + \left(V + e\Phi'\right)\psi'. \tag{12.143}$$

To show that this equation coincides with (12.141) we rewrite it in the form

$$i\hbar e^{-i(e/\hbar c)\chi}\frac{\partial\psi'}{\partial t} = \frac{e^{-i(e/\hbar c)\chi}}{2m}\left(-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}'\right)^2\psi' + \left(V + e\Phi'\right)\psi. \tag{12.144}$$

Since

$$\begin{aligned} i\hbar e^{-i(e/\hbar c)\chi}\frac{\partial\psi'}{\partial t} &= i\hbar e^{-i(e/\hbar c)\chi}\frac{\partial}{\partial t}\left[\psi e^{i(e/\hbar c)\chi}\right] \\ &= i\hbar\frac{\partial\psi}{\partial t} - \frac{e}{c}\frac{\partial\chi}{\partial t}\psi = i\hbar\frac{\partial\psi}{\partial t} + \left[e\Phi' - e\Phi\right]\psi, \end{aligned} \tag{12.145}$$

Eq. (12.144) reduces to

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}e^{-i(e/\hbar c)\chi}\left(-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}'\right)^2\psi' + (V + e\Phi)\,\psi. \tag{12.146}$$

Now we observe that

$$\begin{aligned} &e^{-i(e/\hbar c)\chi}\left(-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}'\right)\psi e^{i(e/\hbar c)\chi} \\ &= e^{-i(e/\hbar c)\chi}\left[-i\hbar e^{i(e/\hbar c)\chi}\left(\nabla\psi + i\psi\,(e/\hbar c)\,\nabla\chi\right) - \frac{e}{c}\left(\boldsymbol{A} + \nabla\chi\right)\psi e^{i(e/\hbar c)\chi}\right] \\ &= -i\hbar\left(\nabla\psi + i\,(e/\hbar c)\,\psi\nabla\chi\right) - \frac{e}{c}\left(\boldsymbol{A} + \nabla\chi\right)\psi = \left(-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}\right)\psi. \end{aligned} \tag{12.147}$$

With this result, the transformed equation is effectively equal to the original.

We now need to look at what happens to important expectation values, such as momentum or velocity. From Eq. (12.147) it follows that

$$\psi'^*\left(-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}'\right)\psi' = \psi^*\left(-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}\right)\psi, \tag{12.148}$$

which shows that the expectation value of the velocity $\boldsymbol{v} = \left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)/m$ is gauge invariant, but the expectation value of the mechanical momentum $\boldsymbol{p}$ is not. This result confirms that in the presence of an electromagnetic field it is preferable to work with the canonical momentum rather than the mechanical momentum. Note that although the expression $-i\hbar\nabla - \frac{e}{c}\boldsymbol{A}$ explicitly depends on the norm, its expectation and eigenvalues are gauge invariant (the change in phase of the wave function compensates for the change in potential). It follows from Eq. (12.148) that the current density (12.123) is also gauge invariant.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

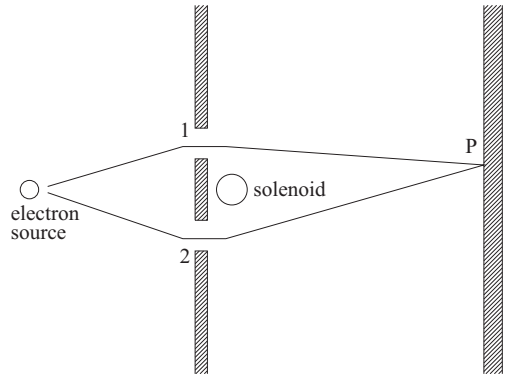


Figure 12.5 Schematic of an Aharonov–Bohm interference experiment. Even though outside of the solenoid $B = 0$, the current through the solenoid causes a shift of the interference pattern on the screen.

12.7.3.1 The Aharonov–Bohm effect

As mentioned earlier, in classical electrodynamics the vector and scalar potentials $\boldsymbol{A}, \Phi$ play an auxiliary role; they are introduced as mathematical tools such that the electric and magnetic fields are correctly given by

$$\boldsymbol{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \boldsymbol{A}}{\partial t}, \ \boldsymbol{B} = \nabla \times \boldsymbol{A}. \tag{12.149}$$

This allows different sets of potentials $\boldsymbol{A}', \Phi'$ to represent the same fields, provided they are related to the original set by the gauge transformation (12.140).

As shown earlier, the Schrödinger equation is also gauge invariant, as are the average values (and eigenvalues) of the dynamical variables. However, in contrast to the classical case where the potentials have no direct physical meaning, there are quantum situations where the electromagnetic potentials do play a role. One case that has gained great importance is the *Aharonov–Bohm effect,* predicted by Aharonov and Bohm in 1959.[10] The effect was experimentally verified by G. Möllenstedt and W. Bayh in 1962 and conclusively demonstrated by A. Tonomura in 2006, using electron-interference experiments.

The apparatus for producing the Aharonov–Bohm effect is shown schematically in Fig. 12.5. As can be seen, it is a variant of the two-slit electron diffraction experiment, similar to that shown in Figure 4.1, with the addition of a very thin and long solenoid placed immediately behind the slits. Because of its size and position, the solenoid is located in a region of space inaccessible to the electrons. When a constant electric current is passed through it, a magnetic field is produced inside it, but the field outside the solenoid is zero, even though the vector potential itself is not zero in this

[10] The effect had been predicted by W. Ehrenberg and R. E. Siday in 1949. When Aharonov and Bohm published their work in 1959 they were unaware of Ehrenberg and Siday's work, but they credited it in a subsequent paper in 1961.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

outer region: $\nabla \times \boldsymbol{A}_{\text{ext}}(\boldsymbol{x}) = 0$, but $\boldsymbol{A}_{\text{ext}}(\boldsymbol{x}) \neq 0$. The point is that the presence of the potential is sufficient to produce a *shift* in the diffraction pattern observed on the detection screen.[11]

The magnetic flux inside the solenoid is

$$\Phi = \iint \boldsymbol{B} \cdot d\mathbf{S} = \iint (\nabla \times \boldsymbol{A}(\mathbf{x})) \cdot d\mathbf{S} = \oint \boldsymbol{A} \cdot d\boldsymbol{x}, \tag{12.150}$$

as follows from the application of Stokes' theorem. Outside the solenoid, however, $\nabla \times \boldsymbol{A}_{\text{ext}} = 0$ and $\boldsymbol{A}_{\text{ext}}$ can be expressed as the gradient of a scalar χ, $\boldsymbol{A}_{\text{ext}}(\boldsymbol{x}) = \nabla\chi(\boldsymbol{x})$. On the other hand, as mentioned earlier, the presence of $\boldsymbol{A}_{\text{ext}}$ is counteracted by the gauge transformation $\psi = \psi^0 e^{i(e/\hbar c)\chi}$, where ψ^0 is the solution in the absence of the potential. Applying this idea to the paths on either side of the solenoid, numbered $i = 1, 2$, we can write $\psi_1 = \psi_1^0 e^{i(e/\hbar c)\chi_1}$, $\psi_2 = \psi_2^0 e^{i(e/\hbar c)\chi_2}$, where $\chi_i = \int_i \boldsymbol{A} \cdot d\boldsymbol{x}$. Since $\boldsymbol{A}$ is irrotational in each of the two regions, these integrals depend only on the endpoints of the trajectories. We can now determine the wave function at a point P on the screen *that is common to both trajectories*,

$$\begin{aligned} \psi_P &= \psi_1^0 e^{i(e/\hbar c)\chi_1} + \psi_2^0 e^{i(e/\hbar c)\chi_2} \\ &= e^{i(e/\hbar c)\chi_1} \left(\psi_1^0 + \psi_2^0 e^{i(e/\hbar c)(\chi_2 - \chi_1)} \right) \\ &= e^{i(e/\hbar c)\chi_1} \left(\psi_1^0 + \psi_2^0 e^{i(e/\hbar c) \oint_S \boldsymbol{A} \cdot d\boldsymbol{x}} \right), \end{aligned} \tag{12.151}$$

that is,

$$\psi_P = \psi_1^0 + \psi_2^0 e^{i(e/\hbar c)\Phi}. \tag{12.152}$$

In the final result, a global phase has been omitted, as it has no observable effect. The fact that the phase difference depends on the magnetic flux in the solenoid, makes the relative position of the observed diffraction pattern dependent on this flux, even though the particles travel through regions of space where there is no magnetic field and therefore do not experience any of the usual forces that would deflect them.

This observation is important because it suggests a more general view of the problem: an effect can occur when the action over closed trajectories is modified by an external field, be it electromagnetic, gravitational, due to spin effects, and so on. This occurs naturally in quantum particle interferometry, and the effects appear to be due to topological phases generated by the presence of the fields. More recent analyses suggest that the phase shift can be viewed as being produced by the vector potential of a solenoid acting on the electron, or the vector potential of the electron acting on the solenoid, or the electron and solenoid currents acting on the quantized vector potential. In any case, there is still no general consensus on the ultimate physical significance of the Aharonov–Bohm effect.

[11] As shown in figure 7 of Möllenstedt and Bayh (1962), it is only the diffraction pattern that is shifted; the envelope in which it is contained does not suffer any deviation.

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

Problems

P12.1 Consider a diatomic molecule made up of ions with charge $\pm q$ and masses m_1 and m_2, respectively. Show that:

(a) The external gravitational field (near the earth's surface) produces an effect on the movement of the CM of the molecule, but not on its internal (relative) motion;

(b) An external uniform electric field $\mathcal{E}$ along the z-axis does not affect the CM motion, but it does affect the internal one, since it induces a dipole electric moment given by $\frac{\partial}{\partial \mathcal{E}}\,(q\mathcal{E}\cdot \boldsymbol{r}) = qz$. *Hint*: study the general case corresponding to the potential $V(r) = f_1 z_1 + f_2 z_2$ and take the particular case.

P12.2 Two oscillators interact with each other linearly, in such a way that the Hamiltonian of the system is

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \tfrac{1}{2}m_1\omega^2 x_1^2 + \tfrac{1}{2}m_2\omega^2 x_2^2 + \tfrac{1}{2}m\omega^2\beta(x_1 - x_2)^2. \quad (12.153)$$

Show that the relative and CM coordinates coincide with the normal coordinates, separate these variables, and determine the eigenvalues of the energy. Study the energy spectrum for the attractive ($\beta > 0$) and repulsive ($\beta < 0$) cases, in the limits $|\beta| \ll 1$ and $|\beta| \gg 1$.

P12.3 Determine the normalization coefficient of the radial wave function of the hydrogen-like atom.

P12.4 By comparing the corresponding differential equations, show that the Laguerre polynomials can be written as a confluent hypergeometric function in the form

$$Q_k^{2l+1}(\rho) = {}_1F_1(-k, 2(l+1); \rho). \quad (12.154)$$

Use this result to obtain the physically acceptable values of the quantum number k.

P12.5 Show that the eccentricity of the hydrogen-like orbits can be taken as $\epsilon = \sqrt{1 - l(l+1)/n^2}$. Note from here that the minimum eccentricity (closest to circular orbits) corresponds to $l = n - 1$ and is $\epsilon_{\min} = 1/\sqrt{n}$, which tends to zero as $n \to \infty$.

P12.6 Derive the following results for the expectation value of r^n for the H atom, where $\rho_{\rm at} = r/a_0$ is measured in atomic units ($m = \hbar = c = 1$), that is, $\rho_{\rm at} = (2n/Z)\rho$:

$$\langle \rho_{\rm at} \rangle = \frac{1}{2Z}\left[3n^2 - l(l+1)\right]; \quad \langle \rho_{\rm at}^2 \rangle = \frac{n^2}{2Z^2}\left[5n^2 + 1 - 3l(l+1)\right];$$
$$\left\langle \frac{1}{\rho_{\rm at}} \right\rangle = \frac{Z}{n^2}; \quad \left\langle \frac{1}{\rho_{\rm at}^2} \right\rangle = \frac{Z^2}{n^3(l+\frac{1}{2})}; \quad \left\langle \frac{1}{\rho_{\rm at}^3} \right\rangle = \frac{Z^3}{n^3 l(l+1)(l+\frac{1}{2})}. \quad (12.155)$$

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

P12.7 Derive the recurrence relation for $\langle r^s \rangle$ for the potential $V = qr^n$. Verify that the results of Exercise E12.2 are particular cases of this expression.

P12.8 Show that in the ground state of the H atom the expectation value of r^n is

$$\langle 100|r^n|100\rangle = \frac{1}{2}\left(\frac{a_0}{2Z}\right)^n (n+2)! \tag{12.156}$$

P12.9 Solve the H atom problem with an additional potential γ/r^2 and show that for any value of the parameter $\gamma \neq 0$, the degeneracy with respect to l is broken.

P12.10 Find the probability that in a hydrogen atom in its ground state, the electron and the proton separate beyond the value allowed by classical mechanics at the same energy.

P12.11 An H atom is in the state $n = 2, l = 1, m = 0$. Express the corresponding electronic wave function in momentum space.

P12.12 In classical electrodynamics the magnetic moment μ_z produced by an electric current density $\boldsymbol{J}_{\text{el}}$ is given by

$$\mu_z = \frac{1}{2c}\int (\boldsymbol{r} \times \boldsymbol{J}_{\text{el}})_z d^3x. \tag{12.157}$$

Show that for discrete charges q this expression reduces to $\mu_z = \frac{q}{2m_0c}L_z$ and, transferring this result to the quantum case, show that

$$\langle \hat{\mu}_z \rangle = e\frac{\langle \hat{L}_z \rangle}{2m_e c} = \frac{e\hbar}{2m_e c}m \tag{12.158}$$

if the wave function has the form $\psi = \Phi(r,\theta)e^{im\varphi}$, with Φ a real function.

P12.13 Show that when the quadratic effects of the magnetic field are taken into account, the magnetic moment of an atom is

$$\mu = -\mu_0 m - \frac{e^2 B}{6m_e c^2}\langle r^2 \rangle. \tag{12.159}$$

Notes: The first term represents a permanent magnetic moment (independent of the external field) and can have any sign; this is the *paramagnetic component* of the magnetic moment. The second term (which, because it comes from a quadratic effect, is generally very small for weak fields) represents an induced magnetic moment (it vanishes when $B = 0$), it is always negative and exists for all atoms; this is the *diamagnetic moment*.

P12.14 Using (17.134) for the Einstein A coefficient, derive in detail Eqs. (12.102) and (12.103).

P12.15 Calculate the mean lifetime of the hydrogen-like $3s$ state.

P12.16 Show that when a quantum system has two or more operators that commute with the Hamiltonian but not with each other, in general the states of the system are degenerate. What general property of the system does this fact reflect?

P12.17 Prove that in the presence of a magnetic field, $m\hat{v}_i = \hat{p}_i - \frac{e}{c}A_i$, and the velocities $\hat{v}_i = \dot{x}_i$ satisfy the commutation rules

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press

$$\left[\hat{v}_i, \hat{v}_j\right] = \frac{ie\hbar}{m^2c}\varepsilon_{ijk}B_k. \tag{12.160}$$

P12.18 Determine the wavelength of the three Zeeman lines produced at the $3d \to 2p$ transition of an H atom placed in a 10^4 Gauss magnetic field.

Bibliographical Notes

For a detailed discussion of the Aharonov–Bohm effect (up to 1987), see Peshkin and Tonomura (1989). More recent discussions of the A-B question show that the physical explanation is still controversial; see, for example, Boyer (2000, 2023) and the review by Cohen et al. (2019).

https://doi.org/10.1017/9781009679633.013 Published online by Cambridge University Press