

Exercises

*0.1 Calculate the size of the quanta involved in the excitation of (a) an electronic motion of period 1.0 fs, (b) a molecular vibration of period 10 fs, and (c) a pendulum of period 1.0 s.

*0.2 The peak in the Sun's emitted energy occurs at about 480 nm. Estimate the temperature of its surface on the basis of it being regarded as a black-body emitter.

*0.3 An unknown metal has a specific heat capacity of $0.91 \text{ J K}^{-1} \text{ g}^{-1}$ at room temperature. Use Dulong and Petit's law to identify the metal.

*0.4 Calculate the energy of 1.00 mol photons of wavelength (a) 510 nm (green), (b) 100 m (radio), (c) 130 pm (X-ray).

*0.5 Calculate the wavelength of the radiation scattered through an angle of 60° when X-rays of wavelength 25.878 pm impinge upon a graphite target.

*0.6 Calculate the speed of an electron emitted from a clean potassium surface ($\Phi = 2.3 \text{ eV}$) by light of wavelength (a) 300 nm, (b) 600 nm.

*0.7 Compute the highest and lowest wavenumbers of the spectral lines in the Balmer series for atomic hydrogen. What are the corresponding wavelengths?

*0.8 Compute the energies (in joules and electronvolts) for the two lowest energy levels of an electron in a hydrogen atom.

*0.9 Calculate the de Broglie wavelength of a tennis ball of mass 57 g travelling at 80 km h^{-1} .

Problems

*0.1 Find the wavelength corresponding to the maximum in the Planck distribution for a given temperature, and show that the expression reduces to the Wien displacement law at short wavelengths. Determine an expression for the constant in the law in terms of fundamental constants. (This constant is called the *second radiation constant*, c_2 .)

0.2 Show that the Planck distribution reduces to the Rayleigh-Jeans law at long wavelengths.

0.3 Compute the power emitted by the Sun regarding it as a black-body radiator at 6 kK; the Sun has a surface area of $6 \times 10^{18} \text{ m}^2$. What energy is emitted during a 24-hour period?

*0.4 Derive the Einstein formula for the heat capacity of a collection of harmonic oscillators. To do so, use the quantum mechanical result that the energy of a harmonic oscillator of force constant k_f and mass m is one of the values $(n + \frac{1}{2})h\nu$ with $\nu = (1/2\pi)(k_f/m)^{1/2}$ and $n = 0, 1, 2, \dots$. *Hint*. Calculate the mean energy, E , of a collection of oscillators by substituting these energies into the Boltzmann distribution, and then evaluate $C = dE/dT$.

0.5 Find the (a) low temperature, (b) high temperature forms of the Einstein heat capacity function.

0.6 Show that the Debye expression for the heat capacity is proportional to T^3 as $T \rightarrow 0$.

*0.7 Estimate the molar heat capacities of metallic sodium ($\theta_D = 150 \text{ K}$) and diamond ($\theta_D = 1860 \text{ K}$) at room temperature (300 K).

0.8 Calculate the molar entropy of an Einstein solid at $T = \theta_E$. *Hint*. The entropy is $S(T) = \int_0^T (C_V/T) dT$. Evaluate the integral numerically.

0.9 How many photons would be emitted per second by a sodium lamp rated at 100 W which radiated all its energy with 100 per cent efficiency as yellow light of wavelength 589 nm?

*0.10 When ultraviolet radiation of wavelength 195 nm strikes a certain metal surface, electrons are ejected at 1.23 Mm s^{-1} . Calculate the speed of electrons ejected from the same metal surface by radiation of wavelength 255 nm.

0.11 At what wavelength of incident radiation do the relativistic and non-relativistic expressions for the ejection of electrons from potassium differ by 10 per cent? That is, find λ such that the non-relativistic and relativistic linear momenta of the photoelectron differ by 10 per cent. Use $\Phi = 2.3 \text{ eV}$.

0.12 Deduce eqn 0.10 for the Compton effect on the basis of the conservation of energy and linear momentum. *Hint*. Use the relativistic expressions. Initially the electron is at rest with energy $m_e c^2$. When it is travelling with momentum p its energy is $(p^2 c^2 + m_e^2 c^4)^{1/2}$. The photon, with initial momentum h/λ_i and energy $h\nu_i$, strikes the stationary electron, is deflected through an angle θ , and emerges with momentum h/λ_f and energy $h\nu_f$. The electron is initially stationary ($p = 0$) but moves off with an angle θ' to the incident photon. Conserve energy and both components of linear momentum (parallel and perpendicular to the

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initial momentum). Eliminate θ' , then p , and so arrive at an expression for $\delta\lambda$.

*0.13 The first few lines of the visible (Balmer) series in the spectrum of atomic hydrogen lie at $\lambda/nm = 656.46, 486.27, 434.17, 410.29, \dots$. Find a value of R_H , the Rydberg constant for hydrogen. The ionization energy, I , is the minimum energy required to remove the electron. Find it from the data and express its value in electronvolts (1 eV = 1.602×10^{-19} J). How is I related to R_H ? *Hint*. The ionization limit corresponds to $n \rightarrow \infty$ for the final state of the electron.

0.14 Use eqn 0.13 for the energy levels of an electron in a hydrogen atom to determine an expression for the Rydberg constant (as a wavenumber) in terms of fundamental constants. Evaluate the Rydberg constant (a) using the reduced mass of a hydrogen atom, (b) substituting the mass of the electron for the reduced mass. (c) What is the percentage difference between the two expressions?

0.15 Derive an expression that could be used to determine the mass of a deuteron from the shift in spectral lines of ^1H and ^2H .

*0.16 A measure of the strength of coupling between the electromagnetic field and an electric charge is the

fine-structure constant, $\alpha = e^2/4\pi\hbar c\epsilon_0$. Express the Rydberg constant (as a wavenumber) in terms of this constant.

0.17 Calculate the de Broglie wavelength of (a) a mass of 1.0 g travelling at 1.0 cm s^{-1} , (b) the same at 95 per cent of the speed of light, (c) a hydrogen atom at room temperature (300 K); estimate the mean speed from the equipartition principle, which implies that the mean kinetic energy of an atom is equal to $\frac{3}{2}kT$, where k is Boltzmann's constant, (d) an electron accelerated from rest through a potential difference of (i) 1.0 V, (ii) 10 kV. *Hint*. For the momentum in (b) use $p = mv/(1 - v^2/c^2)^{1/2}$ and for the speed in (d) use $\frac{1}{2}m_e v^2 = eV$, where V is the potential difference.

0.18 Derive eqn 0.13 for the permitted energy levels for the electron in a hydrogen atom. To do so, use the following (incorrect) postulates of Bohr: (a) the electron moves in a circular orbit of radius r around the nucleus and (b) the angular momentum of the electron is an integral multiple of \hbar , that is $m_e v r = n\hbar$. *Hint*. Mechanical stability of the orbital motion requires that the Coulombic force of attraction between the electron and nucleus equals the centrifugal force due to the circular motion. The energy of the electron is the sum of the kinetic energy and potential (Coulombic) energy. For simplicity, use m_e rather than the reduced mass μ .

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Exercises

*1.1 Which of the following operations are linear and which are non-linear: (a) integration, (b) extraction of a square root, (c) translation (replacement of x by $x + a$, where a is a constant), (d) inversion (replacement of x by $-x$)?

*1.2 Which of the following functions are eigenfunctions of (a) d/dx , (b) d^2/dx^2 : (i) e^{ax} , (ii) e^{ax^2} , (iii) x , (iv) x^2 , (v) $ax + b$, (vi) $\sin x$? If it is an eigenfunction, identify the eigenvalue.

*1.3 Demonstrate that the linear combinations $A + iB$ and $A - iB$ are not Hermitian if A and B are Hermitian operators.

*1.4 An electron is confined to a linear box of length 0.10 nm. What are the minimum uncertainties in (a) its velocity and (b) its kinetic energy?

*1.5 Calculate the value of $\Delta x \Delta p_x$ for the first excited state ($n = 2$) of a particle of mass m in a box of length L . Can you infer a general trend for the uncertainty product as n increases?

*1.6 A particle is confined to the region $0 \leq x \leq \infty$ and its state is described by the unnormalized wavefunction $\psi(x) = e^{-2x}$. What is the probability of finding the particle at a distance $x \geq 1$?

*1.7 Confirm that the z -component of angular momentum, $l_z = (\hbar/i) d/d\phi$, is a constant of the motion for a particle on a ring with uniform potential energy $V(\phi) = V$.

*1.8 A state of a system is described by the wavefunction $\psi(x) = Nxe^{-x^2/2r^2}$. Where is the most probable location of the particle?

*1.9 On the basis of the information in Problem 1.7, calculate the probability density of finding the electron (a) at the nucleus, (b) at a point in space at a distance a_0 from the nucleus. Calculate the probabilities of finding the electron inside a region of volume 1.0 pm^3 located at these points assuming that the probability density is constant inside the small volume region.

Problems

*1.1 Evaluate the expectation values of the operators p_x and p_x^2 for a particle with wavefunction $(2/L)^{1/2} \sin(\pi x/L)$ in the range 0 to L .

1.2 Are the linear combinations $2x - y - z$, $2y - x - z$, $2z - x - y$ linearly independent?

1.3 Evaluate the commutators (a) $[x, y]$, (b) $[p_x, p_y]$, (c) $[x, p_x]$, (d) $[x^2, p_x]$, (e) $[x^n, p_x]$.

*1.4 Show that (a) $[A, B] = -[B, A]$, (b) $[A^m, A^n] = 0$ for all m, n , (c) $[A^2, B] = A[A, B] + [A, B]A$, (d) $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$.

1.5 Evaluate the commutator $[l_y, [l_y, l_z]]$ given that $[l_x, l_y] = i\hbar l_z$, $[l_y, l_z] = i\hbar l_x$, and $[l_z, l_x] = i\hbar l_y$.

1.6 A particle in an infinite one-dimensional system was described by the wavefunction $\psi(x) = Ne^{-x^2/2r^2}$. Normalize this function. Calculate the probability of finding the particle in the range $-r \leq x \leq r$. *Hint.* The integral encountered in the second part is the error function. It is available in mathematical software.

*1.7 The ground-state wavefunction of a hydrogen atom has the form $\psi(r) = Ne^{-br}$, b being a collection of fundamental constants with the magnitude $1/a_0$, with $a_0 = 53 \text{ pm}$. Normalize this spherically symmetrical function. *Hint.* The volume element is $d\tau = \sin\theta d\theta d\phi r^2 dr$, with $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$, and $0 \leq r < \infty$. 'Normalize' always means 'normalize to 1' in this text.

1.8 Confirm that the operators (a) $T = -(\hbar^2/2m)(d^2/dx^2)$ and (b) $l_z = (\hbar/i)(d/d\phi)$ are Hermitian. *Hint.* Consider

the integrals $\int_0^L \psi_a^* T \psi_b dx$ and $\int_0^{2\pi} \psi_a^* l_z \psi_b d\phi$ and integrate by parts.

1.9 Find the operator for position x if the operator for momentum p is taken to be $(\hbar/2m)^{1/2}(A + B)$, with $[A, B] = 1$ and all other commutators zero. *Hint.* Write $x = aA + bB$ and find one set of solutions for a and b .

*1.10 Evaluate the commutators (a) $[(1/x), p_x]$, (b) $[(1/x), p_x^2]$, (c) $[xp_y - yp_x, yp_x - zp_x]$, (d) $[x^2(\partial^2/\partial y^2), y(\partial/\partial x)]$.

1.11 Evaluate the commutators (a) $[H, p_x]$ and (b) $[H, x]$, where $H = p_x^2/2m + V(x)$. Choose (i) $V(x) = V$, a constant, (ii) $V(x) = \frac{1}{2}kx^2$, (iii) $V(x) \rightarrow V(r) = e^2/4\pi\epsilon_0 r$. *Hint.* For part (b), case (iii), use $(\partial r^{-1}/\partial x) = -x/r^3$.

1.12 Use the momentum representation and a general function $f(p_x)$ of the linear momentum to confirm that the position and momentum operators in this representation do not commute, and find the value of their commutator.

*1.13 Construct quantum mechanical operators in the position representation for the following observables: (a) kinetic energy in one and in three dimensions, (b) the inverse separation, $1/x$, (c) electric dipole moment ($\sum_i Q_i r_i$ where r_i is the position of a charge Q_i), (d) z -component of angular momentum ($xp_y - yp_x$), (e) the mean square deviations of the position and momentum of a particle from the mean values.

1.14 Repeat Problem 1.13, but find operators in the momentum representation. *Hint.* The observable $1/x$ should be regarded as x^{-1} ; hence the operator required is the inverse of the operator for x .

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1.15 In relativistic mechanics, energy and momentum are related by the expression $E^2 = p^2c^2 + m^2c^4$. (a) Show that when $p^2c^2 \ll m^2c^4$ this expression reduces to $E = p^2/2m + mc^2$. (b) Construct the relativistic analogue of the Schrödinger equation from the relativistic expression. (c) What can be said about the conservation of probability? *Hint:* For part (b), use $i\hbar(\partial/\partial t)$ for the energy operator. For part (c), see Problem 1.16.

*1.16 Show that if the Schrödinger equation had the form of a true wave equation, then the integrated probability would be time dependent. *Hint:* A wave equation has $\kappa\partial^2/\partial t^2$ in place of $i\hbar\partial/\partial t$, where κ is a constant with the appropriate dimensions (what are they?). Solve the time component of the separable equation and investigate the behaviour of $\int \Psi^* \Psi \, d\tau$.

1.17 The operator e^A has a meaning if it is expanded as a power series: $e^A = \sum_n (1/n!)A^n$. Show that if $|a\rangle$ is an eigenstate of A with eigenvalue a , then it is also an eigenstate of e^A . Find the latter's eigenvalue.

1.18 Evaluate the expectation value of e^{iLp_x} for a particle in a square well of length L and described by the wavefunction $(2/L)^{1/2} \sin(\pi x/L)$ in the range 0 to L . *Hint:* $e^{iA} = \cos A + i \sin A$, $\cos \theta = 1 - (1/2!)\theta^2 + (1/4!)\theta^4 - \dots$, $\sin \theta = \theta - (1/3!)\theta^3 + (1/5!)\theta^5 - \dots$.

*1.19 (a) Show that $e^A e^B = e^{A+B}$ only if $[A, B] = 0$. (b) If $[A, B] \neq 0$ but $[A, [A, B]] = [B, [A, B]] = 0$, show that $e^A e^B = e^{A+B} e^f$, where f is a simple function of $[A, B]$. *Hint:* This is another example of the differences between operators (q -numbers) and ordinary numbers (c -numbers). The simplest approach is to expand the exponentials and to collect and compare terms on both sides of the equality. Note that $e^A e^B$ will give terms like $2AB$ while e^{A+B} will give $AB + BA$. Be careful with order.

1.20 Evaluate (by considering eqn 1.43a) the limitation on the simultaneous specification of the following observables: (a) the position and momentum of a particle, (b) the three components of linear momentum of a particle, (c) the kinetic energy and potential energy of a particle, (d) the electric dipole moment ($-ex$) and the total energy of a one-dimensional system, (e) the kinetic energy and the position of a particle in one dimension.

1.21 Evaluate the quantity $\Delta_x x \Delta_x p_x$ for the ground state ($n = 1$) of a particle of mass m in a box of length L , where $\Delta_x \Omega = \langle (\Omega - \langle \Omega \rangle)^2 \rangle^{1/2}$.

*1.22 Use eqn 1.44 to find expressions for the rate of change of the expectation values of position and momentum of a harmonic oscillator; solve the pair of differential equations, and show that the expectation values change in time in the same way as for a classical oscillator. *Hint:* Use the results of Problem 1.11 part (ii).

1.23 The only non-zero matrix elements of x and p_x for a harmonic oscillator are

$$\langle \nu + 1 | x | \nu \rangle = \left(\frac{\hbar}{2m\omega} \right)^{1/2} (\nu + 1)^{1/2}$$

$$\langle \nu - 1 | x | \nu \rangle = \left(\frac{\hbar}{2m\omega} \right)^{1/2} \nu^{1/2}$$

$$\langle \nu + 1 | p_x | \nu \rangle = i \left(\frac{\hbar m \omega}{2} \right)^{1/2} (\nu + 1)^{1/2}$$

$$\langle \nu - 1 | p_x | \nu \rangle = -i \left(\frac{\hbar m \omega}{2} \right)^{1/2} \nu^{1/2}$$

See Section 2.15. Use the completeness relation, eqn 1.25, to deduce the value of the matrix element $\langle \nu | x p_x^2 x | \nu \rangle$.

1.24 Write the time-independent Schrödinger equations for (a) the hydrogen atom, (b) the helium atom, (c) the hydrogen molecule, (d) a free particle, (e) a particle subjected to a constant, uniform force. *Hint:* Identify the appropriate potential energy terms and express them as operators in the position representation.

*1.25 The time-dependent Schrödinger equation is separable when V is independent of time. (a) Show that it is also separable when V is a function only of time and is uniform in space. (b) Solve the pair of equations. Let $V(t) = V \cos \omega t$; find an expression for $\Psi(x, t)$ in terms of $\Psi(x, 0)$. (c) Is $\Psi(x, t)$ stationary in the sense specified in Section 1.14?

1.26 (a) Calculate the probability of the electron being found anywhere within a sphere of radius a_0 for the atom defined in Problem 1.7. (b) If the radius of the atom is defined as the radius of the sphere inside which there is a 90 per cent probability of finding the electron, what is the atom's radius? *Hint:* For part (b), find the solution numerically (e.g. by successive approximation, using software, or graphically).

1.27 A particle is moving in a circle in the xy plane. The only coordinate of importance is the angle φ which can vary from 0 to 2π as the particle goes around the circle. We are interested in measurements of the angular momentum l_z of the particle. The angular momentum operator for such a system is given by $(\hbar/i)d/d\varphi$. (a) Suppose that the state of the particle is described by the wavefunction $\psi(\varphi) = Ne^{-i\varphi}$ where N is the normalization constant. What values will we find when we measure the angular momentum of the particle? If more than one value is possible, what is the probability of obtaining each result? What is the expectation value of the angular momentum? (b) Now suppose that the state of the particle is described by the normalized wavefunction $\psi(\varphi) = N\{(3/4)^{1/2}e^{-i\varphi} - (i/2)e^{2i\varphi}\}$. When we measure the angular momentum of the particle, what values will we find? If more than one value is possible, what is the probability of obtaining each result? What is the expectation value of the angular momentum?

*1.28 Provide a proof of eqn 1.47; eqns 1.47 and 1.46b jointly form *Ehrenfest's theorem*.

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2.68)

$$\frac{d}{dt}\langle p_x x \rangle = 2\langle T \rangle - \left\langle x \frac{dV}{dx} \right\rangle$$

The time average of this expression is

$$\frac{1}{\tau} \int_0^\tau \frac{d}{dt} \langle p_x x \rangle dt = \frac{1}{\tau} \int_0^\tau \left\{ 2\langle T \rangle - \left\langle x \frac{dV}{dx} \right\rangle \right\} dt$$

Therefore, because the expectation values on the right are independent of time,

$$\frac{1}{\tau} \langle p_x x \rangle \Big|_0^\tau = 2\langle T \rangle - \left\langle x \frac{dV}{dx} \right\rangle$$

The term on the left is zero, for if the motion is periodic we may choose τ to be the period, and if the motion is not periodic, then we may choose τ to be infinite. In the latter case, the value of $\langle p_x x \rangle_\tau - \langle p_x x \rangle_0$ is finite in a bounded system and τ is infinite. Therefore,

(2.69)

$$2\langle T \rangle = \left\langle x \frac{dV}{dx} \right\rangle \quad (2.72)$$

The force experienced by the particle is $F_x = -dV/dx$, so this equation may be written

$$2\langle T \rangle = -\langle x F_x \rangle \quad (2.73)$$

and in three dimensions this expression is the virial theorem:

$$2\langle T \rangle = -\langle \mathbf{r} \cdot \mathbf{F} \rangle \quad (2.74)$$

If the potential energy of the particle has the form $V = ax^s$, then eqn 2.72 gives

$$\langle T \rangle = \frac{1}{2} s \langle V \rangle \quad (2.75)$$

as used in the text. The theorem may be extended to operators other than $p \cdot r$; then, different choices lead to a variety of hypervirial theorems.

Exercises

***2.1** Write the wavefunctions for (a) an electron travelling to the right ($x > 0$) after being accelerated from rest through a potential difference of (i) 1.0 V, (ii) 10 kV, (b) a particle of mass 1.0 g travelling to the right at 10 m s⁻¹.

***2.2** Find expressions for the probability densities of the particles in the preceding exercise.

***2.3** Confirm that the wavefunctions in eqns 2.5 and 2.6 satisfy the time-independent Schrödinger equation, eqn 2.4.

***2.4** Calculate the flux density for a particle with a wavefunction $A \sin kx$.

***2.5** Calculate the kinetic energy of the electron incident on a potential energy barrier of height 2.0 eV and having a penetration depth of 0.40 nm.

***2.6** Calculate the transmission probability for an electron incident upon an Eckart potential barrier with $V_0 = 2.0$ eV, $\beta = 1.0 \times 10^{10}$ m⁻¹, and $E = V_0$.

***2.7** Identify the locations of the nodes in the wavefunction with $n = 4$ for a particle in a one-dimensional square well.

***2.8** Confirm that the $n = 1$ and $n = 2$ wavefunctions for a particle in a box are orthogonal.

***2.9** Identify the locations of (a) the nodes and (b) the maxima in the probability densities for a particle in a geometrically square two-dimensional box of length L and in the state (i) $|n_1 = 2, n_2 = 1\rangle$, (ii) $|n_1 = 3, n_2 = 2\rangle$.

***2.10** For a particle in a three-dimensional cubic box, find the degeneracy of the level that has an energy three times that of the lowest level.

***2.11** Locate the nodes of the harmonic oscillator wavefunction for the state with $\nu = 2$.

***2.12** Calculate the wavelength and wavenumber of the photon needed to excite a transition between the neighbouring vibrational energy levels of a harmonic oscillator of mass 1.33×10^{-25} kg and force constant 275 N m⁻¹.

Problems

***2.1** Use the qualitative 'wavefunction generator' in Fig. 2.4 to sketch the wavefunctions for (a) a particle with a potential energy that decreases linearly to the right, (b) a particle with a potential energy that is constant to $x = 0$, then falls in the shape of a semicircle to a low value to climb back to its original constant value at $x = L$, (c) the same as in part (b), but with the dip replaced by a hump.

2.2 Express the coefficients C and D in eqn 2.6 in terms of the coefficients A and B in eqn 2.5.

2.3 Calculate the flux density (eqn 2.11) for a particle with a wavefunction with coefficients $A = A_0 \cos \zeta$ and $B = A_0 \sin \zeta$, for a particle undergoing free motion in one dimension, with ζ a parameter, and plot J_x as a function of ζ .

***2.4** A particle was prepared travelling to the right with all momenta between $(k - \frac{1}{2}\Delta k)\hbar$ and $(k + \frac{1}{2}\Delta k)\hbar$ contributing equally to the wavepacket. Find the explicit form of the wavepacket at $t = 0$, normalize it, and estimate the range

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of positions, Δx , within which the particle is likely to be found. Compare the last conclusion with a prediction based on the uncertainty principle. *Hint.* Use eqn 2.13 with $g = B$, a constant, inside the range $k - \frac{1}{2}\Delta k$ to $k + \frac{1}{2}\Delta k$ and zero elsewhere, and eqn 2.12 with $t = 0$ for Ψ_k . To evaluate $\int |\Psi_k|^2 dx$ (for the normalization step) use the integral $\int_{-\infty}^{\infty} (\sin x/x)^2 dx = \pi$. Take Δx to be determined (numerically) by the locations where $|\Psi|^2$ falls to half its value at $x = 0$. For the last part use $\Delta p_x \approx \hbar \Delta k$.

2.5 Sketch the form of the wavepacket $|\Psi(x,0)|^2$ constructed in Problem 2.4. Sketch its form $|\Psi(x,t)|^2$ a short time later, when t is non-zero but still small. *Hint.* For the second part use eqn 2.13 but with $e^{-i\hbar k^2 t/2m} \approx 1 - i\hbar k^2 t/2m$.

2.6 Complete the derivation of eqn 2.22a for the transmission probability at energies $E < V$. Show that eqn 2.22a simplifies to eqn 2.22b for barriers that are high and wide (in the sense that $\kappa L \gg 1$).

***2.7** Repeat the evaluation (see the preceding problem) that led to eqn 2.22a but do so for the case $E > V$. Compare your result to the transmission probability in eqn 2.23.

2.8 Demonstrate that eqns 2.22a and 2.23 coincide at $E = V$ and identify the value of T at that energy. *Hint.* To find the value of T , note that $\sin^2 x \rightarrow x^2$ as $x \rightarrow 0$.

2.9 A particle of mass m is incident from the left on a wall of infinite thickness and which may be represented by a potential energy V . Calculate the reflection probability for (a) $E \leq V$, (b) $E > V$. For electrons incident on a metal surface $V = 10$ eV. Evaluate and plot the reflection probability. *Hint.* Proceed as in Problems 2.6 and 2.7 but consider only two domains, inside the barrier and outside it. The reflection probability is the ratio $|B|^2/|A|^2$ in the notation of eqn 2.21a.

***2.10** A particle of mass m is confined to a one-dimensional box of length L . Calculate the probability of finding it in the following regions: (a) $0 \leq x \leq \frac{1}{2}L$, (b) $0 \leq x \leq \frac{1}{4}L$, (c) $\frac{1}{2}L - \delta x \leq x \leq \frac{1}{2}L + \delta x$. Derive expressions for a general value of n . Then evaluate the probabilities (i) for $n = 1$, (ii) in the limit $n \rightarrow \infty$. Compare the latter to the classical expectations.

2.11 An electron is confined to a one-dimensional box of length L . What should be the length of the box in order for its zero-point energy to be equal to its rest mass energy ($m_e c^2$)? Express the result in terms of the Compton wavelength, $\lambda_c = h/m_e c$.

2.12 Energy is required to compress the box when a particle is inside: this suggests that the particle exerts a force on the walls. (a) On the basis that when the length of the box changes by dL the energy changes by $dE = -F dL$, find an expression for the force. (b) At what length does $F = 1$ N when an electron is in the state $n = 1$?

***2.13** The mean position $\langle x \rangle$ of a particle in a one-dimensional well can be calculated by weighting its position x by the probability that it will be found in the

region dx at x , which is $\psi^2(x)dx$, and then summing (i.e. integrating) these values. Show that $\langle x \rangle = \frac{1}{2}L$ for all values of n . *Hint.* Evaluate $\int_0^L x \psi_n^2(x) dx$.

2.14 The root mean square deviation of the particle from its mean position is $\Delta x = \{(\langle x^2 \rangle - \langle x \rangle^2)\}^{1/2}$. Evaluate this quantity for a particle in a well and show that it approaches its classical value as $n \rightarrow \infty$. *Hint.* Evaluate $\langle x^2 \rangle = \int_0^L x^2 \psi^2(x) dx$. In the classical case the distribution is uniform across the box, and so in effect $\psi(x) = 1/L^{1/2}$.

2.15 For a particle in a box, the mean value and mean square value of the linear momentum are given by $\int_0^L \psi^* p \psi dx$ and $\int_0^L \psi^* p^2 \psi dx$, respectively. Evaluate these quantities. Form the root mean square deviation $\Delta p = \{(\langle p^2 \rangle - \langle p \rangle^2)\}^{1/2}$ and investigate the consistency of the outcome with the uncertainty principle. *Hint.* Use $p = (\hbar/i)d/dx$. For $\langle p^2 \rangle$ notice that $E = p^2/2m$ and we already know E for each n . For the last part, form $\Delta x \Delta p$ and show that $\Delta x \Delta p \geq \frac{1}{2}\hbar$, the precise form of the principle, for all n ; evaluate $\Delta x \Delta p$ for $n = 1$.

***2.16** Calculate the energies and wavefunctions for a particle in a one-dimensional square well in which the potential energy rises to a finite value V at each end, and is zero inside the well; that is

$$V(x) = V \quad x \leq 0 \text{ and } x \geq L$$

$$V(x) = 0 \quad 0 < x < L$$

Show that for any V and L there is always at least one bound level, and that as $V \rightarrow \infty$ the solutions coincide with those in eqn 2.31. *Hint.* Divide space into three zones, solve the Schrödinger equations, and impose the boundary conditions (finiteness and continuity of ψ and continuity of $d\psi/dx$ across the zone boundaries: combine the latter continuity requirements into the continuity of the logarithmic derivatives $((1/\psi)(d\psi/dx))$. After some algebra arrive at

$$kL + 2 \arcsin\left\{\frac{k\hbar}{(2mV)^{1/2}}\right\} = n\pi \quad k\hbar = (2mE)^{1/2}$$

Solve this expression graphically for k and hence find the energies for each value of the integer n .

2.17 A very simple model of a polyene is the free electron molecular orbital (FEMO) model. Regard a chain of N conjugated carbon atoms, bond length R_{CC} , as forming a box of length $L = (N - 1)R_{CC}$. Find an expression for the allowed energies. Suppose that the electrons enter the states in pairs so that the lowest $\frac{1}{2}N$ states are occupied. Estimate the wavelength of the lowest energy transition, taking $R_{CC} = 140$ pm and $N = 22$. Repeat the calculation of the wavelength if the length of the chain is taken to be $(N + 1)R_{CC}$ (an assumption that allows for electrons to spill over the ends slightly).

2.18 (a) Show that the variables in the Schrödinger equation for a cubic box may be separated and the overall wavefunctions expressed as $X(x)Y(y)Z(z)$. (b) Deduce the energy levels and wavefunctions. (c) Show that the functions

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are orthonormal. (d) What is the degeneracy of the level with $E = 14(b^2/8mL^2)$?

2.19 Demonstrate that accidental degeneracies can exist in a rectangular infinite square-well potential provided that the lengths of the sides are in a rational proportion, that is when $L_1 = \lambda L_2$, with λ an integer. What is the degeneracy?

2.20 Confirm that the completeness relation, eqn 1.25, may be expressed in terms of wavefunctions as

$$\sum_n \psi_n(r)\psi_n^*(r') = \delta(r-r')$$

where $\delta(r-r')$ is the Dirac δ -function described in Section 2.1.

2.21 For the ground-state wavefunction of a particle in a three-dimensional cubic box of length L , evaluate the matrix element $\langle \psi | \delta | \psi \rangle$ where δ is the Dirac δ -function $\delta(r-r')$ and r' is taken to be the point at the centre of the cube. What is the relation between the matrix element and probability amplitudes? *Hint.* Use the results of Problem 2.18 and the *brief comment* in Section 2.1.

2.22 The Hermite polynomials $H_n(y)$ satisfy the differential equation

$$H_n''(y) - 2yH_n'(y) + 2nH_n(y) = 0$$

Confirm that the wavefunctions in eqn 2.41 are solutions of the harmonic oscillator Schrödinger equation.

2.23 Locate the nodes of the harmonic oscillator wavefunction for the state with $\nu = 6$. *Hint.* Use mathematical software.

2.24 Confirm the expression for the normalization factor of a harmonic oscillator wavefunction, eqn 2.41.

2.25 Evaluate the matrix elements (a) $\langle \nu + 1 | x | \nu \rangle$ and (b) $\langle \nu + 2 | x^2 | \nu \rangle$ of a harmonic oscillator by using the relations given at the bottom of Table 2.1 for the Hermite polynomials.

2.26 The oscillation of the atoms around their equilibrium positions in the molecule HI can be modelled as a harmonic oscillator of mass $m \approx m_{\text{H}}$ (the iodine atom is almost stationary) and force constant $k_f = 313.8 \text{ N m}^{-1}$. Evaluate the separation of the energy levels and predict the wavelength of the light needed to induce a transition between neighbouring levels.

2.27 What is the relative probability of finding the HI molecule with its bond length 10 per cent greater than its equilibrium value (equilibrium bond length of 161 pm) when it is in (a) the $\nu = 0$ state, (b) the $\nu = 4$ state? Use the information in Problem 2.26.

2.28 Determine the probability of finding the ground-state harmonic oscillator stretched to a displacement beyond the classical turning point. *Hint.* Relate the expression for the probability to the error function, $\text{erf } z$, defined as

$$\text{erf } z = 1 - \frac{2}{\pi^{1/2}} \int_z^\infty e^{-y^2} dy$$

and evaluate it using $\text{erf } 1 = 0.8427$. The error function is incorporated into most mathematical software packages.

2.29 Calculate the values of (a) $\langle x \rangle$, (b) $\langle x^2 \rangle$, (c) $\langle p_x \rangle$, (d) $\langle p_x^2 \rangle$ for a harmonic oscillator in its ground state by evaluation of the appropriate integrals (as in Problems 2.13–2.15). Examine the value of $\Delta x \Delta p_x$ in the light of the uncertainty principle. *Hint.* Use the integrals

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$\int_0^{\infty} x e^{-\alpha x^2} dx = \frac{1}{2\alpha}$$

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2} \left(\frac{\pi}{\alpha^3}\right)^{1/2}$$

2.30 Show that the flux density associated with a time-dependent wavefunction Ψ of definite energy is independent of location. *Hint.* Use eqn 2.10 in conjunction with the time-dependent Schrödinger equation (eqn 1.33) to show that J_x is independent of x ; that is, $\partial J_x / \partial x = 0$.

2.31 A particle of mass m is confined in a one-dimensional box of length L . The state of the particle is given by the normalized wavefunction $\psi(x) = \frac{1}{3}\psi_1(x) + \frac{1}{3}i\psi_3(x) - \left(\frac{2}{9}\right)^{1/2}\psi_5(x)$ where $\psi_n(x)$ is a normalized particle-in-a-box wavefunction corresponding to quantum number n (eqn 2.31). (a) What will be the outcome when the energy of the particle is measured? (b) If more than one result is possible, give the probability of obtaining each result. (c) What is the expectation value of the energy?

2.32 Consider a harmonic oscillator of mass m undergoing harmonic motion in two dimensions x and y . The potential energy is given by $V(x,y) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2$. (a) Write down the expression for the hamiltonian operator for such a system. (b) What is the general expression for the allowable energy levels of the two-dimensional harmonic oscillator? (c) What is the energy of the ground state (the lowest energy state)? *Hint.* The hamiltonian operator can be written as a sum of operators.

2.33 Consider a particle of mass $1.00 \times 10^{-25} \text{ g}$ moving freely in a three-dimensional cubic box of side 10.00 nm. The potential energy is zero inside the box and is infinite at the walls and outside of the box.

(a) Evaluate the zero-point energy of the particle.

(b) Consider the energy level that has an energy 9 times greater than the zero-point energy. What is the degeneracy of this level? Identify all the sets of quantum numbers that correspond to this energy. (The energy levels of the cubic box were deduced in Problem 2.18.)

(c) Compute the wavelength, frequency, and wavenumber of the photon responsible for the transition from the ground state of the particle to the energy level of part (b).

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Exercises

(3.97)

*3.1 The rotation of the HI molecule can be pictured as an orbiting of the hydrogen atom at a radius of 160 pm about a virtually stationary I atom. If the rotation is thought of as taking place in a plane, what are the rotational energy levels?

(3.98)

*3.2 What wavelength of radiation is emitted in the transition $m_l = +1 \rightarrow m_l = 0$ in the system described in Exercise 3.1? In what region of the electromagnetic spectrum does this transition occur?

(3.99)

*3.3 Show that $l_z = (\hbar/i)\partial/\partial\varphi$ (that is, confirm eqn 3.10) for a particle confined to a planar surface.

(3.100)

*3.4 Show that the wavefunctions in eqn 3.13 are mutually orthogonal.

(3.101)

*3.5 Calculate the rotational energy levels of a compact disk of radius 10 cm, mass 50 g free to rotate in a plane (refer to Fig. 3.1 for the radius of gyration). To what value of m_l does a rotation rate of 100 Hz correspond?

(3.102)

*3.6 Construct the analogues of Figs 3.5 and 3.6 for the states of a rotor with $m_l = +3$ and $+4$.

*3.7 Confirm that the wavefunctions for a particle on a sphere may be written $\psi(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$ by the method of separation of variables, and find the equation for Θ .

*3.8 Confirm that the Schrödinger equation for a particle free to rotate in three dimensions does indeed separate into equations for the variation with θ and φ .

*3.9 Confirm that $Y_{1,+1}$ and $Y_{2,0}$ as listed in Table 3.2 are solutions of the Schrödinger equation for a particle on a sphere.

*3.10 Confirm by explicit integration that $Y_{1,+1}$ and $Y_{2,0}$ are normalized and mutually orthogonal.

*3.11 Modify Exercise 3.1 so that the molecule is free to rotate in three dimensions. Calculate the energies and degeneracies of the lowest three rotational levels.

*3.12 Predict the wavelength of radiation emitted in the $l = 1 \rightarrow 0$ transition for the system treated in Exercise 3.11.

In which region of the electromagnetic spectrum does this transition occur?

*3.13 Draw the analogues of Fig. 3.30 for $l = 2$. Observe how the maxima of $|Y|^2$ migrate into the equatorial plane as $|m_l|$ increases.

*3.14 Verify that the solutions of eqn 3.45 are separable and that the radial wave equation for a particle in a spherical cavity is eqn 3.47b.

*3.15 Confirm that the radial wavefunctions $u_{1,0}$, $u_{2,0}$, and $u_{3,1}$ satisfy the radial wave equation, eqn 3.58. Use Table 3.4.

*3.16 Locate the radial nodes of the (a) 2s-orbital, (b) 3s-orbital of the hydrogen atom.

*3.17 Confirm that ψ_1 and ψ_2 are mutually orthogonal.

*3.18 A quantity important in some branches of spectroscopy (see, for instance, Section 13.14) is the probability of an electron being found at the same location as the nucleus. Evaluate this probability density for an electron in the 1s-, 2s-, and 3s-orbitals of a hydrogenic atom. Proceed to evaluate this probability density numerically for the hydrogen atom.

*3.19 Another quantity of interest in spectroscopy is the average value of $1/r^3$ (for example, the average magnetic dipole interaction between the electron and nuclear magnetic moments depends on it). Determine $\langle 1/r^3 \rangle$ for an electron in a 2p-orbital of a hydrogenic atom and evaluate it numerically for a hydrogen atom.

*3.20 Calculate the difference in ionization energies of ^1H and ^2H on the basis of differences in their reduced masses. (The experimental difference is 29.838 cm^{-1} .)

*3.21 For a given principal quantum number n , l takes the values $0, 1, \dots, n-1$ and for each l , m_l takes the values $l, l-1, \dots, -l$. Confirm that the degeneracy of the term with principal quantum number n is equal to n^2 in a hydrogenic atom.

Problems

*3.1 Confirm eqn 3.2 for the laplacian in two dimensions.

3.2 Calculate (a) the mean radius, (b) the mean square radius, and (c) the most probable radius of the 1s-, 2s-, and 3s-orbitals of a hydrogenic atom of atomic number Z . *Hint.* For the most probable radius look for the principal

maximum of the radial distribution function. You will find the following integral useful:

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

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3.3 Calculate the probability of finding an electron within a sphere of radius a_0 for (a) a 3s-orbital, (b) a 3p-orbital of the hydrogen atom. *Hint.* Use mathematical software for integration.

***3.4** Calculate the values of (a) $\langle r \rangle$ and (b) $\langle 1/r \rangle$ for a 3s- and a 3p-orbital of a hydrogenic atom of atomic number Z . *Hint.* Use the definite integral given in Problem 3.2.

3.5 (a) Construct a wavepacket $\Psi = N \sum_{m_l=0}^{\infty} (1/m_l!) e^{im_l\phi}$ and normalize it to unity. Sketch the form of $|\Psi|^2$ for $0 \leq \phi \leq 2\pi$. **(b)** Calculate $\langle \phi \rangle$, $\langle \sin \phi \rangle$, and $\langle I_z \rangle$. **(c)** Why is $\langle I_z \rangle \leq \hbar$? *Hint.* Draw on a variety of pieces of information, including $\sum_{n=0}^{\infty} x^n/n! = e^x$ and the following integrals:

$$\int_0^{2\pi} e^{x \cos \phi} d\phi = 2\pi I_0(x) \quad \int_0^{2\pi} \cos \phi e^{x \cos \phi} d\phi = 2\pi I_1(x)$$

with $I_0(2) = 2.280 \dots$, $I_1(2) = 1.591 \dots$; the $I_l(x)$ are modified Bessel functions.

3.6 Investigate the properties of the more general wavepacket $\Psi = N \sum_{m_l=0}^{\infty} (\alpha^{m_l}/m_l!) e^{im_l\phi}$ and show that when α is large $\langle I_z \rangle \approx \alpha \hbar$. *Hint.* Proceed as in the last problem. The large-value expansions of $I_0(x)$ and $I_1(x)$ are $I_0(x) \approx I_1(x) \approx e^x/(2\pi x)^{1/2}$.

***3.7** Use mathematical software to verify that the energies of a particle in a circular square well of radius a are those given in Table 3.1.

3.8 Evaluate the probability that a particle of mass m in the ground state of a circular square well of radius a will be found within the circular area of radius $1/2a$.

3.9 Confirm eqn 3.28 for the laplacian in three dimensions.

***3.10 (a)** Confirm that the radius of gyration of a solid uniform sphere of radius R is $r = (\frac{3}{5})^{1/2} R$. **(b)** What is the radius of gyration of a solid uniform cylinder of radius R and length l about an axis perpendicular to its principal

axis? *Hint.* For part (a), the moment of inertia of a sphere is $\frac{2}{5}MR^2$.

3.11 Calculate the angle that the angular momentum vector makes with the z -axis when the system is described by the wavefunction ψ_{lm} . Show that the minimum angle approaches zero as l approaches infinity. Calculate the allowed angles when l is 1, 2, and 3.

3.12 Confirm the entries for the first five energy levels of a particle in a spherical cavity as listed in Table 3.3.

***3.13** Evaluate the probability that a particle of mass m will be found within a sphere of radius $1/2a$ in the ground state of a spherical cavity of radius a .

3.14 Calculate the most probable radius at which a particle of mass m will be found in the ground state of a spherical cavity of radius a .

3.15 Calculate the mean kinetic and potential energies of an electron in the ground state of the hydrogen atom, and confirm that the virial theorem is satisfied. *Hint.* Evaluate $\langle T \rangle = -(\hbar^2/2\mu) \int \psi_1^* \nabla^2 \psi_1 d\tau$ and $\langle V \rangle = -(e^2/4\pi\epsilon_0) \int \psi_1^*(1/r)\psi_1 d\tau$. The laplacian is given in eqn 3.28 and the virial theorem is dealt with in *Further information 2.4*.

***3.16** Confirm, by drawing pictures like those in Fig. 3.31, that a whimsical Flatlander might be shown that 3s-, 3p-, and 3d-orbitals are degenerate.

3.17 The state of the electron in a He^+ ion is described by the wavefunction: $\psi(r, \theta, \phi) = R_{4,1}(r) Y_{1,1}(\theta, \phi)$. Determine **(a)** the energy of the electron; **(b)** the magnitude of the angular momentum vector of the electron; and **(c)** the projection of the angular momentum vector on to the z -axis. In addition, draw as complete a picture as possible of the vector model of the electron angular momentum. In your picture, specify as many of the lengths and angles as possible. *Hint.* For the last part of this problem, you need not be concerned with the radial component of ψ .

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Exercises

- *4.1 Use a derivation analogous to that of eqn 4.6 to verify the commutation relations in eqn 4.7.
- *4.2 Confirm that $[l_x, l_-] = -\hbar l_-$ and $[l_x, l_+] = 2\hbar l_+$.
- *4.3 Evaluate the effects of l_+ and l_- on the states (a) $|3,3\rangle$, (b) $|3,-3\rangle$.
- *4.4 Evaluate the effects of j^2 and j_z on the states (a) $|3,2\rangle$, (b) $|1,-1\rangle$.
- *4.5 What values of m_l are permitted for (a) $l = 4$, (b) $l = 5/2$?
- *4.6 Confirm that the shift operators s_+ and s_- are each other's Hermitian conjugate by using eqn 4.27 and the effects of the operators on the spin states α and β .
- *4.7 Calculate the matrix elements (a) $\langle 1,0|j_z|1,0\rangle$, (b) $\langle 1,1|j_+|1,0\rangle$.
- *4.8 Evaluate the magnitude of the spin angular momentum and its component on the z -axis for an electron in spin state (a) α , (b) β . Express your results in appropriate SI units.
- *4.9 Using a derivation analogous to that of eqn 4.38, show that the commutation relations in eqn 4.7 are obeyed by the three components of the total angular momentum $j = j_1 + j_2$.
- *4.10 What angular momentum states can arise from a system with two sources of angular momentum, one with $j_1 = 1$ and the other with $j_2 = 3/2$? Specify the states as in Example 4.3.
- *4.11 Construct the state $|j = 1/2, m_j = +1/2\rangle$ for a p-electron from its uncoupled states.
- *4.12 Determine what total spin angular momenta may arise from the spin angular momenta of three electrons.

Problems

- *4.1 Evaluate the commutator $[l_x, l_y]$ in (a) the position representation, (b) the momentum representation.
- 4.2 Evaluate the commutators (a) $[l_y^2, l_x]$, (b) $[l_y^2, l_x^2]$, and (c) $[l_x, [l_x, l_y]]$. *Hint.* Use the basic commutators in eqn 4.7.
- 4.3 Confirm that $[l^2, l_x] = 0$.
- *4.4 Verify that eqn 4.9 expresses the basic angular momentum commutation rules. *Hint.* Expand the left of eqn 4.9 and compare coefficients of the unit vectors. Be careful with the ordering of the vector components when expanding the determinant; the operators in the second row always precede those in the third.
- 4.5 Verify that the three matrices in eqn 4.36 yield the correct results for the applications of the spin operators s_q ($q = x, y, z$) on the spin states α and β .
- 4.6 Find expressions for the matrices σ_+ and σ_- that yield the correct results for the applications of the spin operators $s_q = \frac{1}{2}\hbar\sigma_q$ ($q = +, -$) on the spin states α and β .
- *4.7 (a) Confirm that the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
 satisfy the angular momentum commutation relations when we write $s_q = \frac{1}{2}\hbar\sigma_q$, and hence provide a matrix representation of angular momentum. (b) Why does the representation correspond to $s = 1/2$? *Hint.* For the second part, form the matrix representing s^2 and establish its eigenvalues.
- 4.8 Using the Pauli matrix representation, reduce each of the operators (a) $s_x s_y$, (b) $s_x s_y^2 s_z^2$, and (c) $s_x^2 s_y^2 s_z^2$ to a single spin operator.
- 4.9 Evaluate the effect of (a) $e^{i\alpha/\hbar}$, (b) $e^{i\beta/\hbar}$, (c) $e^{i\gamma/\hbar}$ on an α spin state. *Hint.* Expand the exponential operators as in Problem 1.17 and use arguments like those in Problem 4.8.
- *4.10 Suppose that in place of the actual angular momentum commutation rules, the operators obeyed $[l_x, l_y] = -i\hbar l_z$. What would be the roles of $l_{\pm} = l_x \pm i l_y$?
- 4.11 Calculate the matrix elements (a) $\langle 0,0|l_z|0,0\rangle$, (b) $\langle 2,1|l_+|2,0\rangle$, (c) $\langle 2,2|l_+^2|2,0\rangle$, (d) $\langle 2,0|l_-|2,0\rangle$, (e) $\langle 2,0|l_- l_+|2,0\rangle$, and (f) $\langle 2,0|l_-^2 l_+^2|2,0\rangle$.
- 4.12 Demonstrate that $j_1 - j_2$ is not an angular momentum.
- *4.13 Calculate the values of the following matrix elements between p-orbitals: (a) $\langle p_x|l_z|p_y\rangle$, (b) $\langle p_x|l_+|p_y\rangle$, (c) $\langle p_z|l_y|p_x\rangle$, (d) $\langle p_z|l_x|p_y\rangle$, and (e) $\langle p_z|l_x|p_x\rangle$. *Hint.* Use the relations between p_x, p_y, p_z and p_0, p_{+1}, p_{-1} .
- 4.14 Evaluate the matrix elements (a) $\langle j, m_j + 1|j_x^3|j, m_j\rangle$ and (b) $\langle j, m_j + 3|j_x^3|j, m_j\rangle$.
- 4.15 Verify eqn 4.31 for the shift operators in spherical polar coordinates. Use eqn 4.30.
- *4.16 Confirm that the spherical polar forms of the orbital angular momentum operators in eqn 4.30 satisfy the angular momentum commutation relation $[l_x, l_y] = i\hbar l_z$ and that the shift operators in eqn 4.31 satisfy $[l_+, l_-] = 2\hbar l_z$.

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4.17 Verify that successive application of L_x to ψ_{ll} with $l = 2$ in eqn 4.32 generates the five normalized spherical harmonics Y_{2,m_l} as set out in Table 3.2.

4.18 Verify that successive application of L_x to $\psi_{1,-1}$ in Table 3.2 generates the two other normalized spherical harmonics Y_{1,m_l} shown in the table.

***4.19 (a)** Demonstrate that if $[j_{1q}, j_{2q'}] = 0$ for all q, q' , then $j_1 \times j_2 = -j_2 \times j_1$. **(b)** Go on to show that if $j_1 \times j_1 = i\hbar j_1$ and $j_2 \times j_2 = i\hbar j_2$, then $j \times j = i\hbar j$ where $j = j_1 + j_2$.

4.20 In some cases m_{j_1} and m_{j_2} may be specified at the same time as j because although $[j^2, j_{1z}]$ is non-zero, the effect of $[j^2, j_{1z}]$ on the state with $m_{j_1} = j_1, m_{j_2} = j_2$ is zero. Confirm that $[j^2, j_{1z}]|j_1 j_1; j_2 j_2\rangle = 0$ and $[j^2, j_{1z}]|j_1, -j_1; j_2, -j_2\rangle = 0$.

4.21 Determine what total angular momenta may arise in the following composite systems: **(a)** $j_1 = 3, j_2 = 4$; **(b)** the orbital momenta of two electrons (i) both in p-orbitals, (ii) both in d-orbitals, (iii) the configuration $p^1 d^1$; **(c)** the spin angular momenta of four electrons. *Hint.* Use the Clebsch–Gordan series, eqn 4.42; apply it successively in (c).

***4.22** Construct the vector coupling coefficients for a system with $j_1 = 1$ and $j_2 = 1/2$ and evaluate the matrix elements $\langle j' m'_j | j_{1z} | j m_j \rangle$. *Hint.* Proceed as in Section 4.12 and check the answer against the values in *Resource section 2*. For the matrix element, express the coupled states in the uncoupled representation, and then operate with j_{1z} .

4.23 Use the vector model of angular momentum to derive the value of the angle between the vectors representing **(a)** two α spins, **(b)** an α and a β spin in a state with $S = 1$ and $M_S = +1$ and $M_S = 0$, respectively.

4.24 Set up a quantum mechanical expression that can be used to derive the same result as in Problem 4.23. *Hint.* Consider the expectation value of $s_1 \cdot s_2$.

***4.25** Apply both procedures (of the preceding two problems) to calculate the angle between α spins in the $\alpha\alpha\alpha$ state with $S = 3/2$.

4.26 Consider a system of two electrons that can have either paired or unpaired spins (e.g. a biradical). The energy of the system depends on the relative orientation of their spins. Show that the operator $(\hbar J / \hbar^2) s_1 \cdot s_2$ distinguishes between singlet and triplet states. The system is now exposed to a magnetic field in the z -direction. Because the two electrons are in different environments, they experience different local fields and their interaction energy can be written $(\mu_B / \hbar) \times \mathcal{B}(g_1 s_{1z} + g_2 s_{2z})$ with $g_1 \neq g_2$; μ_B is the Bohr magneton and g is the electron g -value, quantities discussed in Chapter 13. Establish the matrix of the total hamiltonian, and demonstrate that when $\hbar J \gg \mu_B \mathcal{B}$, the coupled representation is ‘better’, but that when $\mu_B \mathcal{B} \gg \hbar J$, the uncoupled representation is ‘better’. Find the eigenvalues of the system in each case. *Hint.* Use the vector coupling coefficients in *Resource section 2* to determine hamiltonian matrix elements.

4.27 What is the expectation value of the z -component of orbital angular momentum of electron 1 in the $|G, M_L\rangle$ state of the configuration d^2 ? *Hint.* Express the coupled state in terms of the uncoupled states, find $\langle G, M_L | l_{1z} | G, M_L \rangle$ in terms of the vector coupling coefficients, and evaluate it for $M_L = +4, +3, \dots, -4$.

***4.28** Prove that $\sum_{m_1, m_2} |C_{m_1, m_2}|^2 = 1$ for a given j_1, j_2, j . *Hint.* Use eqn 4.43 and form $\langle j_1 j_2; j m_j | j_1 j_2; j m_j \rangle$.

4.29 What are the possible outcomes of a single measurement of the z -component of spin angular momentum of an electron in the spin state $(1/4)^{1/2} \alpha - (3/4)^{1/2} \beta$?

* Indicates that the solution can be found in the *Student’s solution manual*, which is available in the Online Resource Centre accompanying this book. Go to www.oxfordtextbooks.co.uk/orc/mqm5e/

Exercises

***5.1** Identify the symmetry elements of **(a)** a planar equilateral triangle, **(b)** a planar isosceles triangle, **(c)** a hexagonal prism.

***5.2** Identify the symmetry elements of **(a)** the letter X, **(b)** the letter S, **(c)** the letter Z.

***5.3** Classify the objects in Exercise 5.1 according to their point group.

***5.4** Classify the objects in Exercise 5.2 according to their point group.

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*5.5 Classify the following molecules according to their point symmetry group: (a) H_2O , (b) CO_2 , (c) C_2H_4 , (d) *cis*- $\text{ClHC}=\text{CHCl}$.

*5.6 Classify the following molecules according to their point symmetry group: (a) *trans*- $\text{ClCH}=\text{CHCl}$, (b) benzene, (c) naphthalene, (d) CHClFBr , (e) $\text{B}(\text{OH})_3$.

*5.7 Identify a molecule or ion that belongs to the following point groups: (a) C_{5v} , (b) D_5 , (c) D_{5d} .

*5.8 Identify a molecule or ion that belongs to each of the cubic point groups.

*5.9 Construct the group multiplication table for the group (a) C_3 , (b) D_2 .

*5.10 The group multiplication table for C_{2v} is shown in Example 5.2. Confirm that the group elements multiply associatively.

*5.11 Find the representatives of the operations of the group C_{2v} using as a basis the valence orbitals of H and O in H_2O (that is, $\text{H}1s_A$, $\text{H}1s_B$, $\text{O}2s$, $\text{O}2p$). *Hint.* The group is of order 4 and so there are four 6-dimensional matrices to find.

*5.12 Confirm that the representatives established in Exercise 5.11 reproduce the group multiplications $C_2^2 = E$, $\sigma_v C_2 = \sigma'_v$.

Problems

*5.1 Determine which symmetry species are spanned by the six orbitals of H_2O described in Exercise 5.11. Find the symmetry-adapted linear combinations, and confirm that the representatives are in block-diagonal form. *Hint.* Decompose the representation established in Exercise 5.11 by analysing the characters. Use the projection operator in eqn 5.30 to establish the symmetry-adapted bases (using the elements of the representatives established in Exercise 5.11), form the matrix of coefficients c_{ji} (Section 5.6) and use eqn 5.7 to construct the irreducible representations.

5.2 Find the representatives of the operations of the group T_d by using as a basis four 1s-orbitals, one at each apex of a regular tetrahedron (as in CH_4). *Hint.* The basis is four-dimensional; the order of the group is 24, and so there are 24 matrices to find.

5.3 Show that in an octahedral array, hydrogen 1s-orbitals span $A_{1g} + E_g + T_{1u}$ of the group O_h .

*5.4 Confirm that the representations established in Problem 5.2 reproduce the group multiplications $C_3^3 C_3 = E$, $S_4 C_3 = S'_4$, and $S_4 C_3 = \sigma_d$.

*5.13 Set up the matrix c and its inverse for a similarity transformation in which the orbitals s_1 and s_2 of the H atoms of H_2O are replaced by the linear combinations $s_1 + s_2$ and $s_1 - s_2$.

*5.14 Establish the representatives for C_2 and σ_v in the new basis (of Exercise 5.13, starting from Exercise 5.11).

*5.15 Demonstrate that there are no non-zero integrals of the form $\int \psi' H \psi \, d\tau$ when ψ' and ψ belong to different symmetry species.

*5.16 What is the maximum degeneracy of the energy levels of a particle confined to the interior of a regular tetrahedron?

*5.17 An atom bearing a single p-electron is trapped in an environment with C_{3v} symmetry. What symmetry species does it span?

*5.18 A molecule of carbon dioxide, initially in a Σ_u^- electronic state, absorbs z-polarized electromagnetic radiation. What is the symmetry of the excited electronic state?

*5.19 Show that C_3^+ and C_3^- are conjugate elements in the group D_3 .

5.5 Confirm the validity of the GOT by using the irreducible representation A_2 and an element of the irreducible representation E for the matrices in Table 5.4.

5.6 Determine which irreducible representations are spanned by the four 1s-orbitals in methane. Find the symmetry-adapted linear combinations, and confirm that the representatives for C_3^+ and S_4 are in block-diagonal form. *Hint.* Decompose the representation into irreducible representations by analysing the characters. Use the projection operator in eqn 5.30 to establish the symmetry-adapted bases.

*5.7 Analyse the following direct products into the symmetry species they span: (a) C_{2v} : $A_2 \times B_1 \times B_2$, (b) C_{3v} : $A_1 \times A_2 \times E$, (c) C_{6v} : $B_2 \times E_1$, (d) $C_{\infty v}$: E_{1g}^2 , (e) O : $T_1 \times T_2 \times E$.

5.8 A function $f(x,y,z)$ was found to be a basis for a representation of C_{2v} , the characters being (4,0,0,0). What symmetry species of irreducible representations does it span? *Hint.* Proceed by inspection to find the a_i in eqn 5.20 or use eqn 5.22.

5.9 Find the representation A_1 , for example $f(x,y,z) +$

*5.10 Classify the configurations $e^1 t_1^1$, $t_1^1 t_2^1$, t_1^2 tables; trip

5.11 Construct D_{6h} . *Hint.* 1 procedure

5.12 Determine $\rho = (\hbar/i)(d/dx)$. *Hint.* Proceed

*5.13 The ξ are 2A_1 and 2E_g . To what symmetry species do the transitions transform?

5.14 Show that the representation $3x^2y - y^3$ is

5.15 In the representation $P_1 = P_A - P_B$ orbitals on which of the

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5.9 Find the components of the function $f(x, y, z)$ from Problem 5.8 acting as a basis for each irreducible representation it spans. *Hint.* Use eqn 5.30. The basis for A_1 , for example, turns out to be $\frac{1}{4}\{f(x, y, z) + f(-x, -y, z) + f(x, -y, z) + f(-x, y, z)\}$.

*5.10 Classify the terms that may arise from the following configurations: (a) C_{2v} : $a_1^2 b_1^1 b_2^1$; (b) C_{3v} : $a_1^1 e^1, e^2$; (c) T_d : $a_1^2 e^1, e^1 t_1^1, t_1^1 t_2^1, t_1^2, t_2^2$; (d) O : $e^2, e^1 t_1^1, t_2^2$. *Hint.* Use the direct-product tables; triplet terms have antisymmetric spatial functions.

5.11 Construct the character tables for the groups O_h and D_{6h} . *Hint.* Use $D_{6h} = D_6 \times C_i$ and $O_h = O \times C_i$ and the procedure in Section 5.15.

5.12 Demonstrate that the linear momentum operator $\hat{p} = (\hbar/i)(d/dx)$ is the generator of infinitesimal translations. *Hint.* Proceed as in eqn 5.43.

*5.13 The ground states of the C_{2v} molecules NO_2 and ClO_2 are 2A_1 and 2B_1 , respectively; the ground state of O_2 is ${}^3\Sigma_g^-$. To what states may (a) electric-dipole, (b) magnetic-dipole transitions take place? *Hint.* The electric-dipole operator transforms as translations, the magnetic as rotations.

5.14 Show that $3x^2y - y^3$ is a basis for an A_1 irreducible representation of C_{3v} . *Hint.* Show that $C_3(3x^2y - y^3) \propto 3x^2y - y^3$; likewise for the other elements of the group.

5.15 In the square-planar xenon tetrafluoride molecule, consider the symmetry-adapted linear combination $p_1 = p_A - p_B + p_C - p_D$ where p_A, p_B, p_C, p_D are the $2p_z$ atomic orbitals on the F atoms (clockwise labelling of the F atoms). Which of the various s, p, and d atomic orbitals on the

central Xe atom can overlap with p_1 to form molecular orbitals? *Hint:* It will be much easier to work in the reduced point group D_4 rather than the full point group (D_{4h}) of the molecule.

*5.16 Identify the symmetry species of the f orbitals in an environment with (a) C_{3v} , (b) T_d symmetry. Use rotational subgroups.

5.17 Regard the naphthalene molecule as having C_{2v} symmetry (with the C_2 axis perpendicular to the plane), which is a subgroup of its full symmetry group. Consider the π -orbitals on each carbon as a basis. What symmetry species do they span? Construct the symmetry-adapted bases. *Hint.* Proceed as in Example 5.9.

5.18 Repeat the process of Problem 5.17 for benzene, using the subgroup C_{6v} of the full symmetry group. After constructing the symmetry-adapted linear combinations, refer to the D_{6h} character table to label them according to the full group.

*5.19 We have seen that the angular momentum commutation rules are generated by considering consecutive infinitesimal rotations about perpendicular axes in three-dimensional space. Could it be that the fundamental quantum mechanical commutation rule $[x, p_x] = i\hbar$ is also just a manifestation of the geometry of three-dimensional space? Present an argument that makes use of the angular momentum result and the definition of the angular momentum operators in terms of position and linear momentum operators that could be used to justify this supposition.

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*6.9 Suggest how you could prepare a degenerate two-level system in a mixed state in which the probability is $\frac{1}{3}$ of finding it in state 2.

*6.10 Calculate the transition rate from the ground state of a molecule to a continuum of states if the transition matrix element has a constant value of 4.50×10^{12} rad s⁻¹ and the

continuum consists of 2.50×10^4 states in an energy range of 1.50 aJ accessed by the transition.

*6.11 Estimate the lifetime of a molecular state if the uncertainty in its energy (that is, the range of energies present in the state) is 1.92×10^{-24} J.

Problems

*6.1 Confirm that substitution of $\psi_{\pm}(x) = \exp(\pm iS_{\pm}(x)/\hbar)$ into eqn 6.1 yields eqn 6.3 for $S_{\pm}(x)$.

6.2 Find the semiclassical expression for the energy levels of a particle subjected to the potential energy $V = ax^6$.

6.3 One excited state of the sodium atom lies at 25 739.86 cm⁻¹ above the ground state, another lies at 50 266.88 cm⁻¹. Suppose they are connected by a perturbation equivalent in energy to (a) 100 cm⁻¹, (b) 1000 cm⁻¹, (c) 5000 cm⁻¹. Calculate the energies and composition of the states of the perturbed system. *Hint.* Use eqn 6.15 for the energies and eqn 6.17 for the states, and express the composition as the contribution of the unperturbed states.

*6.4 Confirm eqn 6.17b for the perturbed wavefunctions (eqn 6.17a) in a two-level system.

6.5 A simple calculation of the energy of the helium atom supposes that each electron occupies the same hydrogenic 1s-orbital (but with $Z = 2$). The electron-electron interaction is regarded as a perturbation, and calculation gives

$$\int \psi_{1s}^2(r_1) \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right) \psi_{1s}^2(r_2) d\tau = \frac{5}{4} \left(\frac{e^2}{4\pi\epsilon_0 a_0} \right)$$

(see Example 7.2). Estimate (a) the binding energy of helium, (b) its first ionization energy. *Hint.* Use eqn 6.15 with $E_1 = E_2 = E_{1s}$. Be careful not to count the electron-electron interaction energy twice.

6.6 Show that the energy of the perturbed levels is related to the mean energy of the unperturbed levels $\bar{E} = \frac{1}{2}(E_1 + E_2)$ by $E_{\pm} - \bar{E} = \pm \frac{1}{2}(E_1 - E_2) \sec 2\zeta$, where ζ is the parameter in eqn 6.17b. Devise a diagrammatic method of showing how $E_{\pm} - \bar{E}$ depends on $E_1 - E_2$ and ζ . *Hint.* Use eqn 6.17b.

*6.7 We normally think of the one-dimensional well as being horizontal. Suppose it is vertical; then the potential energy of the particle depends on x because of the presence of the gravitational field. Calculate the first-order correction to the zero-point energy, and evaluate it for an electron in a box on the surface of the Earth. Account for the result. *Hint.* The energy of the particle depends on its height as mgx where $g = 9.81$ m s⁻². Use eqn 6.24 with $\psi(x)$ given by $n = 1$ in eqn 2.31. Because g is so small, the energy correction is tiny; but it would be significant if the box were on the surface of a neutron star.

6.8 Calculate the second-order correction to the energy for the system described in Problem 6.7 and calculate the ground-state wavefunction. Account for the shape of the distortion caused by the perturbation. *Hint.* Use eqn 6.30 for the energy and eqn 6.27 for the wavefunction. The integrals involved are of the form

$$\int x \sin ax \sin bx dx = -\frac{d}{da} \int \cos ax \sin bx dx$$

$$\int \cos ax \sin bx dx = \frac{\cos(a-b)x}{2(a-b)} - \frac{\cos(a+b)x}{2(a+b)}$$

Evaluate the sum over n numerically.

6.9 We normally think of the one-dimensional harmonic oscillator as lying horizontally. Suppose it is held vertically so that it experiences a perturbation mgx . Calculate the correction to second order of the energy of the harmonic oscillator in state $|\nu\rangle$; specialize to the ground-state oscillator. *Hint.* Use the matrix elements in Table 2.2.

*6.10 Calculate the first-order correction to the energy of a ground-state harmonic oscillator subject to an anharmonic potential of the form $ax^3 + bx^4$ where a and b are small (anharmonicity) constants. Consider the three cases in which the anharmonic perturbation is present (a) during bond expansion ($x \geq 0$) and compression ($x \leq 0$), (b) during expansion only, (c) during compression only.

6.11 In the free-electron molecular orbital method (Problem 2.17) the potential energy may be made slightly more realistic by supposing that it varies sinusoidally along the polyene chain. Select a potential energy of the form $V \sin^2(\pi x/R)$ with R the carbon-carbon bond length, and calculate the first-order correction to the wavelength of the lowest energy transition.

6.12 Show group-theoretically that when a perturbation of the form $H^{(1)} = az$ is applied to a hydrogen atom, the 1s-orbital is contaminated by the admixture of np_z -orbitals. Deduce which orbitals mix into (a) $2p_x$ -orbitals, (b) $2p_z$ -orbitals, (c) $3d_{xy}$ -orbitals.

*6.13 The symmetry of the ground electronic state of the water molecule is A_1 . (a) An electric field, (b) a magnetic field is applied perpendicular to the molecular plane. What symmetry species of excited states may be mixed into the ground state by the perturbations? *Hint.* The electric

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interaction has the form $H^{(1)} = ax$; the magnetic interaction has the form $H^{(1)} = bl_x$.

6.14 Repeat Problem 6.8, but estimate the second-order energy correction using the closure approximation. Compare the two calculations and deduce the appropriate value of ΔE . *Hint.* Use eqn 6.33.

6.15 Calculate the second-order energy correction to the ground state of a particle in a one-dimensional box for a perturbation of the form $H^{(1)} = -\epsilon \sin(\pi x/L)$ by using the closure approximation. Infer a value of ΔE by comparison with the numerical calculation in Example 6.4. These two problems (6.14 and 6.15) show that the parameter ΔE depends on the perturbation and is not simply a characteristic of the system itself.

6.16 Suppose that the potential energy of a particle on a ring depends on the angle φ as $H^{(1)} = \epsilon \sin^2 \varphi$. Calculate the first-order corrections to the energy of the degenerate $m_l = \pm 1$ states, and find the correct linear combinations for the perturbation calculation. Find the second-order correction to the energy. *Hint.* This is an example of degenerate-state perturbation theory, and so find the correct linear combinations by solving eqn 6.42 after deducing the energies from the roots of the secular determinant. For the matrix elements, express $\sin \varphi$ as $(1/2i)(e^{i\varphi} - e^{-i\varphi})$. When evaluating eqn 6.42, do not forget the $m_l = 0$ state lying beneath the degenerate pair. The energies are equal to $m_l^2 \hbar^2 / 2mr^2$; use $\psi_{m_l} = (1/2\pi)^{1/2} e^{im_l \varphi}$ for the unperturbed states.

6.17 A particle of mass m is confined to a one-dimensional square well of the type treated in Chapter 2. Choose trial functions of the form (a) $\sin kx$, (b) $(x - x^2/L) + k(x - x^2/L)^2$, (c) $e^{-k(x-1/2L)} - e^{-kL}$ for $x \geq 1/2L$, and $e^{k(x-1/2L)} - e^{-kL}$ for $x \leq 1/2L$. Find the optimum values of k and the corresponding energies.

6.18 Consider the hypothetical linear H_3 molecule. The wavefunctions may be modelled by expressing them as $\psi = c_A s_A + c_B s_B + c_C s_C$ the s_i denoting hydrogen 1s-orbitals of the relevant atom. Use the Rayleigh-Ritz method to find the optimum values of the coefficients and the energies of the orbital. Make the approximations $H_{ss} = \alpha$, $H_{ss'} = \beta$ for neighbours but 0 for non-neighbours, $S_{ss} = 1$, and $S_{ss'} = 0$. *Hint.* Although the basis can be used as it stands, it leads to a 3×3 determinant and hence to a cubic equation for the energies. A better procedure is to set up symmetry-adapted combinations, and then to use the vanishing of H_{ij} unless $\Gamma^{(i)} = \Gamma^{(j)}$.

6.19 Repeat the last problem but set $H_{s_A s_C} = \gamma$ and $S_{s_A s_C} \neq 0$. Evaluate the overlap integrals between 1s-orbitals on centres separated by R ; use

$$S = \left\{ 1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right\} e^{-R/a_0}$$

Suppose that $\beta/\gamma = S_{s_A s_B} / S_{s_A s_C}$. For a numerical result, take $R = 80$ pm, $a_0 = 53$ pm.

6.20 A hydrogen atom in a $2s^1$ configuration passes into a region where it experiences an electric field in the z -direction

for a time τ . What is its electric dipole moment during its exposure and after it emerges? *Hint.* Use eqn 6.62 with $\omega_{21} = 0$; the dipole moment is the expectation value of $-ez$; use $\int \psi_{2s} z \psi_{2p_z} dt = 3a_0$.

6.21 A biradical is prepared with its two electrons in a singlet state. A magnetic field is present, and because the two electrons are in different environments their interaction with the field is $(\mu_B/\hbar)\mathcal{B}(g_1 s_{1z} + g_2 s_{2z})$ with $g_1 \neq g_2$. Evaluate the time-dependence of the probability that the electron spins will acquire a triplet configuration (that is, the probability that the $S = 1, M_S = 0$ state will be populated). Examine the role of the energy separation $\hbar J$ of the singlet state and the $M_S = 0$ state of the triplet. Suppose $g_1 - g_2 \approx 1 \times 10^{-3}$ and $J \approx 0$; how long does it take for the triplet state to emerge when $\mathcal{B} = 1.0$ T? *Hint.* Use eqn 6.63; take $|0,0\rangle = (1/2^{1/2})(\alpha\beta - \beta\alpha)$ and $|1,0\rangle = (1/2^{1/2})(\alpha\beta + \beta\alpha)$. See Problem 4.26 for the significance of μ_B and g .

6.22 An electric field in the z -direction is increased linearly from zero. What is the probability that a hydrogen atom, initially in the ground state, will be found with its electron in a $2p_z$ -orbital at a time t ? *Hint.* Use eqn 6.71 with $H_E^{(1)} \propto t$.

6.23 At $t = \frac{1}{2}T$ the strength of the field used in Problem 6.22 begins to decrease linearly. What is the probability that the electron is in the $2p_z$ -orbital at $t = T$? What would the probability be if initially the electron was in a $2s$ -orbital?

6.24 Instead of the perturbation in the preceding problem being switched linearly, it was switched on and off exponentially and slowly, the switching off commencing long after the switching on was complete. Calculate the probabilities, long after the perturbation has been extinguished, of the $2p_z$ -orbital being occupied, the initial states being as in Problem 6.22. *Hint.* Take $H^{(1)} \propto 1 - e^{-kt}$ for $0 \leq t \leq T$ and $H^{(1)} \propto e^{-k(t-T)}$ for $t \geq T$. Interpret 'slow' as $k \ll \omega$ and 'long after' as both $kT \gg 1$ (for 'long after switching on') and $k(t-T) \gg 1$ (for 'long after switching off').

6.25 Calculate the rates of stimulated and spontaneous emission for the $3p \rightarrow 2s$ transition in hydrogen when it is inside a cavity at 1000 K.

6.26 Find the complete dependence of the A and B coefficients on atomic number for the $2p \rightarrow 1s$ transitions of hydrogenic atoms. Calculate how the stimulated emission rate depends on Z when the atom is exposed to black-body radiation at 1000 K. *Hint.* The relevant density of states also depends on Z .

6.27 Examine how the A and B coefficients depend on the length of a one-dimensional square well for the transition $n + 1 \rightarrow n$. *Hint.* Use the integrals given in Problem 6.8.

6.28 Estimate the lifetime of the upper state of a spectroscopic transition if the spectrum shows a peak with a full width at half maximum of (a) 0.010 cm^{-1} , (b) 1.5 cm^{-1} , (c) 40 cm^{-1} . *Hint.* Use eqn 6.97.

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*7.5 Which of the following transitions are electric-dipole allowed: (a) $1s \rightarrow 2s$, (b) $1s \rightarrow 2p$, (c) $2p \rightarrow 3d$, (d) $3s \rightarrow 5d$, (e) $3s \rightarrow 5p$?

*7.6 The spectrum of a one-electron ion of an element showed that its ns -orbitals were at 0, 2 057 972 cm^{-1} , 2 439 156 cm^{-1} , and 2 572 563 cm^{-1} for $n=1, 2, 3, 4$, respectively. Identify the species and predict the ionization energy of the ion.

*7.7 Calculate the electric dipole transition moment for the transition $3p_z \leftarrow 1s$ in a hydrogenic atom for z -polarized radiation.

*7.8 Evaluate the spin-orbit coupling constant (in cm^{-1}) for (a) a $2p$ electron, (b) a $3d$ electron in Li^{2+} .

*7.9 Identify the terms that may arise from the ground configurations of the atoms of elements of Period 2 and suggest the order of their energies.

*7.10 Write the hamiltonian for the lithium atom ($Z=3$) and confirm that when electron-electron repulsions are neglected the wavefunction can be written as a product $\psi(1)\psi(2)\psi(3)$ of hydrogenic orbitals and the energy is a sum of the corresponding energies.

*7.11 Write the explicit expression for the Slater determinant corresponding to the $1s^2 2s^1$ ground state of atomic lithium. Demonstrate the antisymmetry of the wavefunction upon interchange of the labels of any two electrons.

*7.12 Confirm the radial integration in Example 7.2.

Problems

*7.1 Demonstrate that for one-electron atoms the selection rules are $\Delta l = \pm 1$, $\Delta m_l = 0, \pm 1$, and Δn unlimited. *Hint.* Evaluate the electric-dipole transition moment $\langle n'l'm_l | \mu | nlm_l \rangle$ with $\mu_x = -er \sin\theta \cos\phi$, $\mu_y = -er \sin\theta \sin\phi$, and $\mu_z = -er \cos\theta$. The easiest way of evaluating the angular integrals is to recognize that the components just listed are proportional to Y_{lm_l} with $l=1$, and to analyse the resulting integral group theoretically.

7.2 The general expression for the transition probability of an atom exposed to electromagnetic radiation of frequency ν travelling in the direction k with the electric field polarized along the unit vector e is proportional to the square modulus of the expression $J_{fi} = e \cdot \langle f | e^{-2i\nu k \cdot r} p | i \rangle$ where p is the linear momentum operator and r is a position (within the molecule) that becomes the integration variable when the bracket is written as an integral. Show that when the dimensions of the molecule are much smaller than the wavelength of the radiation, there are contributions that may be interpreted as magnetic dipole and electric quadrupole transitions as well as electric dipole transitions. *Hint:* Use $p = (im_e/\hbar)[H, r]$ (see Problem 1.11(b) and Further

*7.13 Evaluate the expectation values of (a) r , (b) $1/r$, and (c) $1/r^3$ for a $3p$ Slater orbital of general effective nuclear charge Z_{eff} . Express your result as multiples of a_0 .

*7.14 Confirm that eqn 7.49 is the correct expression for the total energy when an atom consists of four electrons (such as Be).

*7.15 What levels may arise from the following terms: 1S , 2P , 3P , 3D , 2D , 1D , 4D ?

*7.16 Arrange in order of increasing energy the terms that may arise from the following configurations: $1s^1 2p^1$, $2p^1 3p^1$, $3p^1 3d^1$.

*7.17 What terms may arise from (a) a d^2 configuration, (b) an f^2 configuration?

*7.18 Use group theory (specifically, an expression like eqn 7.70) to decide which of the d^2 and f^2 terms may be triplets and which singlets.

*7.19 Calculate the magnetic field required to produce a splitting of 1 cm^{-1} between the states of a 1P_1 level.

*7.20 Calculate the Landé g -factor for (a) a term in which J has its maximum value for a given L and S ; (b) a term in which J has its minimum value.

*7.21 Transitions are observed and ascribed to $^1F \rightarrow ^1D$. How many lines will be observed in a magnetic field of 4.0 T ?

*7.22 Calculate the form of the spectrum for the Zeeman effect on a $^3P \rightarrow ^3S$ transition.

*7.23 Show that the solution of the Thomas-Fermi equation at large distances from the nucleus is $\rho \propto 1/r^6$ and deduce the constant of proportionality.

information 12.2) and the vector identity $(a \cdot b)(c \cdot d) = (a \times c) \cdot (b \times d) + (b \cdot c)(a \cdot d)$.

7.3 Estimate the relative magnitudes of magnetic dipole, electric dipole, and electric quadrupole transition probabilities for light of wavelength 500 nm and a molecule of diameter 400 pm . *Hint:* Use the information derived in Problem 7.2.

*7.4 Confirm that in hydrogenic atoms, the spin-orbit coupling constant depends on n and l as in eqn 7.18.

7.5 Calculate the spin-orbit coupling constant for a $2p$ -electron in a Slater-type atomic orbital, and evaluate it for the neutral atoms of Period 2 of the periodic table (from boron to fluorine).

7.6 Suppose that an electron experiences a shielded Coulomb potential (a Coulomb potential modified by a factor $\exp(-r/r_D)$, where r_D is a constant). Evaluate the ratio of spin-orbit coupling constants ζ_{2p}/ζ_{2p}^0 , where ζ_{2p}^0 is the constant for the unshielded potential. Explore the result of setting $r_D = ka_0$, where k is a variable parameter.

*7.7 Deduce the energy levels of a given l orbital differing by Δn in eqn 7.70. Express your result as multiples of a_0 .

7.8 The energy of a $3d^6 4s^2$ configuration is 3.0 eV relative to the energy of a $3d^5 4s^2$ configuration. The energy of a $3d^5 4s^1$ configuration is 1.0 eV relative to the energy of a $3d^5 4s^2$ configuration. Use the information to deduce the energy of a $3d^6 4s^1$ configuration.

7.9 (a) Calculate the energy of a $3d^5 4s^1$ configuration with the $3d$ orbitals half-filled. Each term is a function of the energy of the $3d$ orbitals. Use the information to deduce the energy of a $3d^5 4s^1$ configuration.

$$\sum_{s=0}^n s = \frac{n(n+1)}{2}$$

$$\sum_{s=0}^n s^3 = \left[\frac{n(n+1)}{2} \right]^2$$

*7.10 Find the energy of the $3d^5 4s^1$ configuration of the element with atomic number 24. The energy of the $3d^5 4s^2$ configuration is 3.0 eV relative to the energy of the $3d^5 4s^1$ configuration. The energy of the $3d^5 4s^1$ configuration is 1.0 eV relative to the energy of the $3d^5 4s^2$ configuration. Use the information to deduce the energy of the $3d^5 4s^1$ configuration.

7.11 Evaluate the energy of a $3d^5 4s^1$ configuration.

7.12 The energy of a $3d^5 4s^1$ configuration is 1.0 eV relative to the energy of a $3d^5 4s^2$ configuration. Confirm that the energy of a $3d^5 4s^1$ configuration is 1.0 eV relative to the energy of a $3d^5 4s^2$ configuration.

*7.13 Calculate the energy of a $3d^5 4s^1$ configuration.

7.14 Take the energy of a $3d^5 4s^1$ configuration to be 1.0 eV relative to the energy of a $3d^5 4s^2$ configuration. Calculate the energy of a $3d^5 4s^1$ configuration. Use the information to deduce the energy of a $3d^5 4s^1$ configuration. Interpret the result in terms of the energy of a $3d^5 4s^1$ configuration and $5d^5 4s^1$.

* Indicates that the solution can be found in the *Student's solution manual*, which is available in the Online Resource Centre accompanying this book. Go to www.oxfordtextbooks.co.uk/orc/mqm5e/

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***7.7** Deduce the *Landé interval rule*, which states that for a given l and s , the energy difference between two levels differing in j by unity is proportional to j . *Hint.* Evaluate E_{so} in eqn 7.24 for j and $j - 1$; use the second line in the equation (in terms of ζ_{nl}).

7.8 The ground-state configuration of an iron atom is $3d^64s^2$, and the 5D term has five levels ($J = 4, 3, \dots, 0$) at relative wavenumbers 0, 415.9, 704.0, 888.1, and 978.1 cm^{-1} . Investigate how well the Landé interval rule (Problem 7.7) is obeyed. Deduce a value of ζ_{3d} .

7.9 (a) Calculate the energy difference between the levels with the greatest and smallest values of j for given l and s . Each term of a level is $(2j + 1)$ -fold degenerate.

(b) Demonstrate that the barycentre (mean energy) of a term is the same as the energy in the absence of spin-orbit coupling. *Hint.* Weight each level with $2j + 1$ and sum the energies given in eqn 7.24 from $j = |l - s|$ to $j = l + s$. Use the relations

$$\sum_{s=0}^n s = \frac{1}{2}n(n+1) \quad \sum_{s=0}^n s^2 = \frac{1}{6}n(n+1)(2n+1)$$

$$\sum_{s=0}^n s^3 = \frac{1}{4}n^2(n+1)^2$$

***7.10** Find the first-order corrections to the energies of the hydrogen atom that result from the relativistic mass increase of the electron. *Hint.* The energy is related to the momentum by $E = (p^2c^2 + m^2c^4)^{1/2} + V$. When $p^2c^2 \ll m^2c^4$, $E \approx \mu c^2 + p^2/2\mu + V - p^4/8\mu^3c^2$, where the reduced mass μ has replaced m . Ignore the rest energy μc^2 , which simply fixes the zero. The term $-p^4/8\mu^3c^2$ is a perturbation; hence calculate $\langle nlm_l | H^{(1)} | nlm_l \rangle = -(1/2\mu c^2) \langle nlm_l | (p^2/2\mu)^2 | nlm_l \rangle = -(1/2\mu c^2) \langle nlm_l | (E_{nlm_l} - V)^2 | nlm_l \rangle$. We know E_{nlm_l} ; therefore calculate the matrix elements of $V = -e^2/4\pi\epsilon_0 r$ and V^2 .

7.11 Evaluate the Coulomb integral J for a hydrogenic configuration $1s^12p^1$.

7.12 The Slater atomic orbitals are normalized but not mutually orthogonal. In the *Schmidt orthogonalization procedure* one orbital ψ is made orthogonal to another orbital ψ' by forming $\psi'' = \psi - c\psi'$, with $c = \int \psi^* \psi' d\tau$. Confirm that ψ'' and ψ' are orthogonal and construct a $2s$ -orbital that is orthogonal to a $1s$ -orbital from an STO basis.

***7.13** Confirm the Condon–Slater rules for a two-electron system by explicit expansion of the relevant Slater determinants.

7.14 Take a trial function for the helium atom as $\psi = \psi(1)\psi(2)$, with $\psi(1) = (\zeta^3/\pi)^{1/2}e^{-\zeta r_1}$ and $\psi(2) = (\zeta^3/\pi)^{1/2}e^{-\zeta r_2}$, ζ being a parameter, and find the best ground-state energy for a function of this form, and the corresponding value of ζ . Calculate the first and second ionization energies. *Hint.* Use the variation theorem. All the integrals are standard; the electron repulsion term is calculated in Example 7.2. Interpret Z in terms of a shielding constant. The experimental ionization energies are 24.58 eV and 54.40 eV.

7.15 On the basis of the same kind of calculation as in Problem 7.14, but for general Z , account for the first ionization energies of the ions Li^+ , Be^{2+} , B^{3+} , and C^{4+} . The experimental values are 73.5, 153, 258, and 389 eV, respectively.

***7.16** The first few S terms of helium lie at the following wavenumbers: $1s^2\ ^1S$: 0; $1s^12s^1\ ^1S$: 166 272 cm^{-1} ; $1s^12s^1\ ^3S$: 159 850 cm^{-1} ; $1s^13s^1\ ^1S$: 184 859 cm^{-1} ; $1s^13s^1\ ^3S$: 183 231 cm^{-1} . What are the values of K in the $1s^12s^1$ and $1s^13s^1$ configurations?

7.17 Consider a one-dimensional square well containing two electrons. One electron has $n = 1$ and the other has $n = 2$. Plot a two-dimensional contour diagram of the probability distribution of the electrons when their spins are **(a)** parallel, **(b)** antiparallel. Devise a measure of the radius of the Fermi hole. *Hint.* Recall the discussion in Section 7.11. When the spins are parallel (for example, $\alpha\alpha$) the antisymmetric combination $\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)$ must be used, and when the spins are antiparallel, the symmetric combination must be used. In each case plot ψ^2 against axes labelled x_1 and x_2 . Computer graphics may be used to obtain striking diagrams, but a sketch is sufficient.

7.18 An excited state of atomic calcium has the electron configuration $1s^22s^22p^63s^23p^63d^14f^1$. **(a)** Derive all the term symbols (with the appropriate specifications of S , L and J) for the electron configuration. **(b)** Which term symbol corresponds to the lowest energy of this electron configuration? **(c)** Consider a 3F_2 level of calcium derived from a different electron configuration than that shown above. Which of the term symbols determined in part (a) can participate in spectroscopic transitions to this 3F_2 level?

***7.19** Write down the Slater determinant for the ground term of the beryllium atom, and find an expression for its energy in terms of Coulomb and exchange integrals. Find expressions for the energy in terms of the Hartree–Fock expression, eqn 7.49. *Hint.* Use eqn 7.49 for the configuration $1s^22s^2$; evaluate the expectation value $\langle \psi | H | \psi \rangle$.

7.20 On the basis of the Thomas–Fermi model of an atom, evaluate the radius within which there is a 50 per cent probability of finding the electron density and evaluate it for the Period 2 elements. *Hint.* Use the radial distribution function $r^2\rho$.

7.21 Devise an argument that the Thomas–Fermi–Dirac method gives worse agreement than the Thomas–Fermi method with Hartree–Fock energies. *Hint.* Consider the signs of those terms that contribute to $E[\rho]$.

***7.22** In their classic account of density functional techniques, Parr and Yang describe a modification of the Thomas–Fermi method that relies on the elimination of the singularity of the electron density at the origin. They do so by imposing the additional constraint that $\int e^{-2kr} \nabla^2 \rho(r) dr < \infty$. Deduce the expression for μ and show that the singularity is eliminated by setting $4k\lambda = Z$ where λ is a Lagrange multiplier for the additional constraint.

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***8.10** Set up and solve the secular determinant for the cyclopropenyl radical in the Hückel π -electron scheme; find the energy levels and estimate the delocalization energy.

***8.11** Within the Hückel π -electron scheme, estimate the delocalization energy of (a) the benzene cation $C_6H_6^+$ and (b) the benzene dianion $C_6H_6^{2-}$.

***8.12** Give the spin multiplicities of all the terms that can arise from d^4 , d^5 , d^6 , and d^7 low-spin complexes.

***8.13** Give the spin multiplicities of all the terms that can arise from d^4 and d^5 high-spin complexes.

***8.14** Determine which symmetry species are spanned by (a) d-orbitals, (b) f-orbitals in a tetrahedral complex.

***8.15** Verify that the Kronig–Penney model results in eqn 8.44.

Problems

***8.1** The dependence of the molecular integrals j' , k' , and S for the hydrogen molecule-ion on the internuclear separation R are specified in Section 8.3. Plot the variation of the integrals α and β and the energies E_+ and E_- against R and identify the equilibrium bond length and the dissociation energy of the molecule-ion.

8.2 Confirm that $\frac{1}{2}(E_- + E_+) - E_1$ is a positive quantity, and hence that the effect of an antibonding orbital outweighs the effect of a bonding orbital. *Hint.* Set up expressions for the quantity using eqns 8.21 and 8.22 and the results of Example 8.1; proceed to plot the quantity against R .

8.3 (a) Evaluate the probability density of the electron in H_2^+ at the mid-point of the bond, and plot it as a function of R . (b) Evaluate the difference densities $\rho_{\pm} = \psi_{\pm}^2 - \frac{1}{2}(\psi_A^2 + \psi_B^2)$ at points along the line joining the two nuclei (including the regions outside the nuclei) for $R = 130$ pm. The difference density shows the modification to the electron distribution brought about by constructive (or destructive) overlap. *Hint.* Use the expressions for the coefficients in eqn 8.17 to obtain ψ_{\pm} . The overlap integral S is given in Example 8.1. (c) Repeat the calculation for several values of R .

***8.4** We shall see in Chapter 10 that the vibrational frequency of a chemical bond is $\omega = (k_f/\mu)^{1/2}$, where $k_f = (d^2E/dR^2)_0$ is the force constant and μ is the effective mass; for a homonuclear diatomic molecule of atoms of mass m , $\mu = \frac{1}{2}m$. Estimate the vibrational frequency of the hydrogen molecule-ion. *Hint.* Use mathematical software to evaluate the second derivative of the energy (eqn 8.23a).

8.5 Evaluate the overlap integral S for two $H2s$ orbitals, components of a basis set for an excited electronic state of H_2^+ .

8.6 Take the hydrogen molecule wavefunction in eqn 8.26 and find an expression for the expectation value of the hamiltonian in terms of molecular integrals. *Hint.* The outcome of this calculation is eqn 8.27.

***8.7** Show that eqn 8.27 for the ground-state energy of the hydrogen molecule can also be obtained by using the Condon–Slater rules (Section 7.15).

8.8 All the integrals involved in the H_2 molecular orbital calculation are listed in eqn 8.28 and *Further information* 8.1.

(a) Write and run a procedure using mathematical software to calculate $E - 2E_1$, as a function of R . (b) Identify the equilibrium bond length and the dissociation energy. (c) Use software to evaluate the force constant for the bond (the experimental value is 575 N m^{-1}).

8.9 Evaluate the probability density for a single electron at a point on a line running between the two nuclei in H_2 and plot the difference density $\rho_1 - 2(\psi_A^2 + \psi_B^2)$ for $R = 74$ pm. *Hint.* Use eqn 8.26. The probability density of electron 1, ρ_1 , is obtained from $\psi^2(1,2)$ by integrating over all locations of electron 2, because the latter's position is irrelevant. Therefore, begin by forming $\rho_1 = \int \psi^2(1,2) d\tau_2$.

***8.10** Predict the ground configuration of (a) CO, (b) NO. For each species, decide which term lies lowest in energy, compute the bond order and identify the HOMO and LUMO.

8.11 Use a minimal basis set for the MO description of the molecule H_2O to show that the secular determinant factorizes into (1×1) , (2×2) , and (3×3) determinants. Set up the secular determinant, denoting the Coulomb integrals α_H , α'_O , and α_O for $H1s$, $O2s$, and $O2p$, respectively, and writing the $(O2p, H1s)$ and $(O2s, H1s)$ resonance integrals as β and β' , respectively. Neglect overlap. First, neglect the $2s$ -orbital, and find expressions for the energies of the molecular orbitals for a bond angle of 90° .

8.12 Now develop the previous calculation by taking into account the $O2s$ -orbital. Set up the secular determinant with the bond angle θ as a parameter. Find expressions for the energies of the molecular orbitals and of the entire molecule. As a first step in analysing the expressions, set $\alpha_H \approx \alpha_O \approx \alpha'_O$, and $\beta \approx \beta'$.

***8.13** Construct the symmetry-adapted linear combinations for methane, CH_4 , using a minimal basis set.

8.14 Set up and solve the secular determinants for (a) hexatriene, (b) the cyclopentadienyl radical in the Hückel π -electron scheme; find the energy levels and molecular orbitals, and estimate the delocalization energy.

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8.15 (a) Confirm that the symmetry-adapted linear combinations of p-orbitals for benzene are those set out above Example 8.5. **(b)** Find the corresponding symmetry-adapted combinations for naphthalene.

***8.16** The allyl radical $\text{CH}_2=\text{CHCH}_2\cdot$ is a conjugated π -system having a p-orbital on the carbon atom adjacent to a double bond. Estimate its π -electron energy by using the Hückel approximation.

8.17 Confirm that the solutions of a tridiagonal determinant are those given in Example 8.4.

8.18 Show that the roots of the secular determinant for a cyclic polyene of N atoms can be constructed by inscribing a regular N -gon in a circle and noting the locations of the corners of the polygon, as in Fig. 8.31. *Hint.* See A.A. Frost and B. Musulin, *J. Chem. Phys.*, 572, 21 (1953).

***8.19** Heterocyclic molecules may be incorporated into the Hückel scheme by modifying the Coulomb integral of the atom concerned and the resonance integrals to which it contributes. Consider pyridine, $\text{C}_5\text{H}_5\text{N}$ (symmetry group C_{2v}). Construct and solve the Hückel secular determinant with $\beta_{\text{CC}} \approx \beta_{\text{CN}} \approx \beta$ and $\alpha_{\text{N}} = \alpha_{\text{C}} + \frac{1}{2}\beta$. Estimate the electron energy and the delocalization energy. *Hint.* The roots of the determinants are best found on a computer.

8.20 Explore the role of p-orbital overlap in π -electron calculations. Take the cyclobutadiene secular determinant, but construct it without neglect of overlap between neighbouring atoms. Show that in place of $x = (\alpha - E)/\beta$ and 1 the elements of the determinant become $\omega = (\alpha - E)/(\beta - ES)$ and 1, respectively. Hence the roots in terms of ω are the same as the roots in terms of x . Solve for E . Typically $S = 0.25$.

8.21 Find the effect of including neighbouring atom overlap on the π -electron energy levels of benzene. Use a computer to explore how the energies depend on the bond lengths, using $\beta \propto S$ and

$$S(2p\pi, 2p\pi) = \left(1 + s + \frac{2}{3}s^2 + \frac{1}{15}s^3\right)e^{-s} \quad s = \frac{Z_{\text{eff}}R}{2a_0}$$

where Z_{eff} is taken from Table 7.3. Consider the difference in delocalization energy between the cases where the

molecule has six equivalent C–C bond lengths of 140 pm (the experimental value) and where it has alternating lengths of 133 pm and 153 pm (typical C=C and C–C lengths, respectively).

***8.22** An ion with the configuration f^2 enters an environment of octahedral symmetry. What terms arise in the free ion, and with which terms do they correlate in the complex? *Hint.* Follow the discussion of Section 8.9.

8.23 In the strong field case, the configuration d^2 gives rise to e_g^2 , $t_{2g}^1e_g^1$, and t_{2g}^2 . **(a)** What terms may arise? **(b)** How do the singlet terms of the complex correlate with the singlet terms of the free ion? **(c)** What configurations arise in a tetrahedral complex, and what are the correlations?

8.24 Find the symmetry-adapted linear combinations of **(a)** σ -orbitals, **(b)** π -orbitals on the ligands of an octahedral complex. *Hint.* Set Cartesian axes on each ligand site, with z pointing towards the central ion, determine how the orbitals are transformed under the operations of the group O_h , and use the procedures for establishing symmetry-adapted orbitals as described in Chapter 5.

***8.25** Repeat Problem 8.24 for a tetrahedral complex. What is the role of π -bonding in such complexes?

8.26 Repeat Problem 8.24 for a square planar complex. What is the role of π -bonding in such complexes? *Hint.* Work in the reduced point group D_{4h} .

8.27 Revisit the tight-binding approximation (Section 8.10) and allow for bond alternation along the chain so that for atoms 1 and 2, the resonance integral is β_1 ; for atoms 2 and 3, β_2 ; for atoms 3 and 4, β_1 ; and so forth. Determine the width of the band as $N \rightarrow \infty$. *Hint.* Determine the width numerically as N increases from 1 to about 15 for a fixed ratio of β_2/β_1 of, for instance, 0.9, plot the results, and infer a result for $N \rightarrow \infty$.

***8.28** Explore the effect of changing the depth of the potential well by finding the solutions of eqn 8.46 for different values of γ . Solve the equations numerically for **(a)** $\gamma = \pi$ and **(b)** $\gamma = 2\pi$.

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- *9.7** How many f-type Gaussian orbitals are there (of a given shell)?
- *9.8** Express the integral $(AA|BB)$ in H_2 in terms of s-type Gaussian orbitals on each nucleus.
- *9.9** How many orbitals would constitute a minimal basis set in (a) NH_3 , (b) CH_3Cl ?
- *9.10** How many orbitals would constitute (a) a split-valence basis set, (b) a DZP basis set in NH_3 ?
- *9.11** Determine the number of basis set functions in a molecular electronic structure calculation on ethanol, CH_3CH_2OH , using (i) a 6-31G; (ii) a 6-31G* (iii) a 6-31G** basis.
- *9.12** Determine the total number of different Slater determinants for an electronic structure calculation on ethanol, CH_3CH_2OH , that can be formed from a 6-31G** basis set.
- *9.13** In a CI calculation on the ground 2S state of lithium, which of the following Slater determinants can contribute to the ground-state wavefunction? (a) $\|\Psi_{1s}^{\alpha}\Psi_{1s}^{\beta}\Psi_{2s}^{\alpha}\|$; (b) $\|\Psi_{1s}^{\alpha}\Psi_{1s}^{\beta}\Psi_{2s}^{\beta}\|$; (c) $\|\Psi_{1s}^{\alpha}\Psi_{1s}^{\beta}\Psi_{2p}^{\alpha}\|$; (d) $\|\Psi_{1s}^{\alpha}\Psi_{2p}^{\alpha}\Psi_{2p}^{\beta}\|$; (e) $\|\Psi_{1s}^{\alpha}\Psi_{3d}^{\alpha}\Psi_{3d}^{\beta}\|$; (f) $\|\Psi_{1s}^{\alpha}\Psi_{2s}^{\alpha}\Psi_{3s}^{\alpha}\|$.
- *9.14** In a CI calculation on the excited $^3\Sigma_u^+$ electronic state of H_2 , which of the following Slater determinants can contribute to the excited-state wavefunction? (a) $\|1\sigma_g^{\alpha}1\sigma_u^{\alpha}\|$; (b) $\|1\sigma_g^{\alpha}1\pi_u^{\alpha}\|$; (c) $\|1\sigma_g^{\alpha}1\pi_g^{\beta}\|$; (d) $\|1\sigma_g^{\beta}2\sigma_g^{\beta}\|$; (e) $\|1\pi_u^{\alpha}1\pi_g^{\alpha}\|$; (f) $\|1\pi_u^{\beta}2\pi_u^{\beta}\|$.

Problems

- *9.1** Show that $(1/N_e!)^{1/2}$ is the correct normalization factor for a single Slater determinant consisting of N_e orthonormal spinorbitals.
- 9.2** Show that in the closed-shell restricted Hartree-Fock case the general spinorbital Hartree-Fock equation (eqn 7.88) can be converted to an HF equation (specifically eqn 9.7) for the spatial wavefunction ψ . (*Hint*. To convert from spinorbitals to spatial orbitals, you will need to integrate out the spin functions. Begin with eqn 7.88 and let $\phi_a(1) = \psi_a(1)\alpha(1)$; an identical result will be obtained if you assume that $\phi_a(1) = \psi_a(1)\beta(1)$.)
- 9.3** Consider the two-electron integrals over the basis functions defined in eqn 9.17. If the basis functions are taken to be real, a number of the integrals are equivalent; for example, $(ab|cd) = (ad|cb)$. Find the other integrals that are equal to $(ab|cd)$.
- *9.4** In a Hartree-Fock calculation on atomic hydrogen using four primitive s-type Gaussian functions (S. Huzinaga, *J. Chem. Phys.*, 1293, 42 (1965)), optimized results were

***9.15** In the *brief illustration* of Møller-Plesset perturbation theory (Section 9.9) we remarked that $\langle \Psi_{1\sigma_1^{\alpha}1\sigma_2^{\alpha}} | H^{(1)} | \Psi_0 \rangle = (N_{1\sigma_1^{\alpha}1\sigma_2^{\alpha}})^2 \{ (AA|AA) - (AB|AA) + \dots + (BB|BB) \}$. Identify the unwritten integrals.

***9.16** In the discussion of the coupled-cluster method, we deduced the expression $Q\hat{t}^2 - \Delta E\hat{t} - Q = 0$. Show that when $Q \ll \Delta E$, the energy is the same as that calculated in the MP2 approximation of MPPT.

***9.17** Equation 7.65 is the starting point for the sequence of iterations needed for the Thomas-Fermi and DFT calculations. Set up an expression for $\rho(r)$ for the H_2 molecule using the molecular orbital $\phi(r) = \psi_A(r) + \psi_B(r)$.

***9.18** Calculate the Hessian matrix H for the function $f = \sin ax \cos by$.

***9.19** (a) Which of the following methods are capable of yielding an energy below the exact ground-state energy? (b) Which of the following methods are not assured of being size-consistent? (i) HF-SCF; (ii) full CI; (iii) SDCl; (iv) MP2; (v) MP4; (vi) CCSD; (vii) DFT.

***9.20** Show that the first derivative of a p-type Gaussian orbital generates an s-type and a d-type GTO.

***9.21** Refer to Exercise 9.4: which of the integrals vanish in the ZDO approximation?

***9.22** Show that if the force field specified in eqn 9.58 is adopted, then for small torsional displacements, the molecule undergoes harmonic oscillation.

(a) Show themselves (corresponding two linear $S = 1$, $M_S = 0$.)

9.6 Show R_A with e with explicit Gaussian

***9.7** Prove hamiltonian Φ_0 and its *Hint*. Use

9.8 Cons by only c

$$\Phi_1 = \parallel$$

$$\Phi_2 = \parallel$$

Derive th

$$\langle \Phi_1 | E$$

where we

$$[\phi_a \phi_b]$$

9.9 Using problem show that $= [\phi_a \phi_b] \phi$

***9.10** (a) wavefunction for the d active, in and active an RASS orbitals l

obtained with a linear combination of Gaussians with coefficients c_{ij} and exponents α of 0.509 07, 0.123 317; 0.474 49, 0.453 757; 0.134 24, 2.013 30; and 0.019 06, 13.3615. Describe how these primitives would be utilized in a (4s)/[2s] contraction scheme.

9.5 A single Slater determinant is not necessarily an eigenfunction of the total electron spin operator. Therefore, even within the Hartree-Fock approximation, for the wavefunction Φ_0 to be an eigenfunction of S^2 , it might have to be expressed as a linear combination of Slater determinants. The linear combination is referred to as a *spin-adapted configuration*. As a simple example, consider a two-electron system with four possible Slater determinants:

$$\Phi_1 = \left(\frac{1}{2}\right)^{1/2} \det |\psi_1(r_1)\alpha(1)\psi_2(r_2)\alpha(2)|$$

$$\Phi_2 = \left(\frac{1}{2}\right)^{1/2} \det |\psi_1(r_1)\alpha(1)\psi_2(r_2)\beta(2)|$$

$$\Phi_3 = \left(\frac{1}{2}\right)^{1/2} \det |\psi_1(r_1)\beta(1)\psi_2(r_2)\alpha(2)|$$

$$\Phi_4 = \left(\frac{1}{2}\right)^{1/2} \det |\psi_1(r_1)\beta(1)\psi_2(r_2)\beta(2)|$$

* Indicates that the solution can be found in the *Student's solution manual*, which is available in the Online Resource Centre accompanying this book. Go to www.oxfordtextbooks.co.uk/orc/mqm5e/

(a) Show that the Slater determinants Φ_1 and Φ_4 are themselves eigenfunctions of S^2 with eigenvalue $2\hbar^2$ (corresponding to $S = 1$). (b) From Φ_2 and Φ_3 , determine two linear combinations, one of which corresponds to $S = 1$, $M_S = 0$ and the other of which corresponds to $S = 0$, $M_S = 0$.

9.6 Show that the product of an s-type Gaussian centred at R_A with exponent α_A and an s-type Gaussian centred at R_B with exponent α_B can be written in terms of a single s-type Gaussian centred between R_A and R_B .

*9.7 Prove *Brillouin's theorem*; that is, show that hamiltonian matrix elements between the HF wavefunction Φ_0 and singly excited determinants are identically zero. *Hint.* Use the Condon–Slater rules.

9.8 Consider two Slater determinants Φ_1 and Φ_2 that differ by only one spinorbital; that is,

$$\Phi_1 = \|\cdots \varphi_m \varphi_i \cdots\|$$

$$\Phi_2 = \|\cdots \varphi_p \varphi_i \cdots\|$$

Derive the following Condon–Slater rule:

$$\langle \Phi_1 | H | \Phi_2 \rangle = \langle \varphi_m(1) | h_1 | \varphi_p(1) \rangle + \sum_i \{ [\varphi_m \varphi_i | \varphi_p \varphi_i] - [\varphi_m \varphi_i | \varphi_i \varphi_p] \}$$

where we have used the notation

$$[\varphi_a \varphi_b | \varphi_c \varphi_d] = \int \int \varphi_a^*(1) \varphi_b^*(2) \left(\frac{1}{r_{12}} \right) \varphi_c(1) \varphi_d(2) dr_1 dr_2$$

9.9 Using the notation $[\varphi_a \varphi_b | \varphi_c \varphi_d]$ given in the preceding problem for a two-electron integral over the spinorbitals, show that (a) $[\varphi_a \varphi_b | \varphi_c \varphi_d] = [\varphi_b \varphi_a | \varphi_c \varphi_d]$ and (b) $[\varphi_a \varphi_b | \varphi_c \varphi_d] = [\varphi_c \varphi_d | \varphi_a \varphi_b]^*$.

*9.10 (a) For a CASSCF calculation of the ground-state wavefunction of diatomic C_2 , describe a reasonable choice for the distribution of σ and π molecular orbitals into active, inactive and virtual orbitals. (b) How many inactive and active electrons are there in the calculation? (c) In an RASSCF calculation, how might the set of active orbitals be further divided?

9.11 Show that the Møller–Plesset perturbation $H^{(1)}$ can be written in terms of the Coulomb and exchange operators as

$$H^{(1)} = \sum_{i,j=1}^{N_e} \left\{ \frac{J_0}{2r_{ij}} - J_i(i) + K_i(i) \right\}$$

9.12 Use Møller–Plesset perturbation theory to obtain an expression for the ground-state wavefunction corrected to first order in the perturbation.

*9.13 Show that the expression for $\tau(r)$ in the meta-generalized gradient approximation of DFT represents a kinetic energy density.

9.14 Demonstrate explicitly the relation between the PPP and the HMO methods described in the last paragraph of Section 9.17.

9.15 Which of the following two-electron integrals (over real basis functions) are *not* neglected in (i) CNDO; (ii) INDO; (iii) MNDO? (a) $(ij|ij)$ with θ_i and θ_j belonging to different atoms; (b) $(ij|ji)$ with θ_i and θ_j belonging to the same atom; (c) $(ij|ji)$ with θ_i and θ_j belonging to different atoms; (d) $(ik|ji)$ with θ_i , θ_j and θ_k belonging to the same atom; (e) $(ik|jl)$ with θ_i and θ_j belonging to one atom and θ_k and θ_l belonging to another; (f) $(ii|ii)$.

*9.16 Using appropriate electronic structure software, perform HF-SCF calculations for the ground electronic states of H_2 and F_2 using (a) 6-31G and (b) 6-31G** basis sets. Determine ground-state energies and equilibrium geometries.

9.17 Repeat Problem 9.16 with the indicated basis sets but, rather than HF-SCF, perform calculations using (i) SDCl, (ii) MP2, (iii) DFT (B3LYP functional).

9.18 Repeat Problems 9.16 and 9.17 for the triatomic H_2O and CO_2 . In addition, compute the vibrational wavenumbers in each case.

*9.19 Use the AM1 and PM3 semiempirical methods to compute the equilibrium bond lengths and enthalpies of formation of (a) ethanol, (b) 1,4-dichlorobenzene.

9.20 Devise a simple spreadsheet program for evaluating a two-electron integral in the H_2 molecule.

* Indicates that the solution can be found in the *Student's solution manual*, which is available in the Online Resource Centre accompanying this book. Go to www.oxfordtextbooks.co.uk/orc/mqm5e/