Chapter 0

Introduction and orientation

Exercises

0.1 Use $E = h\nu$; $h = 6.626 \times 10^{-34}$ J s; $\nu = 1/T$ [T: period]

(a) $E = (6.626 \times 10^{-34}\text{ J s})/(1.0 \times 10^{-15}\text{ s}) = \underline{6.626 \times 10^{-19}\text{ J}}$

(b) $E = h/(1.0 \times 10^{-14}\text{ s}) = \underline{6.626 \times 10^{-20}\text{ J}}$

(c) $E = h/(1.0\text{ s}) = \underline{6.626 \times 10^{-34}\text{ J}}$

0.2 Use Wien's law: $\lambda_{\max}T$ = const.; const. = $hc/5k$ [Problem 0.1] = 2.878 mm K [End paper 1 of text]. Hence

$$T = (2.878\text{ mm K})/(480 \times 10^{-9}\text{ m}) \approx \underline{6 \times 10^{3}\text{ K}}$$

0.3 Use the Law of Dulong and Petit (Section 0.2):

molar heat capacity = 25 J K^{-1} mole^{-1} = specific heat capacity × molar mass

The molar mass is therefore 25 J K^{-1} mole^{-1}/0.91 J K^{-1} g^{-1} = 27 g mol^{-1}

and the metal is $\underline{\text{Al}}$.

0.4 The energy of 1.00 mol of photons is given by

$$E = (hc/\lambda) \times 6.02214 \times 10^{23}\text{ photons/mole}$$

giving **(a)** $\underline{2.3 \times 10^{5}\text{ J}}$, **(b)** $\underline{1.20 \times 10^{-3}\text{ J}}$, **(c)** $\underline{9.2 \times 10^{8}\text{ J}}$.

0.5 Use eqn 0.10: $\delta\lambda = 2\lambda_C \sin^2 \frac{1}{2}\theta$

with $\lambda_C = 2.426$ pm and $\theta = 60^0$. Hence $\delta\lambda = 1.213$ pm and the wavelength of the scattered radiation is $\lambda_f = \lambda_i + \delta\lambda = 25.878$ pm + 1.213 pm = $\underline{27.091 \text{ pm}}$.

0.6 2.3 eV corresponds to $2.3 \times (1.602 \times 10^{-19}$ C) V = 3.7×10^{-19} J. Then use eqn 0.7 in the form

$$v = \{(2/m_e)(h\nu - \Phi)\}^{1/2} \quad \text{so long as } h\nu \geq \Phi$$

(a) $h\nu = hc/\lambda = 6.62 \times 10^{-19}$ J when $\lambda = 300$ nm:

$$v = \{[2/(9.10938 \times 10^{-31}\text{ kg})] \times (2.9 \times 10^{-19}\text{ J})\}^{1/2} = \underline{8.0 \times 10^5 \text{ m s}^{-1}}$$

(b) $h\nu = 3.31 \times 10^{-19}$ J $< \Phi$; hence no electrons are emitted.

Exercise: Examine the case where the ejection speed is so great that it must be treated relativistically.

0.7 Use eqn 0.11 for the Balmer series wavenumbers:

$$\tilde{\nu} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

with $R_H = 1.097 \times 10^5\text{ cm}^{-1}$.

The highest wavenumber corresponds to $n = \infty$ and is $\underline{2.743 \times 10^4\text{ cm}^{-1}}$, corresponding to a wavelength of $1/(2.743 \times 10^4\text{ cm}^{-1}) = 3.646 \times 10^{-5}$ cm = $\underline{364.6 \text{ nm}}$.

The lowest wavenumber corresponds to $n = 3$ and is $\underline{1.524 \times 10^4\text{ cm}^{-1}}$, corresponding to a wavelength of $1/(1.524 \times 10^4\text{ cm}^{-1}) = 6.563 \times 10^{-5}$ cm = $\underline{656.3 \text{ nm}}$.

0.8 The permitted energy levels of the electron in a hydrogen atom are given by eqn 0.13:

$$E_n = -\frac{\mu e^4}{8h^2\varepsilon_0^2}\cdot\frac{1}{n^2} = -\frac{2.18\times10^{-18}\,\mathrm{J}}{n^2} = -\frac{13.6\,\mathrm{eV}}{n^2}$$

The two lowest levels are therefore

$n = 1$: $E_1 = \underline{-2.18\times10^{-18}\ \mathrm{J}} = \underline{-13.6\ \mathrm{eV}}$

$n = 2$: $E_2 = \underline{-5.45\times10^{-19}\ \mathrm{J}} = \underline{-3.40\ \mathrm{eV}}$

0.9 The de Broglie wavelength is given by eqn 0.14:

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\mathrm{Js}}{57\mathrm{g}\times\frac{1\ \mathrm{kg}}{1000\mathrm{g}}\times 80\mathrm{km\ hr}^{-1}\times\frac{1000\mathrm{m}}{1\ \mathrm{km}}\times\frac{1\mathrm{hr}}{3600\mathrm{s}}}$$
$$= 5.2\times10^{-34}\,\mathrm{m}$$

Problems

0.1

$$\rho = \left(\frac{8\pi hc}{\lambda^5}\right)\frac{\mathrm{e}^{-hc/\lambda kT}}{1-\mathrm{e}^{-hc/\lambda kT}} \quad \text{[eqn 0.5]}$$

$$= \frac{(8\pi hc/\lambda^5)}{\mathrm{e}^{hc/\lambda kT}-1}$$

$$\frac{\mathrm{d}\rho}{\mathrm{d}\lambda} = -\frac{40\pi hc/\lambda^6}{\mathrm{e}^{hc/\lambda kT}-1} + \frac{(8\pi hc/\lambda^5)(hc/\lambda^2 kT)\mathrm{e}^{hc/\lambda kT}}{(\mathrm{e}^{hc/\lambda kT}-1)^2} = 0$$

That is, at the maximum

$$\frac{5}{\lambda} = \frac{(hc/\lambda^2 kT)\mathrm{e}^{hc/\lambda kT}}{\mathrm{e}^{hc/\lambda kT}-1} = \frac{(hc/\lambda^2 kT)}{1-\mathrm{e}^{-hc/\lambda kT}}$$

and hence

$$\frac{hc}{5\lambda kT} = 1 - \mathrm{e}^{-hc/\lambda kT}$$

At short wavelengths ($hc/\lambda kT >> 1$)

$$\frac{hc}{5\lambda kT} \approx 1\text{, which implies that } \underline{\lambda T \approx hc/5k}$$

Exercise: Confirm that the extremum of ρ is in fact a maximum.

0.4 The Boltzmann distribution is

$$p_i = \frac{\mathrm{e}^{-\beta\varepsilon_i}}{\sum_i \mathrm{e}^{-\beta\varepsilon_i}} \qquad [\beta = 1/kT]$$

Hence

$$\langle\varepsilon\rangle = \sum_i p_i\varepsilon_i = -\frac{1}{q}\left(\frac{\mathrm{d}q}{\mathrm{d}\beta}\right) \quad \left[q = \sum_i \mathrm{e}^{-\beta\varepsilon_i}\right]$$

In this case, $\varepsilon_i \to \varepsilon_v = (v + \frac{1}{2})h\nu$, so

$$q = \sum_{v=0}^{\infty} \mathrm{e}^{-(v+\frac{1}{2})h\nu\beta} = \mathrm{e}^{-\frac{1}{2}h\nu\beta}\sum_{v=0}^{\infty}(\mathrm{e}^{-h\nu\beta})^v$$

$$= \frac{\mathrm{e}^{-\frac{1}{2}h\nu\beta}}{1-\mathrm{e}^{-h\nu\beta}} \quad \left[\sum_n x^n = (1-x)^{-1}\right]$$

Hence

$$\langle\varepsilon\rangle = \tfrac{1}{2}h\nu + \left\{\frac{h\nu\mathrm{e}^{-h\nu\beta}}{1-\mathrm{e}^{-h\nu\beta}}\right\} = \tfrac{1}{2}h\nu + \frac{h\nu}{\mathrm{e}^{h\nu\beta}-1}$$

$$C_\mathrm{V} = \frac{N\mathrm{d}\langle\varepsilon\rangle}{\mathrm{d}T} = \frac{N\mathrm{d}\langle\varepsilon\rangle}{\mathrm{d}\beta}\cdot\frac{\mathrm{d}\beta}{\mathrm{d}T} = -\frac{N}{kT^2}\frac{\mathrm{d}\langle\varepsilon\rangle}{\mathrm{d}\beta}$$

$$= \frac{N(h\nu)^2}{kT^2}\frac{\mathrm{e}^{h\nu\beta}}{(\mathrm{e}^{h\nu\beta}-1)^2} = \frac{Nk(\theta_\mathrm{E}/T)^2\mathrm{e}^{h\nu\beta}}{(\mathrm{e}^{h\nu\beta}-1)^2} \quad [\theta_\mathrm{E} = h\nu/k]$$

There are three modes of oscillation for each atom in a solid, so

$$C_\mathrm{V,m} = 3Rf \quad f = \frac{(\theta_\mathrm{E}/T)^2\mathrm{e}^{\theta_\mathrm{E}/T}}{(1-\mathrm{e}^{\theta_\mathrm{E}/T})^2}$$

as in eqn 0.6a.

Exercise: Derive an expression for the heat capacity of a two-level system, and plot it as a function of temperature.

0.7 For sodium $\theta_\mathrm{D}/T = 0.50$; for diamond $\theta_\mathrm{D}/T = 6.20$. If we use the Einstein formula (with $\theta_\mathrm{E} \approx \theta_\mathrm{D}$), then

Na(s): $f = 0.979$; hence $\underline{C_\mathrm{V,m}/R = 2.94}$

C(d): $f = 0.078$; hence $\underline{C_\mathrm{V,m}/R = 0.23}$

The Debye formula can be evaluated by numerical integration but it is also tabulated. See the *American Institute of Physics Handbook*, D.E. Gray (ed.), McGraw-Hill (1972), p.4.113. Then

Na(s): $f(\theta_\mathrm{D}/T = 0.50) = 0.988$; hence $\underline{C_\mathrm{V,m}/R = 2.96}$

C(d): $f(\theta_\mathrm{D}/T = 6.20) = 0.249$; hence $\underline{C_\mathrm{V,m}/R = 0.747}$

Exercise: Evaluate $C_\mathrm{V,m}$ at 300 K for the Group 1 metals.

0.10 Use the experimental data at 195 nm and eqn 0.7 to compute the work function of the metal surface.

$$\Phi = h\nu - E_{\mathrm{K}} = (hc/\lambda) - \tfrac{1}{2}m_{\mathrm{e}}v^2$$

$$= (6.626 \times 10^{-34}\ \mathrm{J\ s})(3.00 \times 10^{8}\ \mathrm{m\ s^{-1}})/(195 \times 10^{-9}\ \mathrm{m}) -$$

$$\tfrac{1}{2}(9.10938 \times 10^{-31}\ \mathrm{kg})(1.23 \times 10^{6}\ \mathrm{m\ s^{-1}})^2$$

$$= 3.303 \times 10^{-19}\ \mathrm{J}$$

When light of wavelength 255 nm is used, the kinetic energy of the ejected electron is

$$E_{\mathrm{K}} = (hc/\lambda) - \Phi$$

$$= (6.626 \times 10^{-34}\ \mathrm{J\ s})(3.00 \times 10^{8}\ \mathrm{m\ s^{-1}})/(255 \times 10^{-9}\ \mathrm{m}) - 3.303 \times 10^{-19}\ \mathrm{J}$$

$$= 4.492 \times 10^{-19}\ \mathrm{J}$$

corresponding to a speed of

$$v = \left(\frac{2E_K}{m_{\mathrm{e}}}\right)^{1/2} = \underline{9.93 \times 10^{5}\ \mathrm{m\ s^{-1}}}$$

Exercise: For the above problem, what is the longest wavelength of light capable of ejecting electrons from the metal surface?

0.13 From eqn 0.11, $1/\lambda = R_{\mathrm{H}}\{(1/2^2) - (1/n^2)\}$, $n = 3, 4, \ldots$

Hence, plot $1/\lambda$ against $1/n^2$, and find R_{H} from the intercept at $n = \infty$ (since then $1/\lambda_\infty = R_{\mathrm{H}}/4$). The data extrapolate (linear regression) to

$$1/\lambda_\infty = 2.743 \times 10^{6}\ \mathrm{m^{-1}} = 2.743 \times 10^{4}\ \mathrm{cm^{-1}}$$

hence

$$R_\mathrm{H} = 4 \times (2.743 \times 10^4\ \mathrm{cm}^{-1}) = \underline{1.097 \times 10^5\ \mathrm{cm}^{-1}}$$

The ionization energy (I) is the energy required for the transition $n_2 = \infty \leftarrow n_1 = 1$;

hence $\underline{I = hc\mathrm{R}_\mathrm{H}}$ $= 2.179 \times 10^{-18}$ J. Because 1 eV = 1.602×10^{-19} J, $I =$ $\underline{13.6\ \mathrm{eV}}$.

0.16 The square of the fine structure constant is

$$\alpha^2 = \frac{e^4}{16\pi^2\hbar^2c^2\varepsilon_0^2} = \frac{e^4}{4h^2c^2\varepsilon_0^2}$$

from which it follows that (using the mass of the electron for the reduced mass in the Rydberg constant):

$$R = \frac{m_e e^4}{8h^3c\varepsilon_0^2} = \frac{m_e c\alpha^2}{2h}$$

Chapter 1

The foundations of quantum mechanics

Exercises

1.1 **(a)** $\int(f+g)\mathrm{d}x = \int f\mathrm{d}x + \int g\mathrm{d}x$; linear.

(b) $(f+g)^{1/2} \neq f^{1/2} + g^{1/2}$; nonlinear.

(c) $f(x+a) + g(x+a) = f(x+a) + g(x+a)$; linear.

(d) $f(-x) + g(-x) = f(-x) + g(-x)$; linear.

Exercise: Repeat the exercise for (a) differentiation, (b) exponentiation.

1.2 **(a)** $(\mathrm{d}/\mathrm{d}x)\mathrm{e}^{ax} = a\mathrm{e}^{ax}$; e^{ax} is an eigenfunction, eigenvalue a.

$(\mathrm{d}/\mathrm{d}x)\mathrm{e}^{ax^2} = 2ax\mathrm{e}^{ax^2} = 2a\{x\mathrm{e}^{ax^2}\}$; e^{ax^2} not an e.f.

$(\mathrm{d}/\mathrm{d}x)x = 1$; x not an e.f.

$(\mathrm{d}/\mathrm{d}x)x^2 = 2x$; x^2 not an e.f.

$(\mathrm{d}/\mathrm{d}x)(ax+b) = a$; $ax+b$ not an e.f.

$(\mathrm{d}/\mathrm{d}x)\sin x = \cos x$; $\sin x$ not an e.f.

(b) $(\mathrm{d}^2/\mathrm{d}x^2)\mathrm{e}^{ax} = a^2\mathrm{e}^{ax}$; e^{ax} is an eigenfunction, eigenvalue a^2.

$(\mathrm{d}^2/\mathrm{d}x^2)\mathrm{e}^{ax^2} = 2a\mathrm{e}^{ax^2} + 4a^2x^2\mathrm{e}^{ax^2}$; e^{ax^2} not an e.f.

$(\mathrm{d}^2/\mathrm{d}x^2)x = 0 = 0x$; x is an e.f.; e.v. is 0.

$(\mathrm{d}^2/\mathrm{d}x^2)x^2 = 2$; x^2 not an e.f.

$(\mathrm{d}^2/\mathrm{d}x^2)(ax+b) = 0 = 0(ax+b)$; $ax+b$ is an e.f.; e.v. is 0.

$(\mathrm{d}^2/\mathrm{d}x^2)\sin x = -\sin x$; $\sin x$ is an e.f.; e.v. is -1.

Exercise: Find the operator of which e^{ax^2} is an eigenfunction. Find the eigenfunction of the operator ‘multiplication by x^2’.

1.3

$$\langle m|A + \mathrm{i}B|n\rangle = \langle m|A|n\rangle + \mathrm{i}\langle m|B|n\rangle$$

$$= \langle n|A|m\rangle^* + \mathrm{i}\langle n|B|m\rangle^* \text{ [}A, B \text{ hermitian, eqn 1.26]}$$

$$= \{\langle n|A|m\rangle - \mathrm{i}\langle n|B|m\rangle\}^* = \langle n|A - \mathrm{i}B|m\rangle^*.$$

Hence, $A - \mathrm{i}B$ is the hermitian conjugate of $A + \mathrm{i}B$ (and $A + \mathrm{i}B$ is not *self-conjugate*, another term for hermitian).

Exercise: Confirm that $x + (\mathrm{d}/\mathrm{d}x)$ and $x - (\mathrm{d}/\mathrm{d}x)$ are hermitian conjugates.

1.4 If the maximum uncertainty in the position x of the electron is Δx, the minimum uncertainty in the momentum p_x will be given by $\Delta x \Delta p_x = \frac{1}{2}\hbar$. Since the electron is confined to the linear box, $\Delta x = 0.10$ nm. Therefore

$$\Delta p_x = \frac{\hbar}{2\Delta x}$$

$$= \frac{1.055 \times 10^{-34}\ \mathrm{J\ s}}{2 \times 0.10 \times 10^{-9}\ \mathrm{m}}$$

$$= 5.3 \times 10^{-25}\ \mathrm{kg\ m\ s^{-1}}$$

(a) Since $p_x = m_\mathrm{e}v$, the uncertainty in the velocity is

$$\Delta v = \Delta p_x/m_\mathrm{e}$$

$$= (5.3 \times 10^{-25}\ \mathrm{kg\ m\ s^{-1}})/(9.109\,38 \times 10^{-31}\ \mathrm{kg})$$

$$= \underline{5.8 \times 10^{5}\ \mathrm{m\ s^{-1}}}$$

(b) Since, $E_K = p_x^2/2m_e$

$$\Delta E_K = (\Delta p_x)^2/2m_e$$

$$= (5.3 \times 10^{-25}\ \text{kg m s}^{-1})^2/(2 \times 9.109\ 38 \times 10^{-31}\ \text{kg})$$

$$= \underline{1.5 \times 10^{-19}\ \text{J}}$$

Exercise: If the length of the box is doubled to 0.20 nm, what are the minimum uncertainties? If a proton is confined to a linear box of length 0.20 nm, what are the minimum uncertainties?

1.5

Use the integral

$$\int x^2 \sin^2 ax\mathrm{d}x = \tfrac{1}{6}x^3 + (1/4a^3)\{\tfrac{1}{2}\sin(2ax) - ax\cos(2ax) - a^2x^2\sin(2ax)\}$$

$$\langle x^2\rangle_n = (2/L)\int_0^L x^2\sin^2(n\pi x/L)\mathrm{d}x = \underline{\tfrac{1}{3}L^2\{1-(3/2n^2\pi^2)\}}$$

$$\langle x^2\rangle_2 = \tfrac{1}{3}L^2\{1-(3/8\pi^2)\}$$

Since the particle is equally likely to be found in the right-hand side of the box (between $L/2$ and L) and in the left-hand side of the box (between 0 and $L/2$), the average value $< x > = L/2$ for all values of n. Therefore,

$$\Delta x_n = \{\langle x^2\rangle_n - \langle x\rangle_n^2\}^{1/2} = \{\tfrac{1}{3}L^2 - (1/2n^2\pi^2)L^2 - \tfrac{1}{4}L^2\}^{1/2}$$

$$= \underline{(L/2\sqrt{3})\{1-(6/n^2\pi^2)\}^{1/2}}$$

$$\Delta x_2 = \underline{(L/2\sqrt{3})\{1-(3/2\pi^2)\}^{1/2}}$$

As for the momentum, the intuitive solution is $\langle p\rangle_n = 0$ because the wavefunction is a standing wave. The elegant solution is

$$\langle p\rangle = \langle n|p|n\rangle = \langle n|p|n\rangle^* \text{ [hermiticity]} = \langle n|p^*|n\rangle = -\langle n|p|n\rangle[p^* = -p].$$

Therefore since $\langle p\rangle = -\langle p\rangle$, $\langle p\rangle = 0$.

The straightforward solution is:

$$\langle p\rangle_n = (\hbar/i)(2/L)\int_0^L \sin(n\pi x/L)(\mathrm{d}/\mathrm{d}x)\sin(n\pi x/L)\mathrm{d}x$$

$$= (2\hbar/\mathrm{i}L)(n\pi/L)\int_0^L \sin(n\pi x/L)\cos(n\pi x/L)\mathrm{d}x = 0$$

Also, note that

$$\langle p^2\rangle_n = 2mE_n = \underline{n^2h^2/4L^2}$$

Thus, $\Delta p_n = \{\langle p^2\rangle_n - \langle p\rangle_n^2\}^{1/2} = \langle p^2\rangle_n^{1/2} = \underline{nh/2L}$

Therefore:

$$\Delta x_n\Delta p_n = (L/2\sqrt{3})\{1 - (6/n^2\pi^2)\}^{1/2}(nh/2L)$$

$$= (n/4\sqrt{3})\{1 - (6/n^2\pi^2)\}^{1/2}h = \underline{(n\pi/\sqrt{3})\{1-(6/n^2\pi^2)\}^{1/2}(\hbar/2)}$$

$$\Delta x_2\Delta p_2 = (2\pi/\sqrt{3})\{1 - (3/2\pi^2)\}^{1/2}(\hbar/2) = \underline{3.3406(\hbar/2)} > \hbar/2$$

as required. As n increases, the uncertainty product $\Delta x_n\Delta p_n$ increases.

Exercise: Repeat the calculation for the mixed state $\psi_1 \cos\beta + \psi_2 \sin\beta$.

What value of β minimizes the uncertainty product?

1.6 To use the Born interpretation to find the probability, we need to first normalize the wavefunction, $\psi(x) = N\mathrm{e}^{-2x}$. Normalization requires that

$$\int_0^\infty \psi^*\psi\ \mathrm{d}x = \int_0^\infty N^2\mathrm{e}^{-4x}\mathrm{d}x = 1$$

which yields $N = 2$. The probability of finding the particle at a distance $x \geq 1$ is given by

$$\text{Probability} = \int_1^{\infty} (2\mathrm{e}^{-2x})^2 \mathrm{d}x$$

$$= \underline{\mathrm{e}^{-4}}$$

Exercise: Suppose that the particle is now described by the unnormalized wavefunction $\psi(x) = \mathrm{e}^{-3x}$. Between 0 and what other distance is the probability of finding the particle equal to $\frac{1}{2}$?

1.7 Use eqn 1.44. Since $l_z = (\hbar/\mathrm{i})(\partial/\partial\phi)$, $V(\phi) = V$, a constant, and $H = (1/2mr^2)\,l_z^2 + V$:

$$[H, l_z] = (1/2mr^2)[l_z^2, l_z] + [V, l_z] = 0 \;\{[V, l_z] \propto \mathrm{d}V/\mathrm{d}\phi = 0\},$$

Hence, $(\mathrm{d}/\mathrm{d}t)\langle l_z\rangle = 0$

Exercise: Find the equation of motion for the expectation value of l_z for a particle on a vertical ring in a uniform gravitational field. Examine the equations for small displacements from the lowest point.

1.8 The most probable location is given by the value of x corresponding to the maximum (or maxima) of $|\psi|^2$; write this location x_*. In the present case

$$|\psi|^2 = N^2x^2\mathrm{e}^{-x^2/\Gamma^2}$$

$$(\mathrm{d}/\mathrm{d}x)|\psi|^2 = N^2\{2x\mathrm{e}^{-x^2/\Gamma^2} - 2(x^3/\Gamma^2)\mathrm{e}^{-x^2/\Gamma^2}\} = 0 \text{ at } x = x_*$$

Hence, $1 - x_*^2/\Gamma^2 = 0$, so $\underline{x_* = \pm\Gamma}$

Exercise: Evaluate N for the wavefunction. Consider then another excited state wavefunction $\{2(x/\Gamma)^2 - 1\}\mathrm{e}^{-x^2/2\Gamma^2}$, and locate x_*.

1.9 Base the answer on $|\psi|^2 = (b^3/\pi)\mathrm{e}^{-2br}$. The probability densities are

(a) $|\psi(0)|^2 = b^3/\pi = 1/(53\text{ pm})^3\pi = \underline{2.1 \times 10^{-6}\text{ pm}^{-3}}$

(b) $|\psi(r = 1/b, \theta, \phi)|^2 = (b^3/\pi)\mathrm{e}^{-2} = \underline{2.9 \times 10^{-7}\text{ pm}^{-3}}$

[The values of θ and ϕ do not matter because ψ is spherically symmetrical.] The probabilities are given by

$$P = \int_{\text{volume}} \psi^2 d\tau \approx |\psi|^2\ \delta V$$

because $|\psi|^2$ is virtually constant over the small volume of integration $\delta V = 1\ \text{pm}^3$.

Hence:

(a) $P = |\psi(0)|^2 \delta V = \underline{2.1 \times 10^{-6}}$;

(b) $P = |\psi(1/b, \theta, \phi)|^2 \delta V = \underline{2.9 \times 10^{-7}}$

Problems

1.1 **(a)**

$$\langle p_x \rangle \propto \langle \sin(\pi x/L) \left| \frac{\mathrm{d}}{\mathrm{d}x} \right| \sin(\pi x/L) \rangle$$

$$\propto \langle \sin(\pi x/L) | \cos(\pi x/L) \rangle = \underline{0}$$

(b)

$$\langle p_x^2 \rangle = 2m\langle T \rangle = 2mE\ [V = 0] \quad \text{[see eqn 2.30]}$$

$$= 2m\left(\frac{h^2}{8mL^2}\right) [\text{for } n = 1] = \underline{h^2/4L^2}$$

Alternatively, integrate explicitly.

Exercise: Evaluate **(a)** $\langle p_x^3 \rangle$, **(b)** $\langle p_x^4 \rangle$.

1.4 **(a)** $[A, B] = AB - BA = -(BA - AB) = -[B, A]$

(b) $[A^m, A^n] = A^m A^n - A^n A^m = A^{m+n} - A^{m+n} = 0$

(c)

$$[A^2, B] = AAB - BAA = ABA + (AAB - ABA) - ABA + (ABA - BAA)$$

$$= A[A, B] + [A, B]A$$

(d)

$$[A, [B, C]] + [B, [C, A]] + [C, [A, B]]$$

$$= (ABC - ACB - BCA + CBA) + (BCA - BAC - CAB + ACB)$$

$$+ (CAB - CBA - ABC + BAC) = 0$$

Exercise: Express $[A^2, B^2]$, $[A^3, B]$, and $[A, [B, [C, [D, E]]]]$ in terms of individual commutators.

1.7 Find a normalization constant N such that eqn 1.18 is satisfied.

$$\int |\psi|^2 \,\mathrm{d}\tau = N^2 \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \sin\theta \mathrm{d}\theta \int_0^{\infty} r^2 \mathrm{e}^{-2br} \mathrm{d}r$$

$$= N^2\{2\pi\}\{2\} \int_0^{\infty} r^2 \mathrm{e}^{-2br} \mathrm{d}r = 4\pi N^2\{2!/(2b)^3\}$$

$$= N^2\pi/b^3.$$

Hence $\underline{N = (b^3/\pi)^{1/2} = 1.5 \times 10^{15}\ \mathrm{m}^{-3/2}}$

Consequently, $\psi = (b^3/\pi)^{1/2}\mathrm{e}^{-br}$

Exercise: ψ depends on Z as e^{-Zbr}. Find N for general Z.

1.10 **(a)** $[1/x, p_x]$; use the position representation.

$$[1/x,\, p_x] = [x^{-1},\, (\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}x] = (\hbar/\mathrm{i})\{x^{-1}(\mathrm{d}/\mathrm{d}x) - (\mathrm{d}/\mathrm{d}x)x^{-1}\}$$

$$= (\hbar/\mathrm{i})\{x^{-1}(\mathrm{d}/\mathrm{d}x) - (\mathrm{d}x^{-1}/\mathrm{d}x) - x^{-1}(\mathrm{d}/\mathrm{d}x)\}$$

$$= -(\hbar/\mathrm{i})(\mathrm{d}x^{-1}/\mathrm{d}x) = \underline{(\hbar/\mathrm{i})x^{-2}}$$

(b)

$$[1/x,\ p_x^2] = [x^{-1},\, -\hbar^2(\mathrm{d}^2/\mathrm{d}x^2)]$$

$$= -\hbar^2\{x^{-1}(\mathrm{d}^2/\mathrm{d}x^2) - (\mathrm{d}^2/\mathrm{d}x^2)x^{-1}\}$$

$$= -\hbar^2\{x^{-1}(\mathrm{d}^2/\mathrm{d}x^2) - (\mathrm{d}/\mathrm{d}x)[(\mathrm{d}x^{-1}/\mathrm{d}x) + x^{-1}(\mathrm{d}/\mathrm{d}x)]\}$$

$$= -\hbar^2\{x^{-1}(\mathrm{d}^2/\mathrm{d}x^2) - (\mathrm{d}/\mathrm{d}x)[-x^{-2} + x^{-1}(\mathrm{d}/\mathrm{d}x)]\}$$

$$= -\hbar^2\{x^{-1}(\mathrm{d}^2/\mathrm{d}x^2) + (\mathrm{d}x^{-2}/\mathrm{d}x) + x^{-2}(\mathrm{d}/\mathrm{d}x)$$

$$-(\mathrm{d}x^{-1}/\mathrm{d}x)(\mathrm{d}/\mathrm{d}x) - x^{-1}(\mathrm{d}^2/\mathrm{d}x^2)\}$$

$$= -\hbar^2\{-2x^{-3} + 2x^{-2}(\mathrm{d}/\mathrm{d}x)\}$$

$$= 2\hbar^2/x^3 - 2\hbar^2x^{-2}(\mathrm{i}/\hbar)p_x = \underline{(2\hbar/x^3)(\hbar - \mathrm{i}xp_x)}$$

(c)

$$[xp_y - yp_x,\, yp_z - zp_y]$$

$$= [xp_y,\, yp_z] - [xp_y,\, zp_y] - [yp_x,\, yp_z] + [yp_x,\, zp_y]$$

$$= x[p_y,\, y]p_z - 0 - 0 + p_x[y,\, p_y]z$$

$$= x(-\mathrm{i}\hbar)p_z + p_x(\mathrm{i}\hbar)z = \underline{\mathrm{i}\hbar(zp_x - xp_z)}$$

(d)

$$[x^2(\partial^2/\partial y^2), y(\partial/\partial x)]$$

$$= x^2(\partial^2/\partial y^2)y(\partial/\partial x) - y(\partial/\partial x)x^2(\partial^2/\partial y^2)$$

$$= x^2(\partial/\partial x)(\partial^2/\partial y^2)y - (\partial/\partial x)x^2y(\partial^2/\partial y^2)$$

$$= x^2(\partial/\partial x)(\partial/\partial y)\{1 + y(\partial/\partial y)\} - \{2x + x^2(\partial/\partial x)\}y(\partial^2/\partial y^2)$$

$$= x^2(\partial/\partial x)\{2(\partial/\partial y) + y(\partial^2/\partial y^2)\} - 2xy(\partial^2/\partial y^2) - x^2(\partial/\partial x)y(\partial^2/\partial y^2)$$

$$= 2x^2(\partial/\partial x)(\partial/\partial y) - 2xy(\partial^2/\partial y^2)$$

$$= \underline{2x^2(\partial^2/\partial x\partial y) - 2xy(\partial^2/\partial y^2)}$$

Exercise: Evaluate $[xy(\partial^2/\partial x\partial y), x^2(\partial^2/\partial y^2)]$.

1.13 Use the correspondence in Section 1.5.

(a)

$$T = p^2/2m = \underline{-(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}x^2)} \text{ in one dimension.}$$

$$T = p^2/2m = -(\hbar^2/2m)\{(\partial^2/\partial x^2) + (\partial^2/\partial y^2) + (\partial^2/\partial z^2)\}$$

$$= \underline{-(\hbar^2/2m)\nabla^2} \text{ in three dimensions.}$$

(b) $1/x \rightarrow$ <u>multiplication by $(1/x)$</u>

(c) $\mu = \sum_i Q_i \boldsymbol{r}_i \rightarrow \underline{\text{multiplication by } \sum_i Q_i \boldsymbol{r}_i}$

(d)

$$l_z = xp_y - yp_x = \underline{(\hbar/\mathrm{i})\{x(\partial/\partial y) - y(\partial/\partial x)\}}$$

$$= \underline{(\hbar/\mathrm{i})(\partial/\partial\phi)} \text{ for } x = r\cos\phi,\ y = r\sin\phi$$

(e) $\delta x^2 = x^2 - \langle x\rangle^2 \rightarrow$ multiplication by $\{x^2 - \langle x\rangle^2\}$

$\delta p^2 = p^2 - \langle p\rangle^2 \rightarrow \{-\hbar^2(\partial^2/\partial x^2) - \langle p\rangle^2\}$

Exercise: Devise operators for $1/r$, xp_x, and $\mathrm{e}^{\alpha x}$.

1.16 Take $H\Psi = \kappa(\partial^2\Psi/\partial t^2)$. Because H has the dimensions of energy, κ must have the dimensions of energy × time^2, or ML^2. Try $\Psi = \psi\theta$, with H an operator on x, not t. The equation separates into $H\psi = E\psi$, $\mathrm{d}^2\theta/\mathrm{d}t^2 = (E/\kappa)\theta$. The latter admits solutions of the form $\theta \propto \cos(E/\kappa)^{1/2}t$. Then

$$\int |\Psi|^2 \mathrm{d}\tau \propto \int |\psi|^2 \,\mathrm{d}\tau \cos^2(E/\kappa)^{1/2} t$$

which oscillates in time between 0 and 1; hence the total probability is not conserved.

1.19 **(a)**

$$\begin{aligned} \mathrm{e}^A\mathrm{e}^B &= (1 + A + \tfrac{1}{2}A^2 + \ldots)(1 + B + \tfrac{1}{2}B^2 + \ldots) \\ &= 1 + (A + B) + \tfrac{1}{2}(A^2 + 2AB + B^2) + \ldots \\ \mathrm{e}^{A+B} &= 1 + (A + B) + \tfrac{1}{2}(A + B)^2 + \ldots \\ &= 1 + (A + B) + \tfrac{1}{2}(A^2 + AB + BA + B^2) + \ldots \end{aligned}$$

Therefore, $\mathrm{e}^A\mathrm{e}^B = \mathrm{e}^{A+B}$ only if $AB = BA$, which is so if $[A, B] = 0$.

(b) If $[A, [A, B]] = [B, [A, B]] = 0$, then

$$\begin{aligned} e^{A+B} &= 1 + (A+B) + \tfrac{1}{2}(A^2 + AB + BA + B^2) \\ &\quad + (1/3!)(A^3 + A^2B + ABA + BAA + BBA + BAB + ABB + B^3) + \ldots \\ &= 1 + (A+B) + \tfrac{1}{2}(A^2 + 2AB + B^2) - \tfrac{1}{2}[A, B] \\ &\quad + (1/3!)(A^3 + 3A^2B + 3AB^2 + B^3) - \tfrac{1}{2}(A+B)[A, B] + \ldots \\ &= \underline{e^A e^B e^{-\frac{1}{2}[A,B]}} \end{aligned}$$

Therefore, $e^A e^B = e^{A+B} e^f$ where $f = [A, B]/2$.

Exercise: Find expressions for cos A cos B and cos A sin B, where A and B are operators such that

$$[A, [A, B]] = [B, [A, B]] = 0$$

(Use $\cos A = \tfrac{1}{2}(e^{iA} + e^{-iA})$, etc.)

1.22 $(d/dt)\langle\Omega\rangle = (i/\hbar)\langle[H, \Omega]\rangle$ [eqn 1.44].

For a harmonic oscillator, $H = p_x^2/2m + \tfrac{1}{2}k_f x^2$, and

$$[H, x] = [p_x^2/2m, x] = -(i\hbar/m)p_x \qquad \text{[Problem 1.11]}$$

$$[H, p_x] = [\tfrac{1}{2}k_f x^2, p_x] = -i\hbar k_f x \qquad \text{[Problem 1.11]}$$

$$(d/dt)\langle x\rangle = \underline{(1/m)\langle p_x\rangle}\,;\ (d/dt)\langle p_x\rangle = \underline{-k_f\langle x\rangle}$$

Therefore

$$(d^2/dt^2)\langle x\rangle = (1/m)(d/dt)\langle p_x\rangle = -(k_f/m)\langle x\rangle$$

The solution of $(d^2/dt^2)\langle x\rangle = -(k_f/m)\langle x\rangle$ is

$$\langle x\rangle = A\cos\omega t + B\sin\omega t,\quad \omega^2 = k_f/m$$

$$\langle p\rangle = m(\mathrm{d}/\mathrm{d}t)\langle x\rangle = -Am\omega\sin\omega t + Bm\omega\cos\omega t$$

which is the classical trajectory.

Exercise: Find the equation of motion of the expectation values of x and p for a quartic oscillator ($V \propto x^4$).

1.25 $(-\hbar^2/2m)(\mathrm{d}^2\Psi/\mathrm{d}x^2) + V(t)\Psi = \mathrm{i}\hbar(\partial\Psi/\partial t)$.

(a) Try $\Psi = \psi(x)\theta(t)$, then

$$(-\hbar^2/2m)\psi''\theta + V(t)\psi\theta = \mathrm{i}\hbar\,\psi\,\mathrm{d}\theta/\mathrm{d}t$$

$$-(\hbar^2/2m)(\psi''/\psi) + V(t) - \mathrm{i}\hbar(\mathrm{d}\theta/\mathrm{d}t)(1/\theta) = 0$$

By the same argument as that in Section 1.14, $(-\hbar^2/2m)(\psi''/\psi) = \varepsilon$, a constant; hence

$$\psi'' = -(2m\varepsilon/\hbar^2)\psi \qquad (1.1)$$

$\mathrm{i}\hbar(\mathrm{d}\theta/\mathrm{d}t)(1/\theta) - V(t) = \varepsilon$, the same constant; hence

$$(\mathrm{d}/\mathrm{d}t)\ln\theta = \varepsilon + V(t)/\mathrm{i}\hbar \qquad (1.2)$$

(b) Equation (1) has the solution $\psi = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}$, $k = (2m\varepsilon/\hbar^2)^{1/2}$

Equation (2) has the solution $\ln\theta(t) = \ln\theta(0) - (\mathrm{i}/\hbar)\int_0^t\{\varepsilon + V(t)\}\,\mathrm{d}t$

Therefore, on absorbing $\ln\theta(0)$ into A and B,

$$\Psi = \psi(x)\exp\left\{-\mathrm{i}(\varepsilon/\hbar)t - (\mathrm{i}/\hbar)\int_0^t V(t)\mathrm{d}t\right\}$$

Let $V(t) = V\cos\omega t$, then $\int_0^t V(t)\mathrm{d}t = (V/\omega)\sin\omega t$, so

$$\Psi = \psi(x)\exp\{-\mathrm{i}(\varepsilon/\hbar)t - \mathrm{i}(V/\hbar\omega)\sin\omega t\}$$

$$= \psi(x)(\cos\phi - \mathrm{i}\sin\phi),\ \phi = \varepsilon t/\hbar + (V/\hbar\omega)\sin\omega t.$$

The behaviour of the real and imaginary parts of Ψ (essentially the functions $\cos(\tau + \sin\tau)$ and $\sin(\tau + \sin\tau)$) is shown in Fig. 1.1. The dotted line is $\cos(\tau + \sin\tau)$ and the full line is $\sin(\tau + \sin\tau)$.

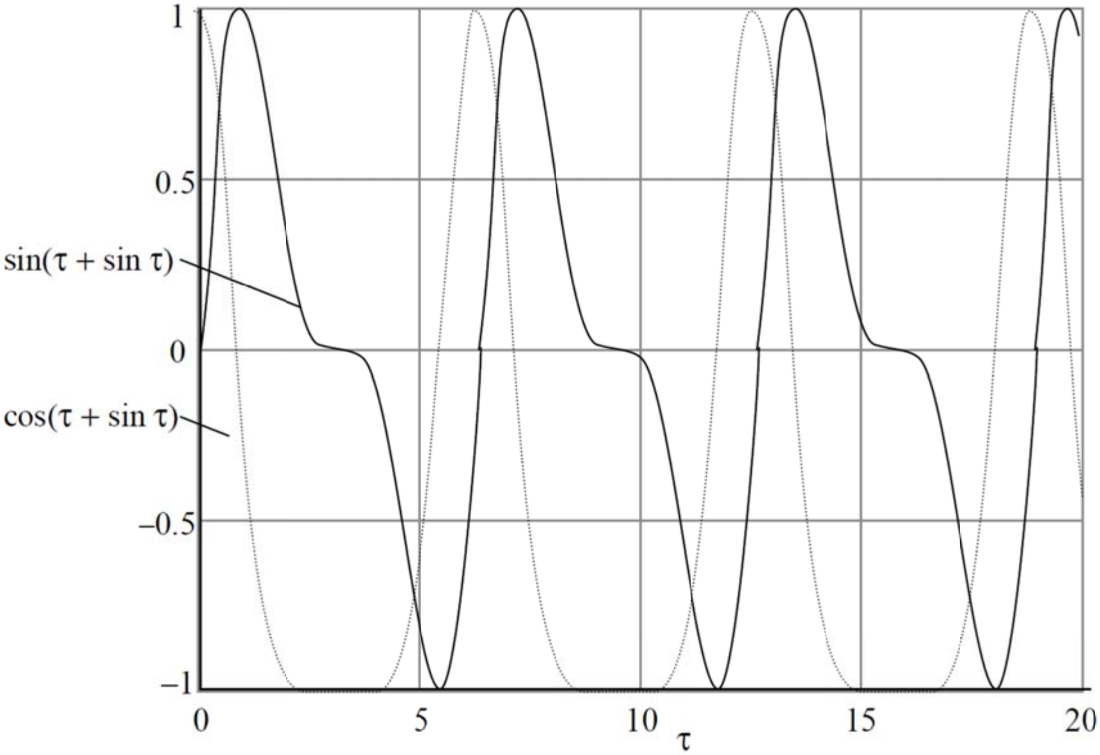


Figure 1.1: The real (dotted line) and imaginary (full line) components of Ψ.

(c) Note that $|\Psi|^2 = |\psi(x)|^2$, and so it is stationary.

Exercise: Consider the form of Ψ for an exponentially switched cosine potential energy, $V(t) = V(1 - e^{-t/T}) \cos \omega t$, for various switching rates.

1.28 From eqn 1.44,

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle [H, x]\rangle$$

The commutator has been evaluated in Problem 1.11(b):

$$\langle [H, x]\rangle = \frac{\hbar}{\mathrm{i}m} p_x$$

and therefore

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{\langle p_x\rangle}{m}$$

which is eqn 1.47.

Chapter 2

Linear motion and the harmonic oscillator

Exercises

2.1 For the energy in **(a)** use $E = e\mathbb{V}$.

(a) $k = (2m_e e\mathbb{V}/\hbar^2)^{1/2} = (5.123 \times 10^9 \text{ m}^{-1}) \times (\mathbb{V}/\text{Volt})^{1/2}$.

(i) $\mathbb{V} = 1.0$ V; $k = 5.123 \times 10^9 \text{ m}^{-1} = 5.123 \text{ nm}^{-1}$;

$\underline{\psi(x) = A \exp\{5.123\,\mathrm{i}(x/\text{nm})\}}$, $A = 1/L^{1/2}$, $L \to \infty$.

(ii) $\mathbb{V} = 10$ kV; $k = 5.123 \times 10^{11} \text{ m}^{-1} = 0.5123 \text{ pm}^{-1}$;

$\underline{\psi(x) = A \exp\{0.5123\,\mathrm{i}(x/\text{pm})\}}$

(b) Because $p = (1.0 \text{ g}) \times (10 \text{ m s}^{-1}) = 1.0 \times 10^{-2} \text{ kg m s}^{-1}$,

$k = p/\hbar$[eqn 2.7] $= 9.48 \times 10^{31} \text{ m}^{-1}$; hence

$$\underline{\psi(x) = A \exp\{9.48\mathrm{i} \times 10^{31}(x/\text{m})\}}$$

Exercise: What value of $\mathbb{V}$ is needed to accelerate an electron so that its wavelength is equal to its Compton wavelength?

2.2 In each case $\underline{|\psi(x)|^2 = A^2}$, a constant ($A^2 = 1/L$; $L \to \infty$)

2.3 Substituting eqn 2.5 for ψ in eqn 2.4 yields:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}\right) = \frac{\hbar^2 k^2}{2m}\left(A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}\right)$$

confirming that the wavefunction is an eigenfunction with eigenvalue $\hbar^2k^2/2m$. The relation between k and E given in eqn 2.5 then follows. Similar substitution of eqn 2.6 for ψ in eqn 2.4 yields:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}(C\cos kx + D\sin kx) = \frac{\hbar^2 k^2}{2m}(C\cos kx + D\sin kx)$$

and the wavefunction is seen to satisfy eqn 2.4.

2.4 The flux density for the wavefunction A sinkx is, using eqn 2.11,

$$J_x\,(A\sin kx) = \frac{1}{2m}\left(\frac{\hbar k}{\mathrm{i}}A^*\sin kx A\cos kx + \frac{\hbar k}{-\mathrm{i}}A\sin kx A^*\cos kx\right) = 0$$

2.5 Use the expression as given in the *brief illustration* in Section 2.7 for the penetration depth $1/\kappa$:

$$\begin{aligned}\frac{1}{\kappa} &= \frac{\hbar}{\{2m(V-E)\}^{1/2}}\\ &= \frac{1.055\times10^{-34}\ \mathrm{Js}}{\{2\times9.109\times10^{-31}\ \mathrm{kg}\times(2.0\ \mathrm{eV}-E)\times1.602\times10^{-19}\ \mathrm{J/eV}\}^{1/2}}\\ &= 4.0\times10^{-10}\ \mathrm{m}\end{aligned}$$

Solving for the kinetic energy yields $E = \underline{1.76\ \mathrm{eV}}$.

2.6 The transmission probability is given in eqn 2.26. Using the Worksheet entitled Equation 2.26 on the text's website and setting

$m = m_\mathrm{e}$ (so that $m/m_\mathrm{e}=1$)

$E = V_0 = 2.0$ eV (so that $E/E_\mathrm{h} = V_0/E_\mathrm{h} = 0.073499$)

$\beta = 1.0\times10^{10}\ \mathrm{m}^{-1}$ (so that $\beta/(1/a_0) = 0.529177$)

yields $T = \underline{6.361\times10^{-1}}$.

2.7 $\psi_4 = (2/L)^{1/2}\sin(4\pi x/L) = 0$ when $x = \underline{0, \tfrac{1}{4}L, \tfrac{1}{2}L, \tfrac{3}{4}L, L,}$ of which the central three are nodes.

Exercise: Repeat the question for $n = 6$.

2.8 To show that the $n = 1$ and $n = 2$ wavefunctions for a particle in a box are orthogonal, we must evaluate the integral

$$\int_0^L \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)\mathrm{d}x = 0$$

The integral can be evaluated using mathematical software or standard integration tables and does indeed vanish.

2.9 The wavefunction for a particle in a geometrically square two-dimensional box of length L is given by (see eqn 2.35)

$$\psi_{n_1 n_2}(x,y) = \frac{2}{L}\sin\left(\frac{n_1 \pi x}{L}\right)\sin\left(\frac{n_2 \pi y}{L}\right)$$

(a) Nodes correspond to points where the wavefunction passes through zero. For (i) $n_1 = 2$, $n_2 = 1$, this occurs at points (x,y) such that $\underline{x = L/2}$. For (ii) $n_1 = 3$, $n_2 = 2$, this occurs at points (x,y) such that $\underline{x = L/3 \text{ or } 2L/3}$ and at points (x,y) such that $\underline{y = L/2}$.

(b) Maxima in the probability densities occur where ψ^2 is maximized. For (i) $n_1 = 2$, $n_2 = 1$, this occurs at points (x,y) such that $\underline{x = L/4 \text{ or } 3L/4}$ and $\underline{y = L/2}$. For (ii) $n_1 = 3$, $n_2 = 2$, this occurs at points (x,y) such that $\underline{x = L/6, L/2 \text{ or } 5L/6}$ and $\underline{y = L/4 \text{ or } 3L/4}$.

2.10 The energy of a particle in a three-dimensional cubic box is given by:

$$E_{n_1 n_2 n_3} = \frac{h^2}{8m}\left(\frac{n_1^2}{L^2}+\frac{n_2^2}{L^2}+\frac{n_3^2}{L^2}\right) \qquad n_1 = 1,2,\ldots \quad n_2 = 1,2,\ldots \quad n_3 = 1,2,\ldots$$

The lowest energy level corresponds to ($n_1 = n_2 = n_3 = 1$) and equals $3h^2/8mL^2$. Three times this energy, that is $9h^2/8mL^2$, can be achieved with the following sets of quantum numbers:

$(n_1 = 2, n_2 = 2, n_3 = 1)$
$(n_1 = 2, n_2 = 1, n_3 = 2)$
$(n_1 = 1, n_2 = 2, n_3 = 2)$

Therefore the degeneracy of the energy level is $\underline{3}$.

2.11 The harmonic oscillator wavefunction is given in eqn 2.41. Nodes correspond to those points x such that the Hermite polynomial $H_v(\alpha x)$ vanishes. Using Table 2.1, we seek values of $z = \alpha x$ such that $4z^2 - 2 = 0$. This equation is satisfied by

$$z = \pm\sqrt{\frac{1}{2}}$$

and therefore $x = \underline{\alpha/\sqrt{2}}$ and $x = \underline{-\alpha/\sqrt{2}}$.

2.12 The energy levels of the harmonic oscillator are given by 2.40. The separation between neighboring vibrational energy levels v and $v+1$ is given by

$$\Delta E = \hbar\omega = \hbar\sqrt{\frac{k_f}{m}} = 1.055 \times 10^{-34}\,\mathrm{Js} \times \sqrt{\frac{275\ \mathrm{Nm}^{-1}}{1.33 \times 10^{-25}\mathrm{kg}}} = 4.797 \times 10^{-21}\mathrm{J}$$

Equating this with the photon energy hc/λ yields a wavelength of $\underline{4.14 \times 10^{-5}\ \mathrm{m}}$ and a corresponding wavenumber of $1/(4.14 \times 10^{-3}\ \mathrm{cm}) = \underline{241\ \mathrm{cm}^{-1}}$.

Problems

2.1 See Fig. 2.1.

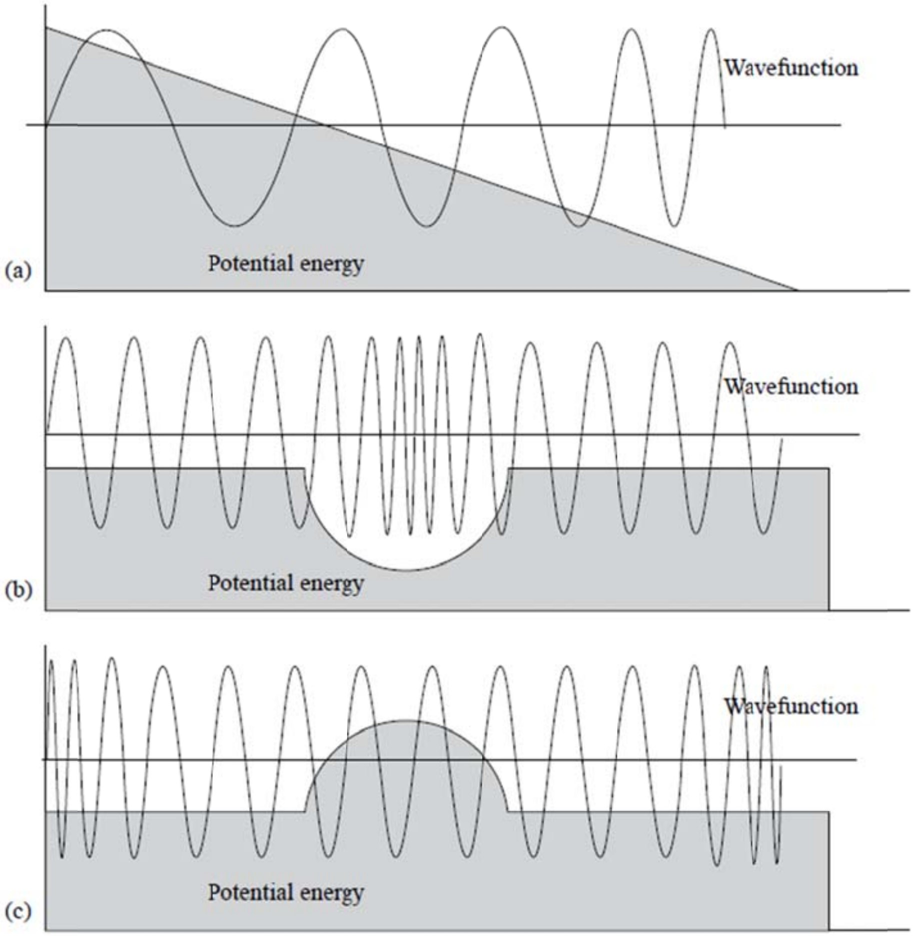


Figure 2.1: The wavefunction in the presence of various potentials.

Exercise: Sketch the general form of the wavefunction for a potential with two parabolic wells separated and surrounded by regions of constant potential.

2.4 From eqns 2.12 and 2.13,

$$\Psi(x,\,t) = \int g(k)\Psi_k(x,t)\mathrm{d}k = AB\int_{k-\frac{1}{2}\Delta k}^{k+\frac{1}{2}\Delta k}\exp\{\mathrm{i}kx - \mathrm{i}k^2\hbar t/2m\}\mathrm{d}k$$

$$\Psi(x,\,0) = AB\int_{k-\frac{1}{2}\Delta k}^{k+\frac{1}{2}\Delta k}\exp\{\mathrm{i}kx\}\mathrm{d}k$$

$$= (AB/\mathrm{i}x)\left\{\mathrm{e}^{\mathrm{i}(k+\frac{1}{2}\Delta k)x} - \mathrm{e}^{\mathrm{i}(k-\frac{1}{2}\Delta k)x}\right\}$$

$$= (AB\mathrm{e}^{\mathrm{i}kx}/\mathrm{i}x)\left\{\mathrm{e}^{\frac{1}{2}\mathrm{i}\Delta kx} - \mathrm{e}^{-\frac{1}{2}\mathrm{i}\Delta kx}\right\} = 2AB(\mathrm{e}^{\mathrm{i}kx}\sin\tfrac{1}{2}\Delta kx)/x$$

$$|\Psi(x,\,0)|^2 = 4A^2B^2\{\sin(\tfrac{1}{2}\Delta kx)/x\}^2$$

For normalization (to unity), write $AB = N$; then

$$\int|\Psi|^2\,\mathrm{d}\tau = 4N^2\int_{-\infty}^{\infty}\{\sin(\tfrac{1}{2}\Delta kx)/x\}^2\mathrm{d}x = 2N^2\Delta k\int_{-\infty}^{\infty}(\sin z/z)^2\mathrm{d}z \;\; [z = \tfrac{1}{2}\Delta kx]$$

$$= 2N^2\Delta k\pi = 1;\text{ hence } N = (2\Delta k\pi)^{-1/2}$$

Therefore, $\Psi(x,0) = (2/\Delta k\pi)^{1/2}(\mathrm{e}^{\mathrm{i}kx}\sin\tfrac{1}{2}\Delta kx)/x$

$$|\Psi(x,\,0)|^2 = (2/\Delta k\pi)(\sin\,\tfrac{1}{2}\Delta kx/x)^2$$

$$|\Psi(0,\,0)|^2 = (2/\Delta k\pi)\,\lim_{x\to 0}(\sin\,\tfrac{1}{2}\Delta kx/x)^2 = (2/\Delta k\pi)(\tfrac{1}{2}\Delta kx/x)^2$$

$$= (2/\Delta k\pi)(\Delta k/2)^2 = \Delta k/(2\pi)$$

We seek the value of x for which $|\Psi(x,\,0)|^2/|\Psi(0,\,0)|^2 = \tfrac{1}{2}$; that is

$$\frac{\{\sin(\frac{1}{2}\Delta kx)/x\}^2}{(\frac{1}{2}\Delta k)^2} = \tfrac{1}{2}$$

or

$$\frac{\sin\frac{1}{2}\Delta kx}{\frac{1}{2}\Delta kx}=\frac{1}{\sqrt{2}}$$

which is satisfied by $\frac{1}{2}\Delta kx = \pm 1.392$ [solve numerically]. Hence the probability density falls to one half its value at $x = 0$ when $x = \pm 2.784/\Delta k$. From the uncertainty principle $\Delta p_x\Delta x \geq \frac{1}{2}\hbar$, so $\Delta k\Delta x \geq \frac{1}{2}$, and hence $\Delta x \geq 0.5/\Delta k$ which is in accord with $\Delta x \approx 2 \times 2.784/\Delta k$.

Exercise: Examine the properties of a Gaussian wavepacket in the same way.

2.7 Consider the zones set out in Fig. 2.5; impose the condition of continuity of ψ and ψ' at each interface.

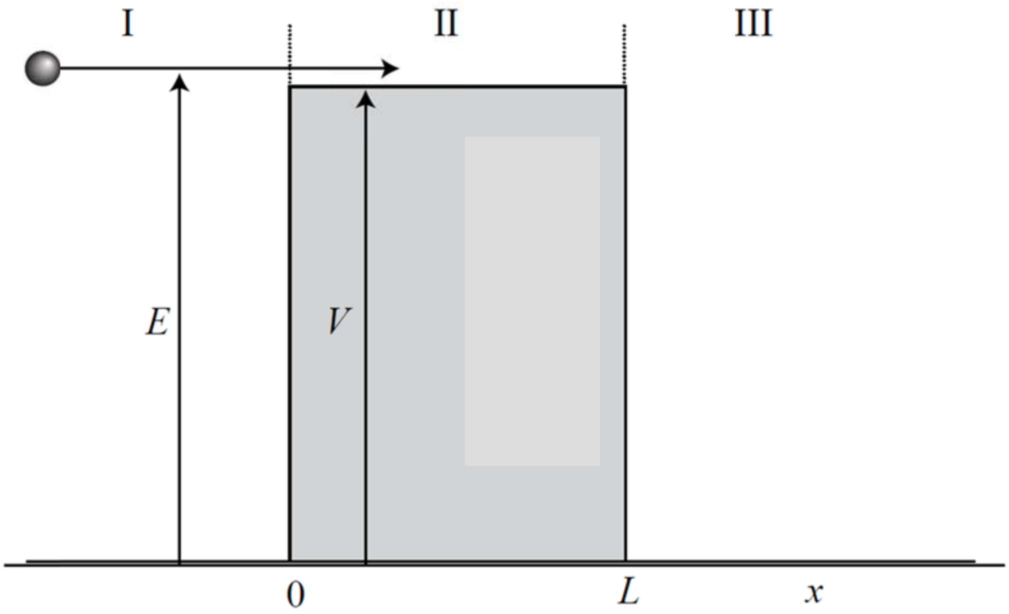


Fig 2.5 The zones of potential energy used in Problem 2.7.

$$\left.\begin{aligned}\psi_{\mathrm{I}} &= A\mathrm{e}^{\mathrm{i}kx}+B\mathrm{e}^{-\mathrm{i}kx}, k^2 = 2mE/\hbar^2\\ \psi_{\mathrm{II}} &= A'\mathrm{e}^{\mathrm{i}k'x}+B'\mathrm{e}^{-\mathrm{i}k'x}, k'^2 = 2m(E-V)/\hbar^2\end{aligned}\right\}\gamma = k/k'$$

$\psi_{\mathrm{III}} = A''\mathrm{e}^{\mathrm{i}kx}$ [no particles incident from right]

(1) $A + B = A' + B'$, [from $\psi_{\rm I}(0) = \psi_{\rm II}(0)$]

(2) $A'{\rm e}^{{\rm i}k'L} + B'{\rm e}^{-{\rm i}k'L} = A''{\rm e}^{{\rm i}kL}$, [from $\psi_{\rm II}(L) = \psi_{\rm III}(L)$]

(3) $kA - kB = k'A' - k'B'$, [from $\psi'_{\rm I}(0) = \psi'_{\rm II}(0)$]

(4) $k'A'{\rm e}^{{\rm i}k'L} - k'B'{\rm e}^{-{\rm i}k'L} = kA''{\rm e}^{{\rm i}kL}$ [from $\psi'_{\rm II}(L) = \psi'_{\rm III}(L)$]

From (1) and (3):

$$A' = \tfrac{1}{2}(1+\gamma)A + \tfrac{1}{2}(1-\gamma)B;\ B' = \tfrac{1}{2}(1-\gamma)A + \tfrac{1}{2}(1+\gamma)B$$

From (2) and (4)

$$A'' = A'{\rm e}^{{\rm i}(k'-k)L} + B'{\rm e}^{-{\rm i}(k'+k)L}$$

$$\gamma A'' = A'{\rm e}^{{\rm i}(k'-k)L} - B'{\rm e}^{-{\rm i}(k'+k)L}$$

so

$$\tfrac{1}{2}(1+\gamma)A'' = A'{\rm e}^{{\rm i}(k'-k)L},\ \tfrac{1}{2}(1-\gamma)A'' = B'{\rm e}^{-{\rm i}(k'+k)L}$$

Then

$$A''{\rm e}^{{\rm i}kL}\left\{(1+\gamma)^2{\rm e}^{-{\rm i}k'L} - (1-\gamma)^2{\rm e}^{{\rm i}k'L}\right\} = 4\gamma A$$

$$A''/A = 2\gamma\,{\rm e}^{-{\rm i}kL}/\{2\gamma\cos k'L - {\rm i}(1+\gamma^2)\sin k'L\}$$

The transmission coefficient (or tunnelling probability) is

$$P = |A''|^2/|A|^2 = |A''/A|^2$$

$$= \underline{4\gamma^2/\{4\gamma^2 + (1-\gamma^2)^2\sin^2 k'L\}},\ \gamma^2 = E/(E-V)$$

Exercise: Find the transmission coefficient for a particle incident on a rectangular dip in the potential energy.

2.10 Use the normalized wavefunctions in eqn 2.31:

$$\psi_n = (2/L)^{1/2} \sin(n\pi x/L)\text{; also use}$$

$$\int \sin^2 ax\mathrm{d}x = \tfrac{1}{2}x - (1/4a)\sin 2ax$$

(a) $P_n = \int_0^{\frac{1}{2}L} \psi_n^2 \mathrm{d}x = (2/L)\int_0^{\frac{1}{2}L} \sin^2(n\pi x/L)\mathrm{d}x = \tfrac{1}{2}$ for all n

(b) $P_n = \int_0^{\frac{1}{4}L} \psi_n^2 \mathrm{d}x = (2/L)\int_0^{\frac{1}{4}L} \sin^2(n\pi x/L)\mathrm{d}x = \underline{\tfrac{1}{4}\{1-(2/\pi n)\sin(\tfrac{1}{2}n\pi)\}}$

$P_1 = \tfrac{1}{4}\{1-(2/\pi)\} = \underline{0.090\ 85}$

(c)

$$P_n = \int_{\frac{1}{2}L-\delta x}^{\frac{1}{2}L+\delta x} \psi_n^2 \mathrm{d}x = (2/L)\int_{\frac{1}{2}L-\delta x}^{\frac{1}{2}L+\delta x} \sin^2(n\pi x/L)\mathrm{d}x$$

$= (2/L)\{\delta x - (L/2\pi n)\cos(n\pi)\sin(2n\pi\delta x/L)\}$

$= \underline{(2/L)\{\delta x - (-1)^n(L/2\pi n)\sin(2n\pi\delta x/L)\}}$

$P_1 = (2/L)\{\delta x + (L/2\pi)\sin(2\pi\delta x/L)\} \approx \underline{4\delta x/L}$ when $\delta x/L << 1$

Note that

$$\lim_{n\to\infty} P_n = \text{(a) } \tfrac{1}{2}\text{, (b) } \tfrac{1}{4}\text{, (c) } 2\delta x/L$$

the last corresponding to a uniform distribution (the classical limit).

Exercise: Find P_n (and P_1) for the particle being in a short region of length δx centred on the general point x.

2.13 Use the wavefunction $\psi_n = (2/L)^{1/2}\sin(n\pi x/L)$ and the integral

$$\int x\sin^2 ax\mathrm{d}x = (1/4a^2)\{a^2x^2 - ax\sin(2ax) - \tfrac{1}{2}\cos(2ax)\}$$

$$\langle x\rangle_n = \int_0^L x\psi_n^2\mathrm{d}x = (2/L)\int_0^L x\sin^2(n\pi x/L)\mathrm{d}x$$

$$= (L/2n^2\pi^2)\{n^2\pi^2 - n\pi\sin(2n\pi) - \tfrac{1}{2}[\cos(2n\pi) - 1]\} = \underline{\tfrac{1}{2}L}$$

The result is also obvious, by symmetry.

Exercise: Evaluate $\langle x\rangle$ when the particle is in the normalized mixed state $\psi_1\cos\beta + \psi_2\sin\beta$. Account for its dependence on the parameter β.

2.16 Refer to Fig. 2.8. Consider the case $E < V$.

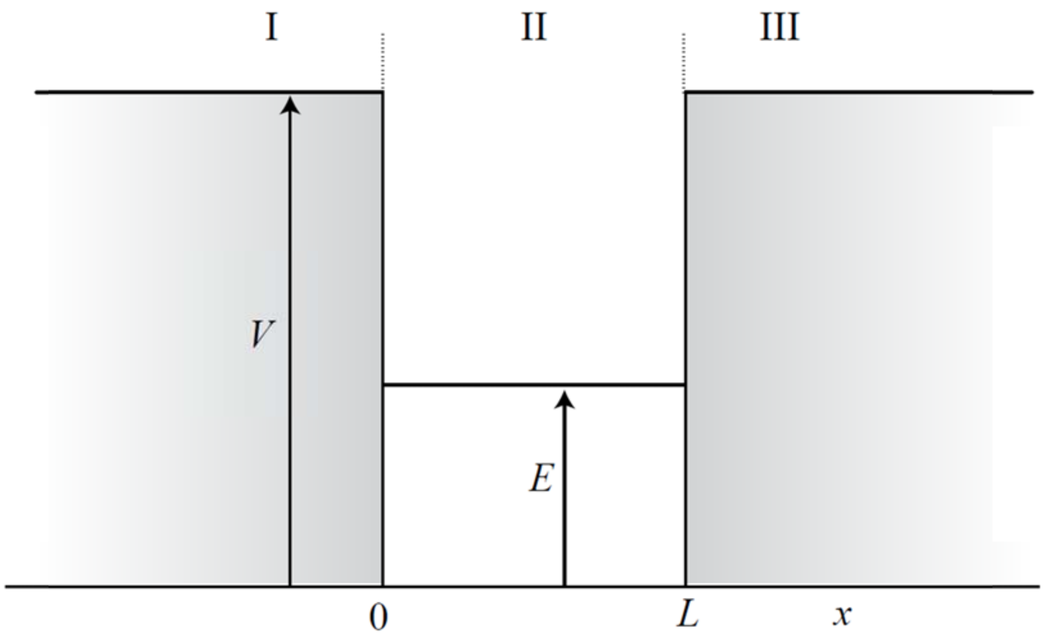


Figure 2.8: The zones of potential energy used in Problem 2.16.

$$\psi_{\mathrm{I}} = A\mathrm{e}^{-\kappa x} + B\mathrm{e}^{\kappa x}, \qquad \kappa^2 = 2m(V-E)/\hbar^2$$

$$\psi_{\mathrm{II}} = A'\mathrm{e}^{\mathrm{i}kx} + B'\mathrm{e}^{-\mathrm{i}kx}, \qquad k^2 = 2mE/\hbar^2$$

$$\psi_{\mathrm{III}} = A''\mathrm{e}^{-\kappa x} + B''\mathrm{e}^{\kappa x}, \qquad \kappa^2 = 2m(V-E)/\hbar^2$$

Because $\psi < \infty$ everywhere, $A = 0$, $B'' = 0$ [consider $x \to -\infty$ and $x \to \infty$ respectively].

At the interfaces of the zones:

$$\psi_{\mathrm{I}}'(0)/\psi_{\mathrm{I}}(0) = -\kappa(A - B)/(A + B) = \kappa \qquad [A = 0]$$

$$\psi_{\mathrm{II}}'(0)/\psi_{\mathrm{II}}(0) = \mathrm{i}k(A' - B')/(A' + B')$$

$$\psi_{\mathrm{II}}'(L)/\psi_{\mathrm{II}}(L) = \mathrm{i}k(A'\mathrm{e}^{\mathrm{i}kL} - B'\mathrm{e}^{-\mathrm{i}kL})/(A'\mathrm{e}^{\mathrm{i}kL} + B'\mathrm{e}^{-\mathrm{i}kL})$$

$$\psi_{\mathrm{III}}'(L)/\psi_{\mathrm{III}}(L) = -\kappa(A''\mathrm{e}^{-\kappa L} - B''\mathrm{e}^{\kappa L})/(A''\mathrm{e}^{-\kappa L} + B''\mathrm{e}^{\kappa L}) = -\kappa \quad [B'' = 0]$$

Because ψ'/ψ is continuous at each boundary,

$$(A' - B')/(A' + B') = \kappa/\mathrm{i}k = -\mathrm{i}\kappa/k = -\mathrm{i}\gamma \quad [\gamma = \kappa/k]$$

$$(A'\mathrm{e}^{\mathrm{i}kL} - B'\mathrm{e}^{-\mathrm{i}kL})/(A'\mathrm{e}^{\mathrm{i}kL} + B'\mathrm{e}^{-\mathrm{i}kL}) = -\kappa/\mathrm{i}k = \mathrm{i}\kappa/k = \mathrm{i}\gamma$$

This pair of equations solves to

$$(1 + \mathrm{i}\gamma)A' = (1 - \mathrm{i}\gamma)B', \quad (1 - \mathrm{i}\gamma)A'\mathrm{e}^{\mathrm{i}kL} = (1 + \mathrm{i}\gamma)B'\mathrm{e}^{-\mathrm{i}kL}$$

It follows that

$$(1 - \gamma^2)\sin kL - 2\gamma\cos kL = 0, \text{ or } \tan kL = 2\gamma/(1 - \gamma^2)$$

Then, since

$$\tan kL = 2\tan(\tfrac{1}{2}kL)/[1 - \tan^2(\tfrac{1}{2}kL)], \quad \tan(\tfrac{1}{2}kL) = \gamma$$

Consequently,

$$\cos(\tfrac{1}{2}kL) = 1/(1 + \gamma^2)^{1/2} = \hbar k/(2mV)^{1/2}$$

Therefore,

$$kL = 2\arccos\{\hbar k/(2mV)^{1/2}\} + n\pi, \quad n = 0, 1, \ldots$$

But $\arccos z = \tfrac{1}{2}\pi - \arcsin z$, so

$$kL + 2\arcsin\{\hbar k/(2mV)^{1/2}\} = n\pi, \quad n = 1, 2, \ldots$$

Solve this equation for k by plotting $y = kL$ and

$$y = n\pi - 2\arcsin(\hbar^2k^2/2mV)^{1/2} \quad \text{for } n = 1, 2, \ldots$$

and finding the values of k at which the two lines coincide, and then form $E_n = \hbar^2k^2/2m$ for each value of n. This procedure is illustrated in Fig. 2.9 for the special case $V = 225\hbar^2/2mL^2$, so, with $kL = z$, $y = z$ and $y = n\pi - 2\arcsin z/15$, $E_n = z_n^2(\hbar^2/2mL^2)$ with z_n the intersection value of n. (Because $E < V$, $z < 15$.) We find $z = 2.9, 5.9, 8.8, 11.7$ for $n = 1, 2, 3, 4$; hence $E/(\hbar^2/2mL^2) = 8.4, 35, 77, 137$ for $n = 1, 2, 3, 4$.

When V is large in the sense $2mV >> \hbar^2k^2$, $\arcsin(\hbar^2k^2/2mV)^{1/2} \approx 0$. Hence the equation to solve is $kL \approx n\pi$. Consequently $E_n \approx n^2h^2/8mL^2$ in accord with the infinitely deep square-well solutions.

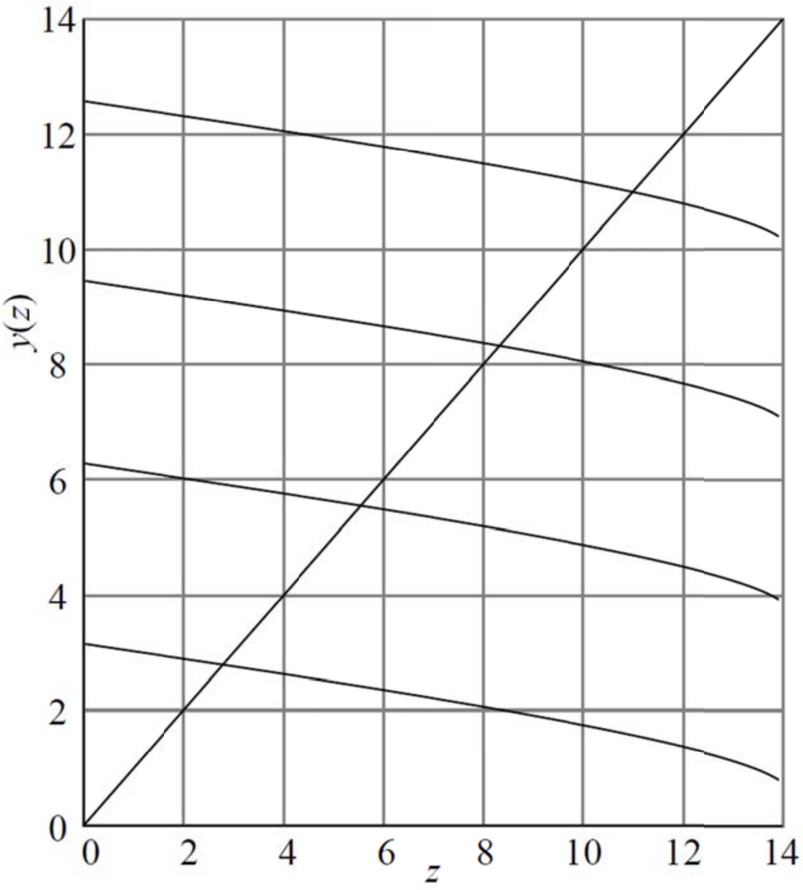


Figure 2.9: The determination of allowed energies.

Exercise: First consider the special case $V = 6\hbar^2/2mL^2$, and find the allowed solutions. Then repeat the calculation for an unsymmetrical well in which the potential energy rises to V on the left and to $4V$ on the right.

2.19 **(a)** $E_{n_1n_2} = \dfrac{h^2}{8m}\left(\dfrac{n_1^2}{L_1^2} + \dfrac{n_2^2}{L_2^2}\right) = \dfrac{h^2}{8mL_2^2}\left(\dfrac{n_1^2}{\lambda^2} + n_2^2\right)$

where $\lambda = L_1/L_2$. Therefore, if λ is an integer, the states (n_1, n_2) and $(\lambda n_2, n_1/\lambda)$ are degenerate.

(b) The states related by the relation in **(a)** are doubly degenerate.

2.22 The Schrödinger equation is

$$-(\hbar^2/2m)(\mathrm{d}^2\psi/\mathrm{d}x^2) + \tfrac{1}{2}k_\mathrm{f}x^2\psi = E\psi$$

Substitute $y = (m\omega/\hbar)^{1/2}x$ with $\omega^2 = k_\mathrm{f}/m$; then $\psi'' - y^2\psi = -\lambda\psi$, with $\lambda = E/\tfrac{1}{2}\hbar\omega$ and

$\psi'' = \mathrm{d}^2\psi/\mathrm{d}y^2$.

Substitute eqn 2.41: $\psi = N_vH_v\mathrm{e}^{-y^2/2}$:

$$(\mathrm{d}^2/\mathrm{d}y^2)(H_v\mathrm{e}^{-y^2/2}) - y^2H_v\mathrm{e}^{-y^2/2} = -\lambda H_v\mathrm{e}^{-y^2/2}$$

Use

$$\begin{aligned}(\mathrm{d}^2/\mathrm{d}y^2)(H_v\mathrm{e}^{-y^2/2}) &= (H_v'' - 2yH_v' - H_v + y^2H_v)\mathrm{e}^{-y^2/2}\\ &= (2yH_v' - 2vH_v - 2yH_v' - H_v + y^2H_v)e^{-y^2/2} \quad \text{[given]}\\ &= \{y^2H_v - (2v+1)H_v\}e^{-y^2/2}\end{aligned}$$

Then

$$\{y^2H_v - (2v+1)H_v - y^2H_v\}\mathrm{e}^{-y^2/2} = -\lambda H_v\mathrm{e}^{-y^2/2}$$

so $\lambda = 2v + 1$, or $E = \tfrac{1}{2}(2v+1)\hbar\omega = (v + \tfrac{1}{2})\hbar\omega$, as required.

2.25 **(a)**

$$\langle v+1|x|v\rangle = N_{v+1}N_v\alpha^{-2}\int_{-\infty}^{\infty} H_{v+1}(y)\,yH_v(y)\mathrm{e}^{-y^2}\,\mathrm{d}y \quad [y=\alpha x]$$

$$= \alpha^{-2}N_{v+1}N_v\int_{-\infty}^{\infty} H_{v+1}\{\tfrac{1}{2}H_{v+1}+vH_{v-1}\}e^{-y^2}\,\mathrm{d}y \quad \text{[Table 2.1]}$$

$$= \tfrac{1}{2}\alpha^{-2}N_{v+1}N_v\int_{-\infty}^{\infty} H_{v+1}^2\mathrm{e}^{-y^2}\,\mathrm{d}y \quad \text{[orthogonality]}$$

$$= \tfrac{1}{2}\alpha^{-2}N_{v+1}N_v\pi^{1/2}2^{v+1}(v+1)!$$

$$= \frac{\pi^{1/2}2^{v+1}(v+1)!}{2\pi^{1/2}\alpha\{2^v2^{v+1}v!(v+1)!\}^{1/2}} = \underline{\frac{1}{\sqrt{2}\alpha}(v+1)^{1/2}}$$

(b)

$$\langle v+2|x^2|v\rangle = N_{v+2}N_v\alpha^{-3}\int_{-\infty}^{\infty} H_{v+2}y^2H_v\mathrm{e}^{-y^2}\,\mathrm{d}y$$

$$= \alpha^{-3}N_{v+2}N_v\int_{-\infty}^{\infty} H_{v+2}y\{\tfrac{1}{2}H_{v+1}+vH_{v-1}\}\mathrm{e}^{-y^2}\,\mathrm{d}y$$

$$= \alpha^{-3}N_{v+2}N_v\int_{-\infty}^{\infty} H_{v+2}\{\tfrac{1}{4}H_{v+2}+\tfrac{1}{2}vH_v+\tfrac{1}{2}vH_v+v^2H_{v-2}\}\mathrm{e}^{-y^2}\,\mathrm{d}y$$

$$= \tfrac{1}{4}\alpha^{-3}N_{v+2}N_v\int_{-\infty}^{\infty} H_{v+2}^2\mathrm{e}^{-y^2}\,\mathrm{d}y \quad \text{[orthogonality]}$$

$$= \tfrac{1}{4}\alpha^{-3}N_{v+2}N_v\pi^{1/2}2^{v+2}(v+2)! \quad \text{[Table 2.1]}$$

$$= \frac{\alpha^{-3}\pi^{1/2}2^{v+2}(v+2)!}{4\{2^{v+2}2^v(v+2)!v!\alpha^{-2}\pi\}^{1/2}} = \underline{\tfrac{1}{2}\alpha^{-2}\{(v+2)(v+1)\}^{1/2}}$$

Exercise: Evaluate $\langle v+3|x^3|v\rangle$ in the same way.

2.28 According to classical mechanics, the turning point x_{tp} occurs when all the energy of the oscillator is potential energy and its kinetic energy is zero. This equality occurs when

$$E = \tfrac{1}{2}k_{\mathrm{f}}x_{\mathrm{tp}}^2 \text{ or } x_{\mathrm{tp}} = \left(\frac{2\mathrm{E}}{k_{\mathrm{f}}}\right)^{1/2}$$

Since we are only considering the stretching of the harmonic oscillator beyond the classical turning point, we only choose the positive square root for x_{tp}. The probability P of finding the ground-state harmonic oscillator stretched beyond a displacement x_{tp} is given by:

$$P = \int_{x_{\mathrm{tp}}}^{\infty} \psi_0^2 \, \mathrm{d}x$$

Using eqn 2.41 and the Hermite polynomial H_0 in Table 2.1, we obtain:

$$P = \frac{\alpha}{\pi^{1/2}} \int_{x_{\mathrm{tp}}}^{\infty} \mathrm{e}^{-\alpha^2 x^2} \, \mathrm{d}x$$

The turning point can be expressed in terms of α, using (i) the definition of α in eqn 2.41 and (ii) the ground-state energy $E = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar(k_{\mathrm{f}}/m)^{1/2}$. This results in $x_{\mathrm{tp}} = 1/\alpha$. Now introduce the variable $y = \alpha x$ so that $\mathrm{d}y = \alpha \mathrm{d}x$, $y^2 = \alpha^2 x^2$ and $y_{\mathrm{tp}} = \alpha x_{\mathrm{tp}} = 1$. The above integral then becomes, in terms of the variable y:

$$P = \frac{1}{\pi^{1/2}} \int_{1}^{\infty} \mathrm{e}^{-y^2} \, \mathrm{d}y$$

The above integral is related to the error function given in the Problem, and using the value of erf 1 given:

$$P = \frac{1}{\pi^{1/2}} \int_1^{\infty} \mathrm{e}^{-y^2} \, \mathrm{d}y = \frac{1}{2}(1 - \mathrm{erf}\ 1) = \frac{1}{2}(1 - 0.8427)$$

The probability is 7.865×10^{-2}.

2.31 The wavefunction $\psi(x)$ is given as a sum of normalized particle-in-a-box eigenfunctions $\psi_n(x)$. Therefore, according to quantum mechanical postulate 3′, a single measurement of the energy yields a single outcome which is one of the eigenvalues E_n (associated with the eigenfunction ψ_n appearing in the expansion of ψ). The probability of obtaining E_n is $|c_n|^2$ where c_n is the coefficient of ψ_n in the expansion.

(a) When the energy of the particle is measured, possible outcomes are

$$E_1 = \frac{h^2}{8mL^2} \quad E_3 = \frac{9h^2}{8mL^2} \quad E_5 = \frac{25h^2}{8mL^2}$$

(b) The probability of obtaining each result is

$$|c_1|^2 = (1/3)^2 = 1/9 \quad \text{for } E_1$$

$$|c_3|^2 = |(\mathrm{i}/3)|^2 = 1/9 \quad \text{for } E_3$$

$$|c_5|^2 = [-(7/9)^{1/2}]^2 = 7/9 \quad \text{for } E_5$$

(c) The expectation value is the weighted sum of the possible eigenvalues:

$$\tfrac{1}{9}E_1 + \tfrac{1}{9}E_3 + \tfrac{7}{9}E_5 = \frac{185h^2}{72mL^2}$$

Exercise: If the linear momentum of the particle described above were measured, what would we expect to find?

Chapter 3

Rotational motion and the hydrogen atom

Exercises

3.1

$$E = m_l^2(\hbar^2/2I)\ [\text{eqn } 3.6]; \quad I = m_\mathrm{H}R^2$$

$$E = m_l^2(\hbar^2/2m_\mathrm{H}R^2)$$

$$m_\mathrm{H} = 1.674 \times 10^{-27}\ \mathrm{kg}, \quad R = 160\ \mathrm{pm}; \quad \hbar^2/2m_\mathrm{H}R^2 = 1.30 \times 10^{-22}\ \mathrm{J}$$

Hence,

$$E = \underline{(1.30 \times 10^{-22}\ \mathrm{J})m_l^2}$$

3.2 Using the energy levels from Exercise 3.1, we obtain

$$\Delta E = (1.30 \times 10^{-22}\ \mathrm{J})(1 - 0) = 1.30 \times 10^{-22}\ \mathrm{J}$$

$$\lambda \quad = hc/\Delta E = 1.53 \times 10^{-3}\ \mathrm{m} = \underline{1.53\ \mathrm{mm}}$$

This wavelength corresponds <u>to microwave</u> radiation.

Exercise: Calculate the effect of deuteration on E and $\lambda(1 \leftarrow 0)$.

3.3 $x = r\cos\phi, \quad y = r\sin\phi, \quad r = (x^2 + y^2)^{1/2}$

$$l_z = \frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$= \frac{\hbar}{\mathrm{i}}\left(x\left\{\frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\phi}{\partial y}\frac{\partial}{\partial\phi}\right\} - y\left\{\frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}\right\}\right)$$

$$= \frac{\hbar}{\mathrm{i}}\left(\left\{\frac{xy}{r}\frac{\partial}{\partial r} + x\frac{\partial\phi}{\partial y}\frac{\partial}{\partial\phi}\right\} - \left\{y\frac{x}{r}\frac{\partial}{\partial r} + y\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}\right\}\right)$$

$$= \frac{\hbar}{\mathrm{i}}\left(x\frac{\partial\phi}{\partial y} - y\frac{\partial\phi}{\partial x}\right)\frac{\partial}{\partial\phi}$$

$$= \frac{\hbar}{\mathrm{i}}\left(\frac{x}{\partial y/\partial\phi} - \frac{y}{\partial x/\partial\phi}\right)\frac{\partial}{\partial\phi}$$

$$= \frac{\hbar}{\mathrm{i}}\left(\frac{r\cos\phi}{r/\cos\phi} + \frac{r\sin\phi}{r/\sin\phi}\right)\frac{\partial}{\partial\phi} = \underline{\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\phi}}$$

3.4
$$\int_0^{2\pi}\phi^*_{m_l'}\phi_{m_l}\,\mathrm{d}\phi = (1/2\pi)\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(m_l-m_l')\phi}\mathrm{d}\phi$$

$$= (1/2\pi)\left\{\frac{\mathrm{e}^{2\mathrm{i}(m_l-m_l')\pi}-1}{(m_l-m_l')\mathrm{i}}\right\} = 0 \quad \text{if } m_l' \neq m_l$$

$$[\mathrm{e}^{2\mathrm{i}n\pi} = 1,\ n \text{ an integer}]$$

(Note that when $m_l' = m_l$ the integral has the value 2π.)

Exercise: Normalize the wavefunction $\mathrm{e}^{\mathrm{i}\phi}\cos\beta + \mathrm{e}^{-\mathrm{i}\phi}\sin\beta$, and find an orthogonal linear combination of $\mathrm{e}^{+\mathrm{i}\phi}$ and $\mathrm{e}^{-\mathrm{i}\phi}$.

3.5 The moment of inertia of a solid uniform disc of mass M and radius R is

$$I = \tfrac{1}{2}MR^2; \quad \text{hence } I = 2.5\times10^{-4}\ \text{kg m}^2$$

Then

$$E = m_l^2(\hbar^2/2I) = \underline{(2.2\times10^{-65}\ \mathrm{J})m_l^2}$$

The rotation rate is 100 Hz. Hence $\omega = 2\pi\nu = 628\ \mathrm{s}^{-1}$. The angular momentum is $I\omega =$ $0.16\ \mathrm{kg\ m^2\ s^{-1}}$. If this is set equal to $|m_l|\hbar$ we require $|m_l| = 1.5\times10^{33}$. Since the disc rotates anticlockwise when seen from below, m_l is negative. Hence, $\underline{m_l = -1.5\times10^{33}}$.

Exercise: How much more energy is required to raise the disc into its next rotational state?

3.6 See Fig. 3.1. We have plotted

$$\mathrm{re}\ \phi_{m_l} = (1/2\pi)^{1/2}\cos m_l\phi = \begin{cases}(1/2\pi)^{1/2}\cos 3\phi & \text{for } m_l = 3\\ (1/2\pi)^{1/2}\cos 4\phi & \text{for } m_l = 4\end{cases}$$

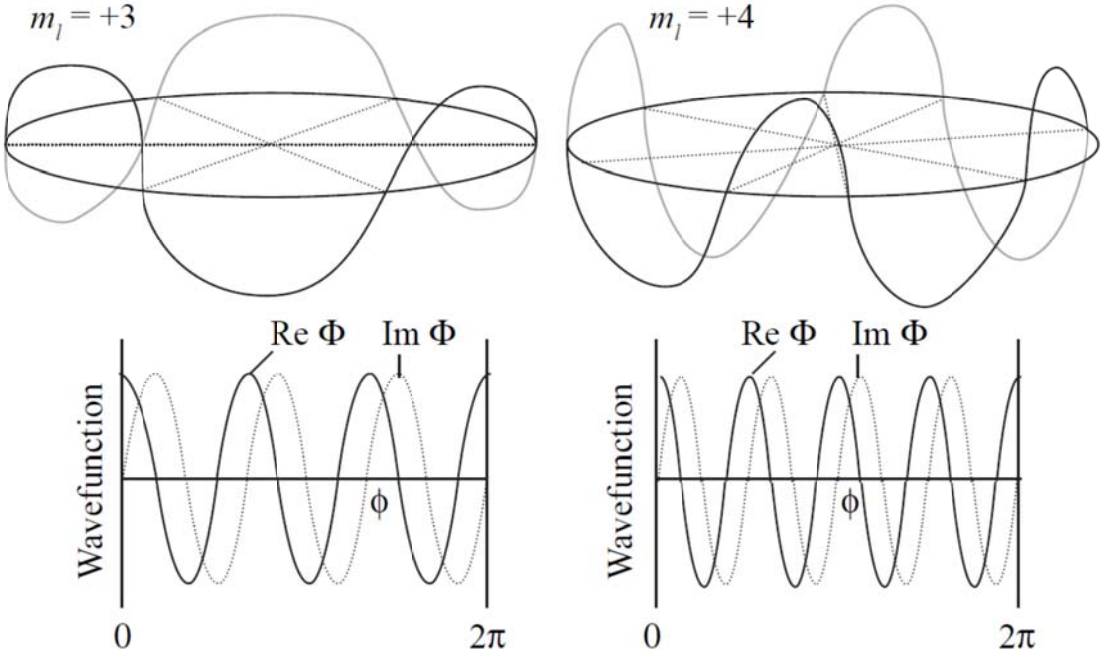


Figure 3.1: A representation of the amplitudes and phases of the wavefunction of a particle on a ring (red, real; green, imaginary).

Exercise: Superimpose the imaginary parts of ϕ_{m_l} on the diagrams. Draw re ϕ for the superposition $e^{i\phi}\cos\beta + e^{-i\phi}\sin\beta$.

3.7 The Schrödinger equation is given in eqn 3.31:

$$\Lambda^2\psi = -(2IE/\hbar^2)\psi\,;\quad \Lambda^2 = (1/\sin^2\theta)(\partial^2/\partial\phi^2) + (1/\sin\theta)(\partial/\partial\theta)\sin\theta\,(\partial/\partial\theta)$$

Write $\psi = \Theta\Phi$; then with $\Theta' = d\Theta/d\theta$ and $\Phi' = d\Phi/d\phi$, etc.

$$(1/\sin^2\theta)\Theta\Phi'' + (1/\sin\theta)\Phi(d/d\theta)\sin\theta\,\Theta' = -(2IE/\hbar^2)\Theta\Phi$$

$$\Phi''/\Phi + (1/\Theta)\sin\theta\,(d/d\theta)\sin\theta\,\Theta' = -(2IE/\hbar^2)\sin^2\theta$$

Write $\Phi''/\Phi = -m_l^2$, a constant; then

$$(1/\Theta)\sin\theta\,(d/d\theta)\sin\theta\,\Theta' = m_l^2 - (2IE/\hbar^2)\sin^2\theta$$

Because $(d/d\theta)\sin\theta\,\Theta' = \Theta'\cos\theta + \Theta''\sin\theta$, this rearranges into

$$\Theta''\sin^2\theta + \Theta'\sin\theta\cos\theta = \{m_l^2 - (2IE/\hbar^2)\sin^2\theta\}\Theta$$

Exercise: Identify this equation in M. Abramowitz and I.A. Stegun, *Handbook of mathematical functions*, and wite down its solutions.

3.8 The Schrödinger equation is

$$\Lambda^2\psi = -(2IE/\hbar)^2\psi \quad \text{[eqn 3.31]}$$

Write $\psi = \Theta(\theta)\Phi(\phi)$, $\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$ [eqn 3.29], and $2IE/\hbar^2 = \varepsilon^2$;

then

$$\frac{1}{\sin^2\theta}\Theta\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\Phi}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} = -\varepsilon^2\Phi\Theta$$

Divide through by $\Theta\Phi$ and multiply through by $\sin^2\theta$:

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} + \varepsilon^2\sin^2\theta = 0$$

Write $\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m_l^2$, so $\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m_l^2\Phi$ which implies that

$$\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} + \varepsilon^2\sin^2\theta = m_l^2$$

and hence that

$$\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} + \varepsilon^2\sin^2\theta\Theta - m_l^2\Theta = 0$$

and the equation is separable.

Exercise: Is the equation separable if $V(\theta, \phi) = af(\theta) + bg(\phi)$?

3.9 It is sufficient to show that the Y_{lm_l} satisfy $\Lambda^2 Y_{lm_l} = -l(l+1)Y_{lm_l}$ [eqn 3.33].

$Y_{11} = -\tfrac{1}{2}(3/2\pi)^{1/2}\sin\theta\,\mathrm{e}^{\mathrm{i}\phi}$

$$\Lambda^2 \sin\theta\, e^{i\phi} = (1/\sin^2\theta)(\partial^2/\partial\phi^2)\sin\theta\, e^{i\phi} + (1/\sin\theta)(\partial/\partial\theta)\sin\theta\,(\partial/\partial\theta)\sin\theta\, e^{i\phi}$$

$$= -(1/\sin\theta)e^{i\phi} + (1/\sin\theta)e^{i\phi}(d/d\theta)\sin\theta\cos\theta$$

$$= -(1/\sin\theta)e^{i\phi} + (1/\sin\theta)e^{i\phi}(\cos^2\theta - \sin^2\theta)$$

$$= -(1/\sin\theta)e^{i\phi} + (1/\sin\theta)e^{i\phi}(1 - 2\sin^2\theta) = -2\sin\theta\, e^{i\phi}$$

Hence, $\Lambda^2 Y_{11} = -2Y_{11}$, in accord with $l = 1$.

$Y_{20} = \frac{1}{4}(5/\pi)^{1/2}(3\cos^2\theta - 1)$

$$\Lambda^2(3\cos^2\theta - 1) = (1/\sin\theta)(d/d\theta)\sin\theta(d/d\theta)(3\cos^2\theta - 1)$$

$$= -6(1/\sin\theta)(d/d\theta)\sin^2\theta\cos\theta$$

$$= -6(1/\sin\theta)\{2\sin\theta\cos^2\theta - \sin^3\theta\}$$

$$= -6\{2\cos^2\theta - \sin^2\theta\} = -6(3\cos^2\theta - 1)$$

Hence, $\Lambda^2 Y_{20} = -6Y_{20}$, in accord with $l = 2$.

3.10

$$\int |Y_{11}|^2\, d\tau = \tfrac{1}{4}(3/2\pi)\int_0^{\pi}\sin^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi$$

$$= \tfrac{3}{4}\int_{-1}^{1}(1-x^2)dx\ [x = \cos\theta] = 1$$

$$\int |Y_{20}|^2\, d\tau = \tfrac{1}{16}(5/\pi)\int_0^{\pi}(3\cos^2\theta - 1)^2\sin\theta d\theta\int_0^{2\pi}d\phi$$

$$= \tfrac{5}{8}\int_{-1}^{1}(3x^2 - 1)^2 dx = 1$$

$$\int Y_{11}^{*} Y_{20} d\tau \propto \int_0^{2\pi} e^{-i\phi} d\phi = 0$$

Exercise: Repeat the calculation for Y_{21} and Y_{31}.

3.11 From eqn 3.44, $E = J(J+1)(\hbar^2/2I) = (1.30 \times 10^{-22}\ \text{J})J(J+1)$ [Exercise 3.1]. Draw up the following Table, using degeneracy $g_J = 2J + 1$:

J	$E/(10^{-22}\ \text{J})$	g_J
0	0	1
1	2.60	3
2	7.80	5

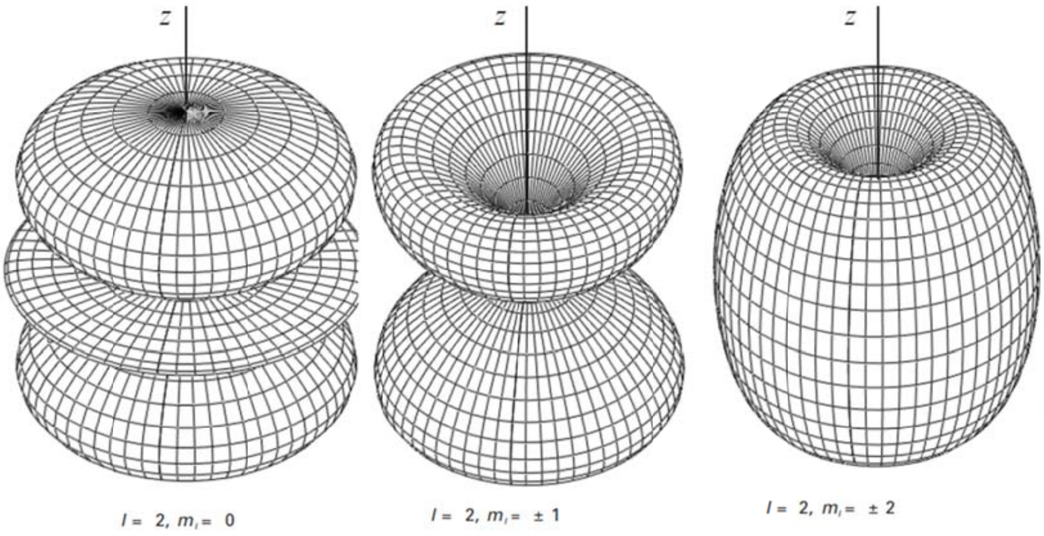
3.12 Using the energies in Exercise 3.11, we find

$$\Delta E(1-0) = 2.60 \times 10^{-22}\ \text{J}$$

$$\lambda(1-0) = hc/\Delta E(1-0) = 7.64 \times 10^{-4}\ \text{m} = \underline{0.764\ \text{mm}}\ (\underline{\text{far infrared}})$$

Exercise: Calculate the same quantities for the deuterated species.

3.13 See Fig. 3.2. From Problem 3.11, when $l = 3$ and $m_l = 0$, $\theta = 90°$, and the angular momentum vector lies in the equatorial plane; therefore $|Y|^2$ will have maxima on the z-axis, as seen in Fig. 3.2. We also see from Problem 3.11 that as $|m_l|$ increases, the deviation of θ from 90° increases; as the projection of the angular momentum vector on the z-axis increases, $|Y|^2$ becomes larger in the equatorial plane.



$l = 2,\ m_l = 0$ $\quad$ $l = 2,\ m_l = \pm 1$ $\quad$ $l = 2,\ m_l = \pm 2$

Figure 3.2: A representation of the wavefunctions and the location of the angular nodes for a particle on a sphere with $l = 2$.

Exercise: Draw the corresponding diagrams for $l = 4$.

3.14 Start with eqn 3.45

$$-\frac{\hbar^2}{2m}\nabla^2\psi = -\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2\right)\psi = E\psi$$

and use the form of the wavefunction in eqn 3.46:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

This yields (using eqn 3.33):

$$\begin{aligned}
-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}rRY + \frac{1}{r^2}\Lambda^2 RY\right) &= -\frac{\hbar^2}{2m}\left(\frac{Y}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}rR + \frac{R}{r^2}\Lambda^2 Y\right) \\
&= -\frac{\hbar^2}{2m}\left(\frac{Y}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}rR + \frac{-Rl(l+1)}{r^2}Y\right) \\
&= ERY
\end{aligned}$$

Dividing the last two lines above by Y and multiplying by $-\hbar^2/2m$ results in

$$\frac{1}{r}\frac{\mathrm{d}^2(rR)}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2}R = -\frac{2m}{\hbar^2}ER$$

which is eqn 3.47a. Writing $k^2 = 2mE/\hbar^2$ and $z = kr$ gives eqn 3.47b.

3.15 Use eqn 3.57 in the form (with $Z = 1$)

$$(1/r)(\mathrm{d}^2/\mathrm{d}r^2)rR + \{(\mu e^2/2\pi\varepsilon_0\hbar^2 r) - l(l+1)/r^2\}R = -(2\mu E/\hbar^2)R$$

with

$$E = -(\mu e^4/32\pi^2\varepsilon_0^2\hbar^2)(1/n^2) \quad \text{[eqn 3.66]}$$

(a) $R_{10}: n = 1, l = 0; E = -(\mu e^4/32\pi^2\varepsilon_0^2\hbar^2); l = 0$

$$(1/r)(\mathrm{d}^2/\mathrm{d}r^2)rR_{10} + (\mu e^2/2\pi\varepsilon_0\hbar^2)(1/r)R_{10} = -(2\mu E/\hbar^2)R_{10}$$

Then, because $R_{10} \propto \mathrm{e}^{-r/a}$,

$$(\mathrm{d}^2/\mathrm{d}r^2)rR_{10} = 2R'_{10} + rR''_{10} = -(2/a)R_{10} + (r/a^2)R_{10}$$

$$-(2/ar) + (1/a^2) + (\mu e^2/2\pi\varepsilon_0\hbar^2)(1/r) = -(2\mu E/\hbar^2)$$

But $2/a = \mu e^2/2\pi\varepsilon_0\hbar^2$; hence $1/a^2 = -2\mu E/\hbar^2$, so $E = -\hbar^2/2\mu a^2$, as required.

(b) $R_{20} \propto (2-\rho)\mathrm{e}^{-\rho/2} = (2 - r/a)\mathrm{e}^{-r/2a}$; $E_{2s} = -\frac{1}{4}(\hbar^2/2\mu a^2)$

$$(\mathrm{d}^2/\mathrm{d}r^2)rR_{20} = 2R'_{20} + rR''_{20} \propto \{-(4/a) + (5r/2a^2) - (r^2/4a^3)\}\mathrm{e}^{-r/2a}$$

$$-(4/ar) + (5/2a^2) - (r/4a^3) + \underbrace{(\mu e^2/2\pi\varepsilon_0\hbar^2)}_{2/a}(1/r)(2 - r/a)$$

$$= -(2\mu E/\hbar^2)(2 - r/a)$$

$$-(4/ar) + (5/2a^2) - (r/4a^3) + (4/ar) - (2/a^2) = (1/2a^2) - (r/4a^3)$$

$$= (1/4a^2)(2 - r/a)$$

Hence, $-2\mu E/\hbar^2 = 1/4a^2$, as required.

(c) $R_{31} \propto (4 - \rho)\rho e^{-\rho/2}$, $\rho = 2r/3a$, $l(l + 1) = 2$; then proceed as above, obtaining

$-2\mu E/\hbar^2 = 1/9a^2$.

Exercise: Confirm that R_{11} and R_{30} satisfy the wave equation.

3.16 The radial nodes are at the zeros of R_{nl}; denote them r_0.

(a) ψ_{2s} : $R_{2s} = 0$ when $2 - \rho = 0$; $\rho = r/a$.

Hence, $r_0/a = 2$ or $\underline{r_0 = 2a = 105.8\ \text{pm}}$

(b) ψ_{3s} : $R_{3s} = 0$ when $6 - 6\rho + \rho^2 = 0$, $\rho = 2r/3a$. The solutions are

$\rho_0 = 3 \pm \sqrt{3}$, or $r_0 = (3 \pm \sqrt{3})(3a/2) = \underline{1.90a,\ 7.10a \text{ or } 101\ \text{pm},\ 376\ \text{pm}}$

Exercise: Find **(a)** the Z-dependence of these node locations, **(b)** the location of the radial nodes of (i) 2p-orbitals, (ii) 4s-orbitals. [A general point in this connection is that A & S lists the locations of zeros of many functions.]

3.17

$$\int \psi_{2s}^{*}\psi_{1s}\,d\tau \propto \int_0^{\infty} R_{20}R_{10}r^2 dr \propto \int_0^{\infty} (2 - Zr/a)e^{-Zr/2a}e^{-Zr/a}r^2 dr$$

$$\propto \int_0^{\infty} (2r^2 - Zr^3/a)e^{-3Zr/2a} dr = (2^5a^3/3^3Z^3) - (2^5a^3/3^3Z^3) = 0$$

Exercise: Confirm that ψ_{2s} and ψ_{3s} are orthogonal.

3.18 Evaluate $|\psi_{ns}|^2 = |Y_{00}|^2 R_{n0}^2 = R_{n0}^2/4\pi$.

$$\psi_{1s}^2(0) = 4(Z/a)^3/4\pi = \underline{(1/\pi)(Z/a)^3} = 2.15 \times 10^{-6}\ \text{pm}^{-3} \text{ for hydrogen}$$

$$\psi_{2s}^2(0) = \tfrac{1}{2}(Z/a)^3/4\pi = \underline{(1/8\pi)(Z/a)^3} = 2.69 \times 10^{-7}\ \text{pm}^{-3}$$

$$\psi_{3s}^2(0) = (6/9\sqrt{3})^2(Z/a)^3/4\pi = \underline{(1/27\pi)(Z/a)^3} = 7.96 \times 10^{-8}\ \text{pm}^{-3}$$

Exercise: Evalute the probability density for a 4s-orbital.

3.19

$$\langle 1/r^3\rangle = \int_0^\infty (1/r^3)R_{21}^2 r^2\mathrm{d}r = \int_0^\infty (1/r)R_{21}^2\mathrm{d}r$$

$$= (Z/a)^3(1/2\sqrt{6})^2(Z/a)^2\int_0^\infty (1/r)r^2\mathrm{e}^{-Zr/a}\mathrm{d}r = \underline{(1/24)(Z/a)^3}$$

For a hydrogen atom, this is 2.82 × 10^{-7} pm^{-3}.

The *general expression* is

$$\langle 1/r^3\rangle_{nlm_l} = \frac{(Z/a)^3}{n^3 l(l+\frac{1}{2})(1+1)}$$

Exercise: Evaluate **(a)** $\langle 1/r^2\rangle$ for a $2p_z$-orbital, **and (b)** $\langle(1 - 3\cos^2\theta)/r^3\rangle$ for (i) a 2s-orbital, (ii) a $2p_z$-orbital.

3.20 $I = hc\mathcal{R}$ (i.e. $I = -E_{1s}$)

$$I(\text{H}) - I(\text{D}) = hc(\mathcal{R}_\text{H} - \mathcal{R}_\text{D}) = hc(\mu_\text{H} - \mu_\text{D})e^4/8h^3\varepsilon_0^2 c$$

$$= (\mu_\text{H} - \mu_\text{D})hc\mathcal{R}_\infty/m_\text{e}$$

$$\mu_\text{H} = m_\text{e}m_\text{p}/(m_\text{e} + m_\text{p}),\ \mu_\text{D} = m_\text{e}m_\text{d}/(m_\text{e} + m_\text{d})$$

$$(\mu_H - \mu_D)/m_e = \frac{m_p}{m_e + m_p} - \frac{m_d}{m_e + m_d}$$

$$= \frac{m_e(m_p - m_d)}{(m_e + m_p)(m_e + m_d)} = \frac{m_e(m_H - m_D)}{m_H m_D}$$

$m_e = 9.109\,38 \times 10^{-31}$ kg, $m_H = 1.6735 \times 10^{-27}$ kg, $m_D = 3.3443 \times 10^{-27}$ kg;

$(\mu_H - \mu_D)/m_e = -2.7195 \times 10^{-4}$

Consequently,

$$I(\text{H}) - I(\text{D}) = -(2.7195 \times 10^{-4}) \times (2.1799 \times 10^{-18}\ \text{J})$$

$$= -5.9282 \times 10^{-22}\ \text{J} = \underline{-0.357\ \text{kJ mol}^{-1}}(-3.70\ \text{meV})$$

The experimental values are 109 678.758 cm^{-1} and 109 708.596 cm^{-1}, so

$$\{I(\text{H}) - I(\text{D})\}/\text{cm}^{-1} = -29.838\ \text{cm}^{-1}(-0.357\ \text{kJ mol}^{-1})$$

Exercise: Evaluate the ionization energy of positronium on the basis of the ionization energy of ^{1}H.

3.21 For a given value of l there are $2l + 1$ values of m_l. For a given n there are n values of l. Hence, the degeneracy g is

$$g = \sum_{l=0}^{n-1}(2l+1) = n(n-1) + n = \underline{n^2}$$

Exercise: Calculate the average value of m_l^2 for an atom in a state with principal quantum number equal to n but with l, m_l unspecified.

Problems

3.1 Write $x = r\cos\phi$, $y = r\sin\phi$, $r = (x^2 + y^2)^{1/2}$, $\phi = \arctan(y/x)$. Then

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial f}{\partial \phi}\frac{\partial \phi}{\partial x} = \left(\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\right)f$$

or

$$\frac{\partial}{\partial x} = \cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}$$

Similarly,

$$\frac{\partial}{\partial y} = \sin\phi\frac{\partial}{\partial r} + \frac{\cos\phi}{r}\frac{\partial}{\partial\phi}$$

Therefore,

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) = \left(\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\right)\left(\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\right)f$$

$$= \left\{\cos^2\phi\frac{\partial^2}{\partial r^2} - \sin\phi\cos\phi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\phi}\right)\right.$$

$$\left. - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}\left(\cos\phi\frac{\partial}{\partial r}\right) + \frac{\sin\phi}{r^2}\frac{\partial}{\partial\phi}\left(\sin\phi\frac{\partial}{\partial\phi}\right)\right\}f$$

That is,

$$\frac{\partial^2}{\partial x^2} = \cos^2\phi\frac{\partial^2}{\partial r^2} - \frac{2\sin\phi\cos\phi}{r}\frac{\partial^2}{\partial r\partial\phi} + \frac{\sin^2\phi}{r^2}\frac{\partial^2}{\partial\phi^2}$$

$$+ \frac{\sin^2\phi}{r}\frac{\partial}{\partial r} + \frac{2\sin\phi\cos\phi}{r^2}\frac{\partial}{\partial\phi}$$

Similarly,

$$\frac{\partial^2}{\partial y^2} = \sin^2\phi\frac{\partial^2}{\partial r^2} + \frac{2\sin\phi\cos\phi}{r}\frac{\partial^2}{\partial r\partial\phi} + \frac{\cos^2\phi}{r^2}\frac{\partial^2}{\partial\phi^2}$$

$$+\frac{\cos^2\phi}{r}\frac{\partial}{\partial r} - \frac{2\sin\phi\cos\phi}{r^2}\frac{\partial}{\partial\phi}$$

It then follows that

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}$$

as in eqn 3.2.

Exercise: Derive an expression for ∇^2 in cylindrical polar coordinates, $x = r\cos\phi$, $y = r\sin\phi$, z.

3.4

$$\langle r\rangle = \int_0^\infty rP(r)\mathrm{d}r = \int_0^\infty R^2r^3\mathrm{d}r \qquad \text{[eqn 3.69]}$$

$$\langle 1/r\rangle = \int_0^\infty r^{-1}P(r)\mathrm{d}r = \int_0^\infty R^2r\mathrm{d}r \qquad \text{[eqn 3.69]}$$

As in Problem 3.3,

(a)

$$\langle r\rangle = \left(\frac{Z^3}{243a_0^3}\right)\left(\frac{3a_0}{2Z}\right)^4\int_0^\infty(6-6\rho+\rho)^2\rho^3\mathrm{e}^{-\rho}\mathrm{d}\rho = \underline{\frac{27a_0}{2Z}}$$

$$\langle 1/r\rangle = \left(\frac{Z^3}{243a_0^3}\right)\left(\frac{3a_0}{2Z}\right)^2\int_0^\infty(6-6\rho+\rho^2)^2\rho\mathrm{e}^{-\rho}\mathrm{d}\rho = \underline{\frac{Z}{9a_0}}$$

(b)

$$\langle r\rangle = \left(\frac{Z^3}{81\times 6a_0^3}\right)\left(\frac{3a_0}{2Z}\right)^4 \int_0^\infty (4-\rho)^2\rho^5 \mathrm{e}^{-\rho}\mathrm{d}\rho = \underline{\frac{25a_0}{2Z}}$$

$$\langle 1/r\rangle = \left(\frac{Z^3}{81\times 6a_0^3}\right)\left(\frac{3a_0}{2Z}\right)^2 \int_0^\infty (4-\rho)^2\rho^3 \mathrm{e}^{-\rho}\mathrm{d}\rho = \underline{\frac{Z}{9a_0}}$$

We have used the integrals

$$\int_0^\infty (6-6x+x^2)^2 x^3\mathrm{e}^{-x}\mathrm{d}x = 648$$

$$\int_0^\infty (6-6x+x^2)^2 x\mathrm{e}^{-x}\mathrm{d}x = 12$$

$$\int_0^\infty (4-x)^2 x^5\mathrm{e}^{-x}\mathrm{d}x = 1200$$

$$\int_0^\infty (4-x)^2 x^3\mathrm{e}^{-x}\mathrm{d}x = 24$$

as obtained by using the symbolic integration procedure in mathematical software.

Exercise: Evaluate $\langle 1/r^3\rangle$ for each orbital.

3.7 Use available mathematical software to find zeroes of the Bessel functions; in particular find values of z such that $J(z) = 0$. With z identified as ka (see eqn 3.25), the energies can be expressed in terms of z as

$$E = \frac{k^2\hbar^2}{2m} = \frac{z^2\hbar^2}{2ma^2}$$

3.10 **(a)** The moment of inertia of a sphere is $I = \frac{2}{5}MR^2$ [Problem 10.1]; therefore, on writing this value as Mr^2, we see that $r = (2/5)^{1/2}R$.

(b) Consider rotation perpendicular to the axis. The mass of a disc of thickness dx, radius R is $\pi\rho R^2\mathrm{d}x$ where ρ is the mass density of the disc. Therefore,

$$I = \int_{-l/2}^{l/2} \pi\rho R^2 x^2 \mathrm{d}x = \tfrac{1}{12}\pi\rho R^2 l^3$$

The mass of the cylinder is $M = \pi\rho R^2 l$; therefore $I = \tfrac{1}{12}Ml^2$.

Setting this value equal to $M r^2$ gives $\underline{r = l/(12)^{1/2}}$

3.13 The wavefunction for a particle in a spherical cavity is given by

$$\psi = Nj(r)Y(\theta,\phi)$$

The ground-state wavefunction is therefore given by $Nj_0Y_{0,0}$. (i) Proceeding as in Problem 3.8, (ii) using eqn 3.48 for j_0 with $k = \pi/a$ (Table 3.3) and (iii) recognizing that the volume element contains a factor of $r^2\mathrm{d}r$, we write the probability for finding the particle within a sphere of radius $a/2$ as:

$$P = \frac{\int_0^{a/2} \frac{\sin^2 kr}{(kr)^2} r^2 \mathrm{d}r}{\int_0^{a} \frac{\sin^2 kr}{(kr)^2} r^2 \mathrm{d}r} = \frac{\int_0^{a/2} \sin^2 kr \,\mathrm{d}r}{\int_0^{a} \sin^2 kr \,\mathrm{d}r} = \frac{\int_0^{a/2} \sin^2 (\frac{\pi r}{a}) \,\mathrm{d}r}{\int_0^{a} \sin^2 (\frac{\pi r}{a}) \,\mathrm{d}r}$$

Using mathematical software or standard integration tables yields $\underline{P = ½}$.

3.16 Refer to Fig. 3.5. The rotation (a)→(b) corresponds to 3p becoming 3d, the rotation (b)→(c) corresponds to 3d becoming 3s.

Exercise: Identify the patterning of the ball that would account for the degeneracy of two-dimensional f-orbitals.

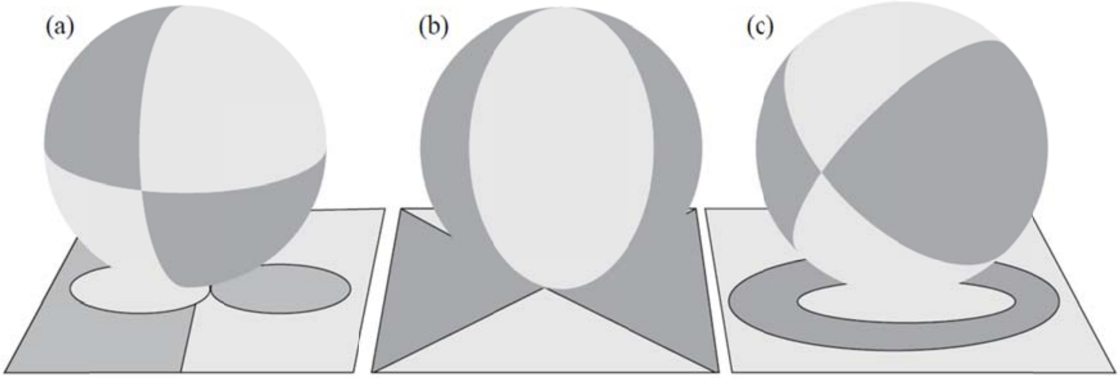


Figure 3.5: The projections of a patterned sphere on a plane (the projection stems from the North Pole).

Chapter 4

Angular momentum

Exercises

4.1 Since $l_y = zp_x - xp_z$ and $l_z = xp_y - yp_x$, one commutator is $[l_y, l_z] = [zp_x - xp_z, xp_y - yp_x]$.

Since in any representation, the operators x, y, z all commute and similarly the operators p_x, p_y, p_z all commute, this commutator is

$$[l_y, l_z] = (zp_xxp_y - xp_yzp_x) - (xxp_zp_y - p_zp_yxx) - (zyp_xp_x - p_xp_xzy) + (xyp_zp_x - p_zp_xxy)$$

Since, again in any representation, y commutes with p_x and p_z, x commutes with p_y and p_z, and z commutes with p_x and p_y, the above expression simplifies to

$$[l_y, l_z] = -zp_y[x,p_x] - 0 - 0 + yp_z[x,p_x]$$

In both the (a) position representation and (b) the momentum representation, $[x,p_x] = \mathrm{i}\hbar$ so

$$[l_y, l_z] = \mathrm{i}\hbar(-zp_y + yp_z) = \underline{\mathrm{i}\hbar l_x}$$

Similarly,

$$[l_z, l_x] = [xp_y - yp_x, yp_z - zp_y]$$

$$= (xp_yyp_z - yp_zxp_y) - (yyp_xp_z - p_xp_zyy) - (xzp_yp_y - p_yp_yxz) + (yzp_xp_y - p_xp_yyz)$$

$$= -xp_z[y,p_y] - 0 - 0 + zp_x[y,p_y]$$

$$= \mathrm{i}\hbar(-xp_z + zp_x) = \underline{\mathrm{i}\hbar l_y}$$

4.2

$$[l_z, l_-] = [l_z, l_x - \mathrm{i}l_y] = [l_z, l_x] - \mathrm{i}[l_z, l_y] = \mathrm{i}\hbar l_y - \mathrm{i}(-\mathrm{i}\hbar l_x) = \hbar(\mathrm{i}l_y - l_x) = -\hbar l_-$$

$$[l_+, l_-] = [l_x + \mathrm{i}l_y, l_x - \mathrm{i}l_y] = [l_x, l_x] - \mathrm{i}[l_x, l_y] + \mathrm{i}[l_y, l_x] - [l_y, l_y]$$

$$= -\mathrm{i}(\mathrm{i}\hbar l_z) + \mathrm{i}(-\mathrm{i}\hbar l_z) = 2\hbar l_z$$

4.3 Using eqns 4.23 and 4.29:

(a)

$$l_+|3,3\rangle = (3 \times 4 - 3 \times 4)^{\frac{1}{2}}\hbar|3,4\rangle = 0$$

$$l_-|3,3\rangle = (3 \times 4 - 3 \times 2)^{\frac{1}{2}}\hbar|3,2\rangle = \sqrt{6}\ \hbar|3,2\rangle$$

(b)

$$l_+|3,-3\rangle = (3 \times 4 - -3 \times -2)^{\frac{1}{2}}\hbar|3,-2\rangle = \sqrt{6}\hbar|3,-2\rangle$$

$$l_-|3,-3\rangle = (3 \times 4 - -3 \times -4)^{\frac{1}{2}}\hbar|3,-4\rangle = 0$$

4.4 Using eqns 4.20 and 4.21:

(a)

$$j^2|3,2\rangle = (3 \times 4)\hbar^2|3,2\rangle = 12\hbar^2|3,2\rangle$$

$$j_z|3,2\rangle = 2\hbar|3,2\rangle$$

(b)

$$j^2|1,-1\rangle = (1 \times 2)\hbar^2|1,-1\rangle = 2\hbar^2|1,-1\rangle$$

$$j_z|1,-1\rangle = -\hbar|1,-1\rangle$$

4.5 **(a)** For $l = 4$, permitted values of m_l are 0, ±1, ±2, ±3, ±4.

(b) For $l = 5/2$, permitted values of m_l are ±1/2, ±3/2, ±5/2.

4.6 Two operators A and B are each other's Hermitian conjugate if

$$\langle a|A|b\rangle = \langle b|B|a\rangle^*$$

To confirm that s_+ and s_- are each other's Hermitian conjugate, we note the following (using eqn 4.34 and the orthonormality of the states α and β):

$$\langle\alpha|s_+|\alpha\rangle = \langle\beta|s_+|\alpha\rangle = \langle\beta|s_+|\beta\rangle = \langle\alpha|s_-|\alpha\rangle = \langle\beta|s_-|\beta\rangle = \langle\alpha|s_-|\beta\rangle = 0$$

The only non-zero matrix elements are

$$\langle\alpha|s_+|\beta\rangle = \hbar$$

$$\langle\beta|s_-|\alpha\rangle = \hbar$$

Therefore, since $\hbar$ is real,

$$\langle\alpha|s_+|\beta\rangle = \langle\beta|s_-|\alpha\rangle^*$$

and s_+ and s_- are each other's Hermitian conjugate.

4.7 **(a)** The matrix element is

$$\langle 1{,}0|j_z|1{,}0\rangle = 0 \times \hbar\langle 1{,}0|1{,}0\rangle = 0$$

(b) The matrix element is

$$\langle 1{,}1|j_+|1{,}0\rangle = \langle 1{,}1\left|\sqrt{1\times 2 - 0\times 1}\hbar\right|1{,}1\rangle = \sqrt{2}\hbar$$

4.8 An electron has a spin angular momentum quantum number $s = ½$ and a quantum number for the z-component of $m_s = +1/2$ (α state) or $m_s = -1/2$ (β state). In general, the magnitude of the angular momentum is given by $\{s(s+1)\}^{1/2}\hbar$ and the z-component is $m_s\hbar$. Therefore, for both **(a)** the α state and **(b)** the β state, the magnitude of the spin angular momentum is

$$\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar = \frac{\sqrt{3}}{2}\hbar = 9.133\times 10^{-35}\,\mathrm{Js}$$

and for the z-component: **(a)** $\hbar/2 = 5.273 \times 10^{-35}$ Js, **(b)** $-\hbar/2 = -5.273 \times 10^{-35}$ Js.

4.9 The three components of ***j*** are $j_x = j_{1x} + j_{2x};\ j_y = j_{1y} + j_{2y};\ j_z = j_{1z} + j_{2z}$. We have shown in eqn 4.38 one of the commutation relations of eqn 4.7, namely $[j_x, j_y] = i\hbar j_z$. The other two commutation relations are confirmed as follows:

$$\begin{aligned}[j_y, j_z] &= [j_{1y} + j_{2y}, j_{1z} + j_{2z}] = [j_{1y}, j_{1z}] + [j_{1y}, j_{2z}] + [j_{2y}, j_{1z}] + [j_{2y}, j_{2z}] \\ &= i\hbar j_{1x} + 0 + 0 + i\hbar j_{2x} = i\hbar j_z\end{aligned}$$

$$[j_z, j_x] = [j_{1z} + j_{2z}, j_{1x} + j_{2x}] = [j_{1z}, j_{1x}] + [j_{1z}, j_{2x}] + [j_{2z}, j_{1x}] + [j_{2z}, j_{2x}]$$
$$= i\hbar j_{1y} + 0 + 0 + i\hbar j_{2y} = i\hbar j_y$$

4.10 A system with two sources of angular momentum, $j_1 = 1$ and $j_2 = 3/2$ can give rise to total angular momenta, using eqn 4.42, j = 5/2, 3/2, 1/2. States can be specified as either

$$|j_1 m_{j1}; j_2 m_{j2}\rangle \text{ or } |j_1 j_2; j m_j\rangle$$

$|j_1 m_{j1}; j_2 m_{j2}>$ states are |1,1; 3/2,3/2>, |1,0; 3/2,3/2>, |1,−1; 3/2,3/2>,

|1,1; 3/2,1/2>, |1,0; 3/2,1/2>, |1,−1; 3/2,1/2>,

|1,1; 3/2,−1/2>, |1,0; 3/2,−1/2>, |1,−1; 3/2,−1/2>,

|1,1; 3/2,−3/2>, |1,0; 3/2,−3/2>, |1,−1; 3/2,−3/2>

$|j_1 j_2; j m_j>$ states are |1, 3/2; 5/2, 5/2>, |1, 3/2; 5/2, 3/2>, |1, 3/2; 5/2, 1/2>,

|1, 3/2; 5/2, −1/2>, |1, 3/2; 5/2, −3/2>, |1, 3/2; 5/2, −5/2>,

|1, 3/2; 3/2, 3/2>, |1, 3/2; 3/2, 1/2>, |1, 3/2; 3/2, −1/2>,

|1, 3/2; 3/2, −3/2>, |1, 3/2; 1/2, 1/2>, |1, 3/2; 1/2, −1/2>

4.11 For a p-electron, l =1 and s = 1/2. We can construct the state $|j, m_j>$ from the uncoupled states $|l,m_l;s,m_s>$ using the vector coupling coefficients of *Resource section* 2:

$$|1/2, 1/2> = (2/3)^{1/2}|1,1;1/2,-1/2> - (1/3)^{1/2}|1,0;1/2,+1/2>$$

4.12 Couple the three spin angular momenta s_1 = ½, s_2 = ½, s_3 = ½. Coupling of s_1 and s_2 yields angular momenta of 1 and 0. Now couple each of these values with s_3. Permitted values from coupling s_3 and 1 are 3/2 and 1/2. Permitted values from coupling s_3 and 0 are 1/2. So the net result is 3/2, 1/2 (twice).

Problems

4.1 **(a)**

$$[l_x, l_y] = (\hbar/\mathrm{i})^2[y(\partial/\partial z) - z(\partial/\partial y), z(\partial/\partial x) - x(\partial/\partial z)] \quad \text{[eqn 4.5]}$$

$$= (\hbar/\mathrm{i})^2\{[y(\partial/\partial z), z(\partial/\partial x)] + [z(\partial/\partial y), x(\partial/\partial z)]\}$$

$$= (\hbar/\mathrm{i})^2\{y[(\partial/\partial z), z](\partial/\partial x) + x[z, (\partial/\partial z)](\partial/\partial y)\}$$

$$[(\partial/\partial z), z] = (\partial/\partial z)z - z(\partial/\partial z) = 1 + z(\partial/\partial z) - z(\partial/\partial z) = 1$$

Therefore,

$$[l_x, l_y] = (\hbar/\mathrm{i})^2\{y(\partial/\partial x) - x(\partial/\partial y)\} = -(\hbar/\mathrm{i})l_z \quad \text{[eqn 4.6]}$$

$$= \underline{\mathrm{i}\hbar l_z}$$

(b)

$$[l_x, l_y] = [yp_z - zp_y, zp_x - xp_z]$$

$$= y[p_z, z]p_x + p_y[z, p_z]x$$

$$= y\left[p_z, -\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial p_z}\right]p_x + p_y\left[-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial p_z}, p_z\right]x$$

$$= \left(-\frac{\hbar}{\mathrm{i}}\right)\left\{y\left[p_z, \frac{\partial}{\partial p_z}\right]p_x - p_y\left[p_z, \frac{\partial}{\partial p_z}\right]x\right\}$$

$$\left[p_z, \frac{\partial}{\partial p_z}\right] = p_z\frac{\partial}{\partial p_z} - \frac{\partial}{\partial p_z}p_z$$

$$= p_z\frac{\partial}{\partial p_z} - 1 - p_z\frac{\partial}{\partial p_z}$$

$$= -1$$

Therefore,

$$[l_x, l_y] = \left(-\frac{\hbar}{\mathrm{i}}\right)\{-yp_x + p_y x\}$$

$$= \left(-\frac{\hbar}{\mathrm{i}}\right) l_z = \mathrm{i}\hbar l_z$$

Exercise: Evaluate $[l_y, l_x]$ in the position representation.

4.4

$$\boldsymbol{l} \times \boldsymbol{l} = \begin{bmatrix} \hat{\boldsymbol{i}} & \hat{\boldsymbol{j}} & \hat{\boldsymbol{k}} \\ l_x & l_y & l_z \\ l_x & l_y & l_z \end{bmatrix}$$

$$= \hat{\boldsymbol{i}}\ (l_y l_z - l_z l_y) - \hat{\boldsymbol{j}}\ (l_x l_z - l_z l_x) + \hat{\boldsymbol{k}}\ (l_x l_y - l_y l_x)$$

$$\mathrm{i}\hbar \boldsymbol{l} = \hat{\boldsymbol{i}}\ (\mathrm{i}\hbar l_x) + \hat{\boldsymbol{j}}\ (\mathrm{i}\hbar l_y) + \hat{\boldsymbol{k}}\ (\mathrm{i}\hbar l_z)$$

Hence, equating both sides term by term reproduces the commutation rules, eqn 4.7.

Exercise: Show that if $\boldsymbol{l}_1 \times \boldsymbol{l}_1 = \mathrm{i}\hbar \boldsymbol{l}_1$ and $\boldsymbol{l}_2 \times \boldsymbol{l}_2 = \mathrm{i}\hbar \boldsymbol{l}_2$, then $\boldsymbol{l} \times \boldsymbol{l} = \mathrm{i}\hbar \boldsymbol{l}$, where $\boldsymbol{l} = \boldsymbol{l}_1 + \boldsymbol{l}_2$, but only if $[l_{1q}, l_{2q'}] = 0$ for all q, q'.

4.7 (a)

$$[s_x, s_y] = \left(\frac{1}{2}\hbar\right)^2 [\sigma_x, \sigma_y]$$

$$= \left(\frac{1}{2}\hbar\right)^2 \left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} - \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\}$$

$$= \left(\frac{1}{2}\hbar\right)^2 \left\{ \begin{pmatrix} \mathrm{i} & 0 \\ 0 & -\mathrm{i} \end{pmatrix} - \begin{pmatrix} -\mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix} \right\} = \frac{1}{2}\mathrm{i}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \underline{\mathrm{i}\hbar s_z}$$

(b)

$$s^2 = s_x^2 + s_y^2 + s_z^2 = \left(\frac{1}{2}\hbar\right)^2 \left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}^2 + \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}^2 + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}^2 \right\}$$

$$= \left(\frac{1}{2}\hbar\right)^2 \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right\} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The eigenvalues of s^2 are therefore $\frac{3}{4}\hbar^2$; hence, identifying these with $s(s + 1)\hbar^2$ identified $s = \frac{1}{2}$.

Exercise: Confirm that the following matrices constitute a representation of an angular momentum with $l = 1$.

$$l_x = (1/\sqrt{2}) \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix},\ l_y = (\mathrm{i}/\sqrt{2}) \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix},\ l_z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

4.10 Suppose $[l_x, l_y] = -\mathrm{i}\hbar l_z$, $l_\pm = l_x \pm \mathrm{i}l_y$; then

$$[l_+, l_z] = \hbar l_+,\ [l_-, l_z] = -\hbar l_-, \text{ and } [l^+, l^-] = -2\hbar l_z$$

Then, following the development that led to eqn 4.17,

$$l_z l_+ |l, m\rangle = \{l_+ l_z + [l_z, l_+]\}|l, m\rangle = \{l_+ l_z - \hbar l_+\}|l, m\rangle$$

$$= \{l_+ m\hbar - \hbar l_+\}|l, m\rangle = (m - 1)\hbar l_+ |l, m\rangle$$

Consequently, $l_+|l, m\rangle \propto |l, m - 1\rangle$ and $l_-|l, m\rangle \propto |l, m + 1\rangle$; therefore l_+ is a *lowering* operator and l_- is a *raising* operator.

Exercise: Find a matrix representation of these l_x and l_y 'angular momenta' corresponding to $L = 1$ (draw on the matrices in the *Exercise* to Problem 4.7).

4.13 In each case $l = 1$ and $\mathrm{p}_x = (\mathrm{p}_- - p_+)/\sqrt{2}$, $\mathrm{p}_y = (\mathrm{p}_- + \mathrm{p}_+)(\mathrm{i}/\sqrt{2})$. Then $\mathrm{p}_+ \rightarrow |1, 1\rangle$, $\mathrm{p}_- \rightarrow |1, -1\rangle$ and $\mathrm{p}_z \rightarrow |1, 0\rangle$ in the notation $|l, m_l\rangle$. The l label will be omitted henceforth.

(a)

$$\langle p_x|l_z|p_y\rangle = (i/2)\{\langle -1| - \langle 1|\}l_z\{| - 1\rangle + |1\rangle\}$$

$$= (i/2)\{\langle -1|l_z| - 1\rangle - \langle 1|l_z|1\rangle\} = (i/2)\{-\hbar - \hbar\}$$

$$= \underline{-i\hbar}$$

(b) $\langle p_x|l_+|p_y\rangle = (i/2)\{\langle -1| - \langle 1|\}l_+\{| - 1\rangle + |1\rangle\} = 0$

(c)

$$\langle p_z|l_y|p_x\rangle = (1/2i)(1/\sqrt{2})\langle 0|(l_+ - l_-)\{| - 1\rangle - |1\rangle\}$$

$$= (1/2i\sqrt{2})\{\langle 0|l_+| - 1\rangle + \langle 0|l_-|1\rangle\}$$

$$= (1/2i\sqrt{2})\{\hbar\sqrt{2} + \hbar\sqrt{2}\} = \underline{-i\hbar}$$

(d)

$$\langle p_z|l_x|p_y\rangle = (1/2)(i/\sqrt{2})\langle 0|(l_+ + l_-)\{| - 1\rangle + |1\rangle\}$$

$$= (i/2\sqrt{2})\{\langle 0|l_+| - 1\rangle + |\langle 0|l_-|1\rangle\}$$

$$= (i/2\sqrt{2})\{\hbar\sqrt{2} + \hbar\sqrt{2}\} = \underline{i\hbar}$$

(e)

$$\langle p_z|l_x|p_x\rangle = (1/2)(1/\sqrt{2})\,\langle 0|(l_+ + l_-)\{| - 1\rangle - |1\rangle\}$$

$$= (1/2\sqrt{2})\{\langle 0|l_+| - 1\rangle - \langle 0|l_-|1\rangle\} = \underline{0}$$

Exercise: Evaluate $\langle p_y|l_-|p_z\rangle$, $\langle p_x|l_y|p_z\rangle$, $\langle p_x|l_+l_-|p_z\rangle$, and $\langle d_{xy}|l_x|d_{xz}\rangle$.

4.16

$$[l_x, l_y] = \hbar^2[\sin\phi(\partial/\partial\theta) + \cot\theta\cos\phi(\partial/\partial\phi), \cos\phi(\partial/\partial\theta) - \cot\theta\sin\phi\,(\partial/\partial\phi)]$$

$$= \hbar^2\{-[\sin\phi(\partial/\partial\theta), \cot\theta\sin\phi\,(\partial/\partial\phi)]$$

$$+ [\cot\theta\cos\phi(\partial/\partial\phi), \cos\phi(\partial/\partial\theta)] - [\cot\theta\cos\phi(\partial/\partial\phi), \cot\theta\sin\phi\,(\partial/\partial\phi)]$$

$$+ [\sin\phi(\partial/\partial\theta), \cos\phi\,(\partial/\partial\theta)]\}$$

$$[\sin\phi(\partial/\partial\theta), \cos\phi(\partial/\partial\theta)] = 0$$

$$[\sin\phi(\partial/\partial\theta), \cot\theta\sin\phi(\partial/\partial\phi)]$$

$$= \sin\phi(\partial/\partial\theta)\cot\theta\sin\phi(\partial/\partial\phi) - \cot\theta\sin\phi(\partial/\partial\phi)\sin\phi(\partial/\partial\theta)$$

$$= \sin^2\phi(\partial\cot\theta/\partial\theta)(\partial/\partial\phi) + \sin^2\phi\cot\theta(\partial^2/\partial\theta\partial\phi)$$

$$- \cot\theta\sin\phi(\partial\sin\phi/\partial\phi)(\partial/\partial\theta) - \cot\theta\sin^2\phi(\partial^2/\partial\theta\partial\phi)$$

$$= -\sin^2\phi\,\mathrm{cosec}^2\theta(\partial/\partial\phi) - \cot\theta\sin\phi\cos\phi(\partial/\partial\theta)$$

$$[\cot\theta\cos\phi(\partial/\partial\phi), \cos\phi(\partial/\partial\theta)]$$

$$= \cot\theta\cos\phi(\partial/\partial\phi)\cos\phi(\partial/\partial\theta) - \cos\phi(\partial/\partial\theta)\cot\theta\cos\phi(\partial/\partial\phi)$$

$$= \cot\theta\cos\phi(\partial\cos\phi/\partial\phi)(\partial/\partial\theta) + \cot\theta\cos^2\phi(\partial^2/\partial\phi\partial\theta)$$

$$- \cos^2\phi(\partial\cot\theta/\partial\theta)(\partial/\partial\phi) - \cos^2\phi\cot\theta(\partial^2/\partial\theta\partial\phi)$$

$$= -\cot\theta\cos\phi\sin\phi(\partial/\partial\theta) + \cos^2\phi\,\mathrm{cosec}^2\theta(\partial/\partial\phi)$$

$$[\cot\theta\cos\phi(\partial/\partial\phi), \cot\theta\sin\phi(\partial/\partial\phi)]$$

$$= \cot^2\theta[\cos\phi(\partial/\partial\phi), \sin\phi(\partial/\partial\phi)]$$

$$= \cot^2\theta\{\cos\phi(\partial/\partial\phi)\sin\phi(\partial/\partial\phi) - \sin\phi(\partial/\partial\phi)\cos\phi(\partial/\partial\phi)\}$$

$$= \cot^2\theta\{\cos^2\phi(\partial/\partial\phi) + \sin^2\phi(\partial/\partial\phi)\} = \cot^2\theta(\partial/\partial\phi)$$

$$[l_x, l_y] = \hbar^2\{\sin^2\phi\,\mathrm{cosec}^2\theta(\partial/\partial\phi) + \cot\theta\sin\phi\cos\phi(\partial/\partial\theta)$$

$$+ \cos^2\phi\,\mathrm{cosec}^2\theta(\partial/\partial\phi) - \cot\theta\cos\phi\sin\phi(\partial/\partial\theta) - \cot^2\theta(\partial/\partial\phi)\}$$

$$= \hbar^2\{(\sin^2\phi + \cos^2\phi)\mathrm{cosec}^2\theta(\partial/\partial\phi) - \cot^2\theta(\partial/\partial\phi)\}$$

$$= \hbar^2\{\mathrm{cosec}^2\theta(\partial/\partial\phi) - \cot^2\theta(\partial/\partial\phi)\} = \hbar^2(\partial/\partial\phi) = \underline{\mathrm{i}\hbar l_z}$$

as required.

$$[l_+, l_-] = \left[\hbar \mathrm{e}^{\mathrm{i}\phi}\left(\frac{\partial}{\partial\theta} + \mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\right), -\hbar \mathrm{e}^{-\mathrm{i}\phi}\left(\frac{\partial}{\partial\theta} - \mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\right)\right]$$

$$= -\hbar^2\left[\mathrm{e}^{\mathrm{i}\phi}\left(\frac{\partial}{\partial\theta} + \mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\right), \mathrm{e}^{-\mathrm{i}\phi}\left(\frac{\partial}{\partial\theta} - \mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\right)\right]$$

$$= -\hbar^2\left\{\left[\mathrm{e}^{\mathrm{i}\phi}\frac{\partial}{\partial\theta}, \mathrm{e}^{-\mathrm{i}\phi}\frac{\partial}{\partial\theta}\right] + \left[\mathrm{e}^{\mathrm{i}\phi}\mathrm{i}\cot\theta\frac{\partial}{\partial\phi}, \mathrm{e}^{-\mathrm{i}\phi}\frac{\partial}{\partial\theta}\right]\right.$$

$$\left. - \left[\mathrm{e}^{\mathrm{i}\phi}\frac{\partial}{\partial\theta}, \mathrm{e}^{-\mathrm{i}\phi}\mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\right] - \left[\mathrm{e}^{\mathrm{i}\phi}\mathrm{i}\cot\theta\frac{\partial}{\partial\phi}, \mathrm{e}^{-\mathrm{i}\phi}\mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\right]\right\}$$

$$= -\hbar^2\left\{\mathrm{i}\mathrm{e}^{\mathrm{i}\phi}\cot\theta\frac{\partial}{\partial\phi}e^{-\mathrm{i}\phi}\frac{\partial}{\partial\theta} - \mathrm{i}\mathrm{e}^{-\mathrm{i}\phi}\frac{\partial}{\partial\theta}e^{\mathrm{i}\phi}\cot\theta\frac{\partial}{\partial\phi}\right.$$

$$- \mathrm{i}\mathrm{e}^{\mathrm{i}\phi}\frac{\partial}{\partial\theta}\mathrm{e}^{-\mathrm{i}\phi}\cot\theta\frac{\partial}{\partial\phi} + \mathrm{i}\mathrm{e}^{-\mathrm{i}\phi}\cot\theta\frac{\partial}{\partial\phi}\mathrm{e}^{\mathrm{i}\phi}\frac{\partial}{\partial\theta}$$

$$\left. + \mathrm{e}^{\mathrm{i}\phi}\cot\theta\frac{\partial}{\partial\phi}\mathrm{e}^{-\mathrm{i}\phi}\cot\theta\frac{\partial}{\partial\phi} - \mathrm{e}^{-\mathrm{i}\phi}\cot\theta\frac{\partial}{\partial\phi}\mathrm{e}^{\mathrm{i}\phi}\cot\theta\frac{\partial}{\partial\phi}\right\}$$

$$= -\hbar^2\left\{\cot\theta\frac{\partial}{\partial\theta} + \mathrm{i}\,\mathrm{cosec}^2\theta\frac{\partial}{\partial\phi} + \mathrm{i}\,\mathrm{cosec}^2\theta\frac{\partial}{\partial\phi}\right.$$

$$\left. - \cot\theta\frac{\partial}{\partial\theta} - 2\mathrm{i}\cot^2\theta\frac{\partial}{\partial\phi}\right\}$$

$$= -2\mathrm{i}\hbar^2\{\mathrm{cosec}^2\theta - \cot^2\theta\}\frac{\partial}{\partial\phi}$$

$$= -2\mathrm{i}\hbar^2\frac{\partial}{\partial\phi}$$

$$= 2\hbar l_z$$

Exercise: Evaluate $[l_z, l_x]$ in this representation.

4.19

$$\boldsymbol{j}_1 \times \boldsymbol{j}_2 = \begin{bmatrix} \hat{\boldsymbol{i}} & \hat{\boldsymbol{j}} & \hat{\boldsymbol{k}} \\ j_{1x} & j_{1y} & j_{1z} \\ j_{2x} & j_{2y} & j_{2z} \end{bmatrix}$$

$$= \hat{\boldsymbol{i}}\ (j_{1y}j_{2z} - j_{1z}j_{2y}) - \hat{\boldsymbol{j}}\ (j_{1x}j_{2z} - j_{1z}j_{2x}) + \hat{\boldsymbol{k}}\ (j_{1x}j_{2y} - j_{1y}j_{2x})$$

$$= \hat{\boldsymbol{i}}\ (j_{2z}j_{1y} - j_{2y}j_{1z}) - \hat{\boldsymbol{j}}\ (j_{2z}j_{1x} - j_{2x}j_{1z}) + \hat{\boldsymbol{k}}\ (j_{2y}j_{1x} - j_{2x}j_{1y})$$

$$= \begin{vmatrix} \hat{\boldsymbol{i}} & \hat{\boldsymbol{j}} & \hat{\boldsymbol{k}} \\ -j_{2x} & -j_{2y} & -j_{2z} \\ j_{1x} & j_{1y} & j_{1z} \end{vmatrix} = -\boldsymbol{j}_2 \times \boldsymbol{j}_1$$

$$\boldsymbol{j} \times \boldsymbol{j} = (\boldsymbol{j}_1 + \boldsymbol{j}_2) \times (\boldsymbol{j}_1 + \boldsymbol{j}_2)$$

$$= \boldsymbol{j}_1 \times \boldsymbol{j}_1 + \boldsymbol{j}_2 \times \boldsymbol{j}_2 + \boldsymbol{j}_1 \times \boldsymbol{j}_2 + \boldsymbol{j}_2 \times \boldsymbol{j}_1 = \boldsymbol{j}_1 \times \boldsymbol{j}_1 + \boldsymbol{j}_2 \times \boldsymbol{j}_2$$

$$= \mathrm{i}\hbar\boldsymbol{j}_1 + \mathrm{i}\hbar\boldsymbol{j}_2 = \mathrm{i}\hbar\boldsymbol{j}$$

Exercise: Under what circumstances do $\boldsymbol{j}_1$ and $\boldsymbol{j}_2$ satisfy the vector relations set out in eqn 4.9?

4.22 $j_1 = 1, j_2 = \frac{1}{2}$ gives the states $j = \frac{3}{2}, \frac{1}{2}$. The state $|j, m_j\rangle = |\frac{3}{2}, +\frac{3}{2}\rangle$ is

$$|j_1, m_{j1}; j_2, m_{j2}\rangle = |1, +1;\ \tfrac{1}{2}, +\tfrac{1}{2}\rangle.$$

Generate $|\frac{3}{2}, +\frac{1}{2}\rangle$ using $j_-|\frac{3}{2}, \frac{3}{2}\rangle = \hbar\sqrt{3}\,|\frac{3}{2}, +\frac{1}{2}\rangle$ and

$$j_-|\tfrac{3}{2}, \tfrac{3}{2}\rangle = (j_{1-} + j_{2-})|1, +1; \tfrac{1}{2}, +\tfrac{1}{2}\rangle$$

$$= \hbar\sqrt{2}\,|1, 0; \tfrac{1}{2}, +\tfrac{1}{2}\rangle + \hbar\,|1, +1; \tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

Therefore,

$$|\tfrac{3}{2},+\tfrac{1}{2}\rangle = \sqrt{(2/3)}\,|1,0;\tfrac{1}{2},+\tfrac{1}{2}\rangle + \sqrt{(1/3)}\,|1,+1;\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

Next, generate $|\tfrac{3}{2},-\tfrac{1}{2}\rangle$ by using

$$j_-\,|\tfrac{3}{2},+\tfrac{1}{2}\rangle = 2\hbar\,|\tfrac{3}{2},-\tfrac{1}{2}\rangle$$

and

$$\begin{aligned} j_-\,|\tfrac{3}{2},+\tfrac{1}{2}\rangle &= (j_{1-}+j_{2-})\left\{\sqrt{(2/3)}\,|1,0;\tfrac{1}{2},+\tfrac{1}{2}\rangle + \sqrt{(1/3)}\,|1,+1;\tfrac{1}{2},-\tfrac{1}{2}\rangle\right\} \\ &= \sqrt{(2/3)}\sqrt{2}\hbar\,|1,-1;\tfrac{1}{2},+\tfrac{1}{2}\rangle + \sqrt{(2/3)}\hbar\,|1,0;\tfrac{1}{2},-\tfrac{1}{2}\rangle \\ &\quad +\sqrt{(1/3)}\sqrt{2}\hbar\,|1,0;\tfrac{1}{2},-\tfrac{1}{2}\rangle + 0 \\ &= (2/\sqrt{3})\hbar\,|1,-1;\tfrac{1}{2},+\tfrac{1}{2}\rangle + (2\sqrt{2}/\sqrt{3})\hbar\,|1,0;\tfrac{1}{2},-\tfrac{1}{2}\rangle \end{aligned}$$

Therefore,

$$|\tfrac{3}{2},-\tfrac{1}{2}\rangle = \sqrt{(1/3)}\,|1,-1;\tfrac{1}{2},+\tfrac{1}{2}\rangle + \sqrt{(2/3)}\,|1,0;\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

We could generate $|\tfrac{3}{2},-\tfrac{3}{2}\rangle$ using $j_-\,|\tfrac{3}{2},-\tfrac{1}{2}\rangle$ or, more simply, by noting that there is only one way to achieve this state since $m_j = m_{j_1} + m_{j_2}$. Therefore,

$$|\tfrac{3}{2},-\tfrac{3}{2}\rangle = |1,-1;\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

The state $|\tfrac{1}{2},+\tfrac{1}{2}\rangle$ is orthogonal to $|\tfrac{3}{2},+\tfrac{1}{2}\rangle$ so we require

$$\begin{aligned} \langle\tfrac{1}{2},+\tfrac{1}{2}\,|\,\tfrac{3}{2},+\tfrac{1}{2}\rangle &= \{a\langle 1,0;\tfrac{1}{2},+\tfrac{1}{2}\,| + b\langle 1,+1;\tfrac{1}{2},-\tfrac{1}{2}\,|\} \\ &\quad \times\left\{\sqrt{(2/3)}\,|1,0;\tfrac{1}{2},+\tfrac{1}{2}\rangle + \sqrt{(1/3)}\,|1,+1;\tfrac{1}{2},-\tfrac{1}{2}\rangle\right\} \\ &= \sqrt{(2/3)}a + \sqrt{(1/3)}b = 0 \end{aligned}$$

Therefore $a = -\sqrt{(1/3)}, b = \sqrt{(2/3)}$ and

$$|\tfrac{1}{2},+\tfrac{1}{2}\rangle = -\sqrt{(1/3)}\,|1,0;\tfrac{1}{2},+\tfrac{1}{2}\rangle + \sqrt{(2/3)}\,|1,+1;\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

The remaining $|\tfrac{1}{2},-\tfrac{1}{2}\rangle$ may be generated using $j_-\,|\tfrac{1}{2},+\tfrac{1}{2}\rangle$ and yields

$$|\tfrac{1}{2},-\tfrac{1}{2}\rangle = \sqrt{(1/3)}\,|1,0;\tfrac{1}{2},-\tfrac{1}{2}\rangle + -\sqrt{(2/3)}\,|1,-1;\tfrac{1}{2},+\tfrac{1}{2}\rangle$$

For the matrix elements, write

$$|\,j,m_j\rangle = \sum_{m_1m_2} c(j_1m_1j_2m_2\,|\,jm_j)\,|\,j_1m_1j_2m_2\rangle$$

Then

$$\langle j',m_j'\,|\,j_{1z}\,|\,j,m_j\rangle \;=\; \sum_{m_1m_2}\sum_{m_1'm_2'} c(j_1m_1'j_2m_2'\,|\,j'm_j')c(j_1m_1j_2m_2\,|\,jm_j)\langle j_1m_1'j_2m_2'\,|\,j_{1z}\,|\,j_1m_1j_2m_2\rangle$$

$$= \sum_{m_1m_2}\sum_{m_1'm_2'} c(j_1m_1'j_2m_2'\,|\,j'm_j')c(j_1m_1j_2m_2\,|\,jm_j)m_1\hbar$$

$$= \delta_{m_1m_1'}\delta_{m_2m_2'}\hbar\sum_{m_1m_2} c(j_1m_1j_2m_2\,|\,j'm_j')c(j_1m_1j_2m_2\,|\,jm_j)m_1$$

$$= \hbar\sum_{m_1m_2} c(j_1m_1j_2m_2\,|j'm_j)c(j_1m_1j_2m_2\,|\,jm_j)m_1$$

Individual numerical values may now be obtained by substituting the coefficients.

Exercise: Repeat the procedure for $j_1 = 2, j_2 = \tfrac{1}{2}$.

4.25 Refer to Fig. 4.3.

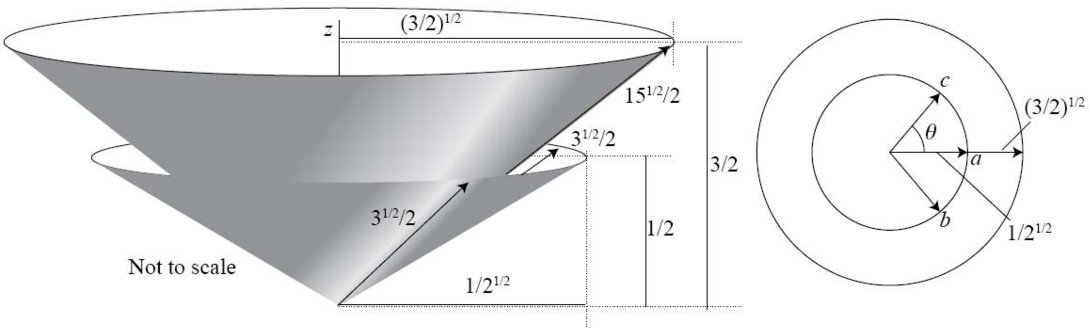


Figure 4.3: The construction used in Problem 4.25.

We shall interpret the question as requiring the angle between the spins projected onto the *xy*-plane. The projection of a spin-$\frac{1}{2}$ vector (of length $\frac{1}{2}\sqrt{3}$) onto the *xy*-plane, given its projection of $\frac{1}{2}$ onto the *z*-axis, is $(\frac{3}{4}-\frac{1}{4})^{1/2}=1/\sqrt{2}$. Similarly, the projection of a spin-$\frac{3}{2}$ vector (of length $\frac{1}{2}\sqrt{15}$), with $m_z=+\frac{3}{2}$, is $(\frac{15}{4}-\frac{9}{4})^{1/2}=\sqrt{\frac{3}{2}}$. Therefore, the projection of the resultant of *b* and *c* must account for $\sqrt{3/2}-\sqrt{1/2}$. Consequently,

$$2\times\frac{1}{\sqrt{2}}\cos\tfrac{1}{2}\theta=(3/2)^{1/2}-(1/2)^{1/2}$$

or

$$\cos\tfrac{1}{2}\theta=\frac{\sqrt{3}-1}{2},\ \theta=2\arccos\left(\frac{\sqrt{3}-1}{2}\right)$$

The angle between *b* and *c* is therefore 137.06°, and that between *a* and *c* (and *a* and *b*) is one-half this angle, or 68.529°.

For the second part, we shall calculate the actual inter-spin angle, θ, by noting that by symmetry the angles between a, b, and c are all the same. Hence

$$\begin{aligned}(\mathbf{s}_1+\mathbf{s}_2+\mathbf{s}_3)\cdot(\mathbf{s}_1+\mathbf{s}_2+\mathbf{s}_3) &= s_1^2+s_2^2+s_3^2+2\mathbf{s}_1\cdot\mathbf{s}_3+2\mathbf{s}_2\cdot\mathbf{s}_3+2\mathbf{s}_1\cdot\mathbf{s}_2\\ &= 3\times\tfrac{3}{4}+3\times\tfrac{3}{2}\cos\theta=\tfrac{9}{4}+\tfrac{9}{2}\cos\theta\\ &= S^2=\tfrac{15}{4}\end{aligned}$$

Therefore,

$$\tfrac{9}{2}\cos\theta=\tfrac{3}{2}, \text{so } \theta=\arccos(\tfrac{1}{3}),\ \text{ or } \underline{70.53°}$$

Exercise: Show, by the second method, that for n spins, the angle between vectors is 70.53° in the state with maximum S and M_s for all n.

4.28

$$\begin{aligned}&\langle j_1j_2;jm_j|j_1j_2;jm_j\rangle\\ &=\sum_{m'_{j1}}\sum_{m'_{j2}}\sum_{m_{j1}}\sum_{m_{j2}}C^*_{m'_{j1}m'_{j2}}C_{m_{j1}m_{j2}}\langle j_1m'_{j1}j_2m'_{j2}\mid j_1m_{j1}j_2m_{j2}\rangle\\ &=\sum_{m'_{j1}}\sum_{m'_{j2}}\sum_{m_{j1}}\sum_{m_{j2}}C^*_{m'_{j1}m'_{j2}}C_{m_{j1}m_{j2}}\delta_{m'_{j1}m_{j1}}\delta_{m'_{j2}m_{j2}}\\ &=\sum_{m_{j1}}\sum_{m_{j2}}C^*_{m_{j1}m_{j2}}C_{m_{j1}m_{j2}}=\sum_{m_{j1},m_{j2}}|C_{m_{j1}m_{j2}}|^2\end{aligned}$$

But $\langle j_1j_2;jm_j|j_1j_2;jm_j\rangle = 1$, which completes the proof.

Exercise: Find a general expression for $\langle j_1j_2;jm_j|j_{1z}|j_1j_2;jm_j\rangle$ and evaluate it for $\langle G, M_L|l_{1z}|G, M_L\rangle$; see Problem 4.27.

Chapter 5

Group theory

Exercises

5.1 **(a)** E, σ_h, $2C_3$, $2S_3$, $3C_2$, $3\sigma_v$;

(b) E, C_2, σ_v, σ'_v;

(c) E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$, i, $2S_3$, $2S_6$, $3C_2$, σ_h, $3\sigma_d$, $3\sigma_v$.

5.2 **(a)** E, $C_2(z)$, $C_2(y)$, $C_2(x)$, i, $\sigma(xy)$, $\sigma(xz)$, $\sigma(yz)$;

(b) E, C_2, i, σ_h;

(c) E, C_2, i, σ_h.

5.3 **(a)** D_{3h}, **(b)** C_{2v}, **(c)** D_{6h}.

5.4 **(a)** D_{2h}, **(b)** C_{2h}, **(c)** C_{2h}.

5.5 **(a)** H_2O: E, C_2, $2\sigma_v$; hence $\underline{C_{2v}}$.

(b) CO_2: E, C_∞, $C_2 \perp C_\infty$, σ_h; hence $\underline{D_{\infty h}}$

(c) C_2H_4: E, C_2, $2C_2' \perp C_2$, σ_h; hence $\underline{D_{2h}}$

(d) *cis*-ClHC=CHCl: E, C_2, $2\sigma_v$; hence $\underline{C_{2v}}$

5.6 **(a)** *trans*-ClHC=CHCl: E, C_2, σ_h; hence $\underline{C_{2h}}$

(b) Benzene: E, C_6, $6C_2'$, σ_h; hence $\underline{D_{6h}}$

(c) Naphthalene: E, C_2, $2C_2'$, σ_h; hence $\underline{D_{2h}}$

(d) CHClFBr: E; hence $\underline{C_1}$

(e) $B(OH)_3$: E, C_3, σ_h; hence $\underline{C_{3h}}$

Exercise: Classify chlorobenzene, anthracene, H_2O_2, S_8

5.7 **(a)** PF_5 (pentagonal pyramid), corannulene $C_{20}H_{10}$,

(b) all *cis*-$C_5H_5F_5$ (planar), **(c)** $Fe(C_5H_5)_2$ (staggered).

5.8 T_d: CH_4; O_h: SF_6; I: C_{60}.

5.9 **(a)** The group multiplication table for C_s is as follows:

First:	E	σ
Second:		
E	E	σ
σ	σ	E

(b) The group multiplication table for D_2 is as follows:

First:	E	$C_2(z)$	$C_2(y)$	$C_2(x)$
Second:				
E	E	$C_2(z)$	$C_2(y)$	$C_2(x)$
$C_2(z)$	$C_2(z)$	E	$C_2(x)$	$C_2(y)$
$C_2(y)$	$C_2(y)$	$C_2(x)$	E	$C_2(z)$
$C_2(x)$	$C_2(x)$	$C_2(y)$	$C_2(z)$	E

5.10 We need to confirm that $(RS)T = R(ST)$ for all elements R, S and T that appear in the group multiplication table for C_{2v} in Example 5.2.

$$(EC_2)\sigma_v = C_2\sigma_v = \sigma_v' = E(C_2\sigma_v)$$

$$(EC_2)\sigma_v' = C_2\sigma_v' = \sigma_v = E(C_2\sigma_v')$$

$$(E\sigma_v)C_2 = \sigma_v C_2 = \sigma_v' = E(\sigma_v C_2)$$

$$(E\sigma_v)\sigma_v' = \sigma_v\sigma_v' = C_2 = E(\sigma_v\sigma_v')$$

$$(E\sigma_V')C_2 = \sigma_V' C_2 = \sigma_V = E(\sigma_V' C_2)$$

$$(E\sigma_v')\sigma_v = \sigma_v'\sigma_v = C_2 = E(\sigma_v'\sigma_v)$$

$$(C_2\sigma_v)E = \sigma_v'E = \sigma_v' = C_2(\sigma_v E)$$

$$(C_2\sigma_v)\sigma_v' = \sigma_v'\sigma_v' = E = C_2(\sigma_v\sigma_v')$$

$$(C_2\sigma_v')E = \sigma_v E = \sigma_v = C_2(\sigma_v')E$$

$$(C_2\sigma_v')\sigma_v = \sigma_v\sigma_v = E = C_2(\sigma_v'\sigma_v)$$

$$(\sigma_v\sigma_v')E = C_2E = C_2 = \sigma_v(\sigma_v'E)$$

$$(\sigma_v\sigma_v')C_2 = C_2C_2 = E = \sigma_v(\sigma_v'C_2)$$

Since the elements commute in the group C_{2v}, if $(RS)T = R(ST)$, then $(SR)T = S(RT)$. For example:

$$(\sigma_v'\sigma_v)C_2 = (\sigma_v\sigma_v')C_2 = \sigma_v(\sigma_v'C_2) = \sigma_v(C_2\sigma_v') = (\sigma_v C_2)\sigma_v' = \sigma_v'(\sigma_v C_2)$$

Exercise: Confirm that the elements in the C_{3v} group multiplication table of Table 5.2 multiply associatively.

5.11 Write $\boldsymbol{f}$ = (H1s$_A$, H1s$_B$, O2s, O2p$_x$, O2p$_y$, O2p$_z$); then $E\boldsymbol{f} = \boldsymbol{f} = \boldsymbol{f}\mathbf{1}$; hence $\boldsymbol{D}(E) = \mathbf{1}$, the 6 × 6 unit matrix.

$$C_2\boldsymbol{f} = (\mathrm{H1s_B}, \mathrm{H1s_A}, \mathrm{O2s}, -\mathrm{O2p}_x, -\mathrm{O2p}_y, \mathrm{O2p}_z)$$

$$= \boldsymbol{f}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{f}\boldsymbol{D}(C_2)$$

$$\sigma_v\boldsymbol{f} = (\mathrm{H1s_B}, \mathrm{H1s_A}, \mathrm{O2s}, \mathrm{O2p}_x, -\mathrm{O2p}_y, \mathrm{O2p}_z)$$

$$= \boldsymbol{f}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{f}\boldsymbol{D}(\sigma_v)$$

$$\sigma_v'\boldsymbol{f} = (\mathrm{H1s_A}, \mathrm{H1s_B}, \mathrm{O2s}, -\mathrm{O2p}_x, \mathrm{O2p}_y, \mathrm{O2p}_z)$$

$$= \boldsymbol{f}\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{f}\boldsymbol{D}(\sigma_v')$$

Exercise: Replace the p-orbitals by d-orbitals, and find the matrix representation.

5.12

$$\boldsymbol{D}(C_2)\boldsymbol{D}(C_2)=\begin{bmatrix}0&1&0&0&0&0\\1&0&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-1&0\\0&0&0&0&0&1\end{bmatrix}\begin{bmatrix}0&1&0&0&0&0\\1&0&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-1&0\\0&0&0&0&0&1\end{bmatrix}$$

$$=\begin{bmatrix}1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{bmatrix}=\boldsymbol{D}(E);\text{ reproducing }C_2^2=E$$

$$\boldsymbol{D}(\sigma_\mathrm{v})\boldsymbol{D}(C_2)=\begin{bmatrix}0&1&0&0&0&0\\1&0&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&-1&0\\0&0&0&0&0&1\end{bmatrix}\begin{bmatrix}0&1&0&0&0&0\\1&0&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-1&0\\0&0&0&0&0&1\end{bmatrix}$$

$$=\begin{bmatrix}1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{bmatrix}=\boldsymbol{D}(\sigma'_\mathrm{v});\text{ reproducing }\sigma_\mathrm{v}C_2=\sigma'_\mathrm{v}$$

Exercise: Confirm these multiplications for the representatives constructed using d-orbitals.

5.13 Denote $s_1 + s_2$ as s' and $s_1 - s_2$ as s''. Since

$$(\mathrm{s}', \mathrm{s}'', \mathrm{O2s}, \mathrm{O2p}_x, \mathrm{O2p}_y, \mathrm{O2p}_z) = (\mathrm{s}_1, \mathrm{s}_2, \mathrm{O2s}, \mathrm{O2p}_x, \mathrm{O2p}_y, \mathrm{O2p}_z)\begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

the matrix $\boldsymbol{c}$ is given by

$$\boldsymbol{c} = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

with an inverse given by

$$\boldsymbol{c}^{-1} = \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 1/2 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

5.14 The representatives for C_2 and σ_v in the basis (H1s$_A$, H1s$_B$, O2s, O2p$_x$, O2p$_y$, O2p$_z$) are given in Exercise 5.11 and denoted $\boldsymbol{D}(C_2)$ and $\boldsymbol{D}(\sigma_v)$, respectively. The representatives in the new basis are given by $\boldsymbol{c}^{-1}\boldsymbol{D}(C_2)\boldsymbol{c}$ and $\boldsymbol{c}^{-1}\boldsymbol{D}(\sigma_v)\boldsymbol{c}$:

$$\boldsymbol{D}'(C_2) = \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 1/2 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ -1/2 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\boldsymbol{D}'(\sigma_{\mathrm{v}}) = \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 1/2 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ -1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

5.15 H has the full symmetry of the system [definition of symmetry operation], and so it is a basis for A_1 or the equivalent totally symmetric irreducible representation. Therefore, $\psi' H\psi$ spans $\Gamma' \times \Gamma$ if ψ' spans Γ' and ψ spans Γ. But $\Gamma' \times \Gamma$ contains A_1 only if $\Gamma' = \Gamma$. Therefore, the integral vanishes when ψ' and ψ belong to different symmetry species.

Exercise: Under what circumstances may a molecule possess a permanent electric dipole moment?

5.16 The point group of a regular tetrahedron is T_{d}: three-dimensional irreducible representations are allowed; therefore the maximum degeneracy is 3. (Accidental degeneracies could increase this number.)

Exercise: What is the maximum degeneracy of molecular obitals of **(a)** benzene, **(b)** anthracene, **(c)** an icosahedral molecule?

5.17 $\chi(C_{120°}) = \sin(\frac{3}{2} \times 120°)/\sin 60° = 0$; $\chi(\mathrm{E}) = 3$

$\chi(\sigma_v) = 1$ [because $p_y \rightarrow -p_y$, $p_x \rightarrow p_x$, $p_z \rightarrow p_z$]

The characters for $(E, 2C_3, 3\sigma_v)$ are therefore (3,0,1). Therefore, the orbitals span

$\underline{\mathrm{A}_1 + \mathrm{E}}$.

Exercise: What symmetry species would be spanned if the p-orbitals were replaced by **(a)** f-orbitals, **(b)** g-orbitals?

5.18 Carbon dioxide is of point group $D_{\infty h}$. The initial wavefunction is assumed to be of symmetry Σ_u^- (or A_{2u}); from the character table in Resource section 1, z spans Σ_u^+ (or A_{1u}). By inspection of the character table,

$$A_{2u} \times A_{1u} = A_{2g}$$

Therefore, the symmetry of the excited state must be $\underline{\Sigma_g^- (\text{or } A_{2g})}$.

Exercise: Repeat for y-polarized radiation.

5.19 We need to show that there is a symmetry transformation of the group that transforms C_3^+ into C_3^-.There are three C_2 rotation axes in the point group D_3, each of which is its own inverse. For any of these C_2 axes, the joint operation $C_2^{-1}\, C_3^+\, C_2$ yields C_3^-.

Problems

5.1 The sums of the diagonal elements in the matrices in Exercise 5.11 are

$$\chi(E) = 6,\ \chi(C_2) = 0,\ \chi(\sigma_v) = 2,\ \chi(\sigma_v') = 4$$

Use eqn 5.22 in the form

$$a_l = (1/4)\{6\chi^{(l)}(E) + 0 + 2\chi^{(l)}(\sigma_v) + 4\chi^{(l)}(\sigma'_v)\}$$

Then

$$a(A_1) = \tfrac{1}{4}\{6 + 0 + 2 + 4\} = 3 \; a(A_2) = \tfrac{1}{4}\{6 + 0 - 2 - 4\} = 0$$

$$a(B_1) = \tfrac{1}{4}\{6 - 0 + 2 - 4\} = 1 \; a(B_2) = \tfrac{1}{4}\{6 - 0 - 2 + 4\} = 2$$

Hence, the reduction is into $\underline{3A_1 + B_1 + 2B_2}$

Draw up the following Table:

	H1s$_A$	H1s$_B$	O2s	O2p$_x$	O2p$_y$	O2p$_z$
E	H1s$_A$	H1s$_B$	O2s	O2p$_x$	O2p$_y$	O2p$_z$
C_2	H1s$_B$	H1s$_A$	O2s	–O2p$_x$	–O2p$_y$	O2p$_z$
σ_v	H1s$_B$	H1s$_A$	O2s	O2p$_x$	–O2p$_y$	O2p$_z$
σ'_v	H1s$_A$	H1s$_B$	O2s	–O2p$_x$	O2p$_y$	O2p$_z$

Form $f^{(A_1)}$ by using $p^{(A_1)} = \frac{1}{4}\sum_R \chi^{(A_1)}(R)R$. From column 1,

$$f^{(A_1)} = \tfrac{1}{4}\{\text{H1s}_A + \text{H1s}_B + \text{H1s}_B + \text{H1s}_A\} = \tfrac{1}{2}\{\text{H1s}_A + \text{H1s}_B\}$$

From column 2, find the same. From column 3, $f^{(A_1)}$ = O2s, from columns 4 and 5 obtain 0. From column 6, $f^{(A_1)}$ = O2p$_z$. Hence

$$\underline{\boldsymbol{f}^{(A_1)} = \{\tfrac{1}{2}(\text{H1}s_A + \text{H1}s_B), \text{O2s}, \text{O2p}_z\}}$$

Form $\boldsymbol{f}^{(B_1)}$: only column 4 gives a non-zero quantity.

$$\underline{\boldsymbol{f}^{(B_1)} = \text{O2p}_x}$$

Form $\boldsymbol{f}^{(\mathrm{B}_2)}$: columns 3,4,6 give zero; columns 1,2, and 5 give

$$\underline{\boldsymbol{f}^{(\mathrm{B}_2)} = \{\tfrac{1}{2}(\mathrm{H1s_B} - \mathrm{H1s_A}), \mathrm{O2p}_y\}}$$

Only $f_1^{(\mathrm{A}_1)}$ and $f_1^{(\mathrm{B}_2)}$ involve linear combinations; the matrix of coefficients (Section 5.6) is therefore given by

$$\{\tfrac{1}{2}(\mathrm{H1s_A} + \mathrm{H1s_B}),\ \tfrac{1}{2}(\mathrm{H1s_B} - \mathrm{H1s_A}),\ \mathrm{O2s},\ \mathrm{O2p}_x,\ \mathrm{O2p}_y,\ \mathrm{O2p}_z\}$$

$$= \{\mathrm{H1s_A},\ \mathrm{H1s_B},\ \mathrm{O2s},\ \mathrm{O2p}_x,\ \mathrm{O2p}_y,\ \mathrm{O2p}_z\}\begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Consequently,

$$\boldsymbol{c} = \begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{c}^{-1} = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Then, from eqn 5.7b, showing only the H1s-combinations:

$$\boldsymbol{D}'(\mathrm{E}) = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\boldsymbol{D}'(\mathrm{C}_2) = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\boldsymbol{D}'(\sigma_{\mathrm{v}}) = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\boldsymbol{D}'(\sigma'_{\mathrm{v}}) = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Because these matrices are diagonal (and therefore also block-diagonal), and the remainder of $\boldsymbol{D}(R)$ are already diagonal, the entire representation is (block-) diagonal.

Exercise: Consider a representation using the basis (p_x, p_y, p_z) on each atom in a $C_{2\mathrm{v}}$ AB_2 molecule. Find the representatives, the symmetry-adapted combinations, and the block-diagonal representations.

5.4

$\boldsymbol{D}(C_3^+(\mathrm{A}))\boldsymbol{D}(C_3^-(\mathrm{A}))$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{D}(E)$$

$\boldsymbol{D}(S_4^+(\mathrm{AC}))\boldsymbol{D}(C_3^-(\mathrm{B}))$

$$= \begin{bmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \boldsymbol{D}(S_4^-(\mathrm{CD}))$$

$\boldsymbol{D}(S_4^+(\mathrm{AC}))\boldsymbol{D}(C_3^-(\mathrm{C}))$

$$= \begin{bmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} = \boldsymbol{D}(\sigma_{\mathrm{d}}(\mathrm{AB}))$$

Exercise: Check three of the group multiplications for the representation developed in the *Exercise* accompanying problem 5.2.

5.7 **(a)** $\chi(A_2) \times \chi(B_1) \times \chi(B_2)$

$= (1, 1, -1, -1) \times (1, -1, 1, -1) \times (1, -1, -1, 1) = (1, 1, 1, 1) = \chi(A_1)$

therefore, $\underline{A_2 \times B_1 \times B_2 = A_1}$ in C_{2v}

(b) $\chi(A_1) \times \chi(A_2) \times \chi(E)$

$= (1, 1, 1) \times (1, 1, -1) \times (2, -1, 0) = (2, -1, 0) = \chi(E)$;

therefore, $\underline{A_1 \times A_2 \times E = E}$ in C_{3v}

(c) $\chi(B_2) \times \chi(E_1) = (1, -1, 1, -1, 1, -1) \times (2, -2, -1, 1, 0, 0)$

$= (2, 2, -1, -1, 0, 0) = \chi(E_2)$

therefore, $\underline{B_2 \times E_1 = E_2}$ in C_{6v}

(d) $\chi(E_1) \times \chi(E_1) = (2, 2\cos\phi, 0) \times (2, 2\cos\phi, 0)$

$= (4, 4\cos^2\phi, 0) = (4, 2 + 2\cos 2\phi, 0)$

$= \chi(A_1) + \chi(A_2) + \chi(E_2)$

therefore, $\underline{E_1 \times E_1 = A_1 + A_2 + E_2}$ in $C_{\infty v}$

(Alternatively: $\Pi \times \Pi = \Sigma^+ + \Sigma^- + \Delta$)

(e) $\chi(T_1) \times \chi(T_2) \times \chi(E)$

$= (3, 0, -1, -1, 1) \times (3, 0, -1, 1, -1) \times (2, -1, 2, 0, 0) = (18, 0, 2, 0, 0)$

Decompose this using $a_l = (1/24)\{18\chi^{(l)}(E) + 6\chi^{(l)}(C_2)\}$ [eqn 5.23].

$a(A_1) = (1/24)\{18 + 6\} = 1 \qquad a(A_2) = (1/24)\{18 + 6\} = 1$

$$a(\mathrm{E}) = (1/24)\{36 + 12\} = 2$$

$$a(\mathrm{T}_1) = (1/24)\{54 - 6\} = 2 \qquad a(\mathrm{T}_2) = (1/24)\{54 - 6\} = 2$$

Therefore,

$$\underline{\mathrm{T}_1 \times \mathrm{T}_2 \times \mathrm{E} = \mathrm{A}_1 + \mathrm{A}_2 + 2\mathrm{E} + 2\mathrm{T}_1 + 2\mathrm{T}_2} \text{ in } O$$

Exercise: Analyse the following direct products: E × E × A_2 in C_{3v}, $A_{2u} \times E_{1u}$ in D_{6h}, and $\mathrm{T}_{1g}^2 \times \mathrm{T}_{2g}^2 \times \mathrm{E}_u$ in O_h.

5.10 **(a)**

$a_1^2b_1b_2$: $A_1 \times A_1 \times B_1 \times B_2 = B_1 \times B_2 = A_2$; $\underline{{}^1A_2 \text{ and } {}^3A_2}$ may arise.

(b) (i) a_2e : $A_2 \times E = E$; $\underline{{}^1E \text{ and } {}^3E}$ may arise.

(ii) e^2 : $E \times E = A_1 + [A_2] + E$; $\underline{{}^1A_1, {}^3A_2, {}^1E}$ may arise.

(c) (i) a_2e : $A_2 \times E = E$; $\underline{{}^1E \text{ and } {}^3E}$ may arise.

(ii) et_1 : $E \times T_1 = T_1 + T_2$; $\underline{{}^1T_1, {}^3T_1, {}^1T_2, \text{ and } {}^3T_2}$ may arise.

(iii) t_1t_2 : $T_1 \times T_2 = A_2 + E + T_1 + T_2$; $\underline{{}^1A_2, {}^3A_2, {}^1E, {}^3E, {}^1T_1, {}^3T_1, {}^1T_2, \text{ and } {}^3T_2}$ may arise.

(iv) t_1^2 : $T_1 \times T_1 = A_1 + E + [T_1] + T_2$; $\underline{{}^1A_1, {}^1E, {}^3T_1, \text{ and } {}^1T_2}$ may arise.

(v) t_2^2 : $T_2 \times T_2 = A_1 + E + [T_1] + T_2$; $\underline{{}^1A_1, {}^1E, {}^3T_1, \text{ and } {}^1T_2}$ may arise.

(d) (i) e^2 : $E \times E = A_1 + [A_2] + E$; $\underline{{}^1A_1, {}^3A_2, \text{ and } {}^1E}$ may arise.

(ii) et_1 : $E \times T_1 = T_1 + T_2$; $\underline{{}^1T_1, {}^3T_1, {}^1T_2, \text{ and } {}^3T_2}$ may arise.

(iii) t_2^2 : $T_2 \times T_2 = A_1 + E + [T_1] + T_2$; $\underline{{}^1A_1, {}^1E, {}^3T_1, \text{ and } {}^1T_2}$ may arise.

Exercise: Classify the term that may arise from d^2 in R_3, $\sigma^1\pi^1$ in $C_{\infty v}$, π^2 in $D_{\infty h}$, $e_g^1t_{1u}^1$ in O_h, and e_{1g}^2 in D_{6h}.

5.13 **(a)** In C_{2v} translations span $A_1 + B_1 + B_2$; hence a $^2A_1$ term may make a transition to $A_1 \times {}^2A_1 = {}^2A_1$, $B_1 \times {}^2A_1 = {}^2B_1$, and $B_2 \times {}^2A_1 = {}^2B_2$ and a $^2B_1$ term may make trantitions to $A_1 \times {}^2B_1 = {}^2B_1$, $B_1 \times {}^2B_1 = {}^2A_1$, and $B_2 \times {}^2B_1 = {}^2A_2$. In $D_{\infty h}$, translations span $\Sigma_u^+ + \Pi_u$. Therefore, because $\Sigma_u^+ \times \Sigma_g^- = \Sigma_u^-$ and $\Pi_u \times \Sigma_g^- = \Pi_u$, transitions to $^3\Sigma_u^-$ and $^3\Pi_u$ are allowed.

(b) In C_{2v} rotations span $A_2 + B_1 + B_2$. Then, because $A_1 \times (A_2 + B_1 + B_2) = A_2 + B_1 + B_2$, transitions to $^2A_2$, $^2B_1$, and $^2B_2$ are allowed for NO_2. Because $B_1 \times (A_2 + B_1 + B_2) = B_2 + A_1 + A_2$, transitions to $^2B_2$, $^2A_1$, and $^2A_2$ are allowed for ClO_2. In $D_{\infty h}$, rotations transform as $\Sigma_g^- + \Pi_g$, and because $\Sigma_g^- \times (\Sigma_g^- + \Pi_g) = \Sigma_g^+ + \Pi_g$, transtions to $^3\Sigma_g^+$ and $^3\Pi_g$ are allowed in O_2.

Exercise: What electric and magnetic dipole transitions may take place from the E_{1g}, E_{2u}, and B_{2g} terms of benzene?

5.16 For an f orbital, $l = 3$. We calculate the characters from eqn 5.47b with $l = 3$. **(a)** For a C_{3v} environment, we only consider the symmetry operations E and C_3 for which angles α can be identified. This is equivalent to working in the rotational subgroup C_3. For E, $\alpha = 0$ and $\chi = 7$; for C_3, $\alpha = 2\pi/3$ and $\chi = 1$. We now use eqn 5.23 with $h = 6$ and find $a(E) = 2$. We can use $h = 6$ because the character for σ_v is zero for the irreducible representation E. However, since the characters for σ_v are nonzero for the irreducible representations A_1 and A_2, we must revert to using the rotational subgroup C_3. In this case the angles are $\alpha = 0$ for E, $\alpha = 2\pi/3$ for C_3 and $\alpha = 4\pi/3$ for C_3^2; this yields characters (7, 1, 1) for (E, C_3, C_3^2) and use of eqn 5.23 with $h = 3$ (the order of the group C_3) yields $a(A) = 3$. Therefore, the symmetry species are 3A + 2E. **(b)** For a T_d environment, we only consider the symmetry operations E, C_2 and C_3 for which angles α can be identified. Therefore we work in the rotational subgroup T. For E, $\alpha = 0$ and $\chi = 7$; for C_3, $\alpha = 2\pi/3$ and $\chi = 1$; for C_3^2, $\alpha = 4\pi/3$ and $\chi = 1$; and for C_2, $\alpha = \pi$ and $\chi = -1$. We now use eqn 5.23 with $h = 12$ (for group T) and find $a(A) = 1$ and $a(T) = 2$. Therefore, the symmetry species are A + 2T.

5.19 We have shown in Section 5.18 that the difference between two infinitesimal rotations is equivalent to a single infinitesimal rotation and that the reverse argument implies the angular momentum commutation rules. We show here that the commutation relation $[l_x, l_y] = i\hbar l_z$ and the definition of angular momentum in terms of position and linear momentum operators implies the fundamental quantum mechanical commutation rule $[q, p_q] = i\hbar$ and, as a result, the latter commutation rule can be considered a manifestation of three-dimensional space. We begin by expanding $[l_x, l_y]$:

$$[l_x, l_y] = [yp_z - zp_y, zp_x - xp_z]$$

$$= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]$$

$$= yp_zzp_x - zp_xyp_z - (yp_zxp_z - xp_zyp_z) - (zp_yzp_x - zp_xzp_y) + (zp_yxp_z - xp_zzp_y)$$

$$= yp_x[p_z, z] - 0 - 0 + xp_y[z, p_z]$$

$$= [z, p_z]\{xp_y - yp_x\}$$

Since $l_z = xp_y - yp_x$, the relation $[l_x, l_y] = \mathrm{i}\hbar l_z$ immediately implies that $[z, p_z] = \mathrm{i}\hbar$, the fundamental quantum mechanical selection rule.

Chapter 6

Techniques of approximation

Exercises

6.1 The first-order WKB wavefunction is given in eqn 6.6 in classically allowed regions (note here that $E > V$ since a and x are positive). With $p(x)$ given by eqn 6.1b,

$$p(x) = \{2m[E - V(x)]\}^{1/2} = (2ma)^{1/2}x$$

The first-order WKB wavefunction is

$$\psi(x) = \frac{C}{(2ma)^{\frac{1}{4}}x^{\frac{1}{2}}}\sin\left(\frac{1}{\hbar}\int_0^x (2ma)^{\frac{1}{2}}x\mathrm{d}x + \delta\right) = \frac{C}{(2ma)^{\frac{1}{4}}x^{\frac{1}{2}}}\sin\left(\frac{(2ma)^{\frac{1}{2}}x^2}{2\hbar} + \delta\right)$$
$$= \frac{C}{(2ma)^{\frac{1}{4}}x^{\frac{1}{2}}}\sin\left(\left[\frac{ma}{2\hbar^2}\right]^{1/2} x^2 + \delta\right)$$

6.2 The energies of a two-level system are given by eqn 6.15. Therefore, with all energies in cm^{-1} units,

$$E_\pm = \tfrac{1}{2}(5000 + 10000) \pm \tfrac{1}{2}\sqrt{(10000 - 5000)^2 + 4 \times 500^2}$$

yielding $E_+ = 10\,049.51\ \mathrm{cm}^{-1}$ and $E_- = 4950.49\ \mathrm{cm}^{-1}$.

6.3 The wavefunction for the ground-state harmonic oscillator is given by

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2} \mathrm{e}^{-\alpha^2x^2/2}$$

The first-order energy correction, eqn 6.24, is

$$E_0^{(1)} = \langle\psi_0|H^{(1)}|\psi_0\rangle = \frac{\alpha}{\pi^{1/2}}\int_0^b ax\mathrm{e}^{-\alpha^2x^2}\mathrm{d}x = \frac{a}{2\alpha\pi^{1/2}}\left(1-\mathrm{e}^{-\alpha^2b^2}\right)$$

6.4 The second-order energy correction is given in eqn 6.30. Here, $H^{(1)} = a$ and $H^{(2)} = 0$. The ground-state wavefunction is given by

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2}\mathrm{e}^{-\alpha^2x^2/2}$$

and the $v = 1$ wavefunction by

$$\psi_1(x) = \left(\frac{2\alpha^3}{\pi^{1/2}}\right)^{1/2}x\mathrm{e}^{-\alpha^2x^2/2}$$

Since the wavefunctions are real, $H_{01}{}^{(1)} = H_{10}{}^{(1)}$; the denominator of the v =1 contribution to $E^{(2)}$ is (0 + ½) $\hbar\omega$ − (1 + ½) $\hbar\omega = -\hbar\omega$. The matrix element $H_{01}{}^{(1)}$ is

$$H_{01}^{(1)} = \int_0^\infty a\left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2}\mathrm{e}^{-\alpha^2x^2/2}\left(\frac{2\alpha^3}{\pi^{1/2}}\right)^{1/2}x\mathrm{e}^{-\alpha^2x^2/2}\mathrm{d}x = a\frac{2^{1/2}\alpha^2}{\pi^{1/2}}\left(\frac{1}{2\alpha^2}\right) = \frac{a}{2^{1/2}\pi^{1/2}}$$

Therefore, the contribution to $E^{(2)}$ from v =1 is

$$\frac{H_{01}^{(1)}H_{10}^{(1)}}{E_0^{(0)} - E_1^{(0)}} = \frac{a^2}{2\pi}\times\left(\frac{1}{-\hbar\omega}\right) = -\frac{a^2}{h\omega}$$

6.5 As discussed in Section 6.3, to know the energy correct to order $2n + 1$ in the perturbation, it is sufficient to know the wavefunctions only to nth order in the perturbation. Therefore, if the perturbed wavefunction is known to second order, the energy is accurately known to 5th order.

6.6 Following Example 6.5 in the text, we need to decide which matrix elements < s | y | n > are non-zero. The function for a s-orbital ($l = 0$) is a component of the basis for $\Gamma^{(0)}$ and y is likewise a component of the basis for $\Gamma^{(1)}$. Because $\Gamma^{(0)} \times \Gamma^{(1)} = \Gamma^{(1)}$ by eqn 5.51, we can infer that only p-orbitals can be mixed into the ground state. Furthermore, because the perturbation is in the *y*-direction, only p_y can be mixed.

6.7 The optimum form of the wavefunction corresponds to a minimum in the Rayleigh ratio. Therefore, we seek the value of *k* such that the derivative of the Rayleigh ratio with respect to *k* vanishes.

$$\frac{\mathrm{d}}{\mathrm{d}k}\left(\frac{\hbar^2 k^2}{2m}-\frac{hcR_{\mathrm{H}}k}{a_0}\right)=\frac{\hbar^2 k}{m}-\frac{hcR_{\mathrm{H}}}{a_0}=0$$

and therefore

$$k=\frac{mhcR_{\mathrm{H}}}{\hbar^2 a_0}=\frac{2\pi mcR_{\mathrm{H}}}{\hbar a_0}$$

6.8 Use the Hellmann-Feynman theorem, eqn 6.48.

$$\frac{\mathrm{d}E}{\mathrm{d}P}=\langle \partial H/\partial P\rangle=\langle x^2\rangle$$

6.9 The probability of finding the system in state 2 for a degenerate two-level system is given by eqn 6.64. Therefore, we should use this formula to find the time for which a perturbation should be applied to result in $P_2(t) = 1/3$, and then immediately extinguish the perturbation:

$$\sin^2|V|t=\frac{1}{3}$$

so

$$t=\frac{\arcsin\sqrt{1/3}}{|V|}$$

The perturbation should be applied for this amount of time and then removed.

6.10 The transition rate to a continuum of states is given by Fermi's golden rule, eqn 6.84. The molecular density of states here is

$$\rho_{\mathrm{M}}=\frac{2.50\times 10^4}{1.50\times 10^{-18}\mathrm{J}}=1.67\ \times 10^{22}\mathrm{J}^{-1}$$

Fermi's golden rule then yields

$$W = 2\pi\hbar|V|^2\rho_M = 2\pi(1.055\times10^{-34}\text{Js})(4.50\times10^{12}\text{s}^{-1})^2(1.67\times10^{22}\text{J}^{-1}) = 2.24\times10^{14}\text{s}^{-1}$$

6.11 Use the lifetime broadening relation, eqn 6.97.

$$\tau = \frac{\hbar}{\delta E} = \frac{1.055\times10^{-34}\text{Js}}{1.92\times10^{-24}\text{J}} = 5.49\times10^{-11}\text{s}$$

Problems

6.1 First consider exp(+i$S_+(x)/\hbar$). Noting that

$$\frac{\mathrm{d}}{\mathrm{d}x}\exp\left(\frac{\mathrm{i}S}{\hbar}\right) = \frac{\mathrm{i}}{\hbar}\frac{\mathrm{d}S}{\mathrm{d}x}\exp\left(\frac{\mathrm{i}S}{\hbar}\right)$$

we obtain upon substitution of exp(+i$S_+(x)/\hbar$) into eqn 6.1:

$$\hbar^2\left\{\frac{\mathrm{i}}{\hbar}\frac{\mathrm{d}^2S}{\mathrm{d}x^2}\exp\left(\frac{\mathrm{i}S}{\hbar}\right) + \left(\frac{\mathrm{i}}{\hbar}\frac{\mathrm{d}S}{\mathrm{d}x}\right)^2\exp\left(\frac{\mathrm{i}S}{\hbar}\right)\right\} + p^2\exp\left(\frac{\mathrm{i}S}{\hbar}\right) = 0$$

After factoring out the common term of exp(+i$S_+(x)/\hbar$), we obtain

$$\mathrm{i}\hbar\frac{\mathrm{d}^2S}{\mathrm{d}x^2} - \left(\frac{\mathrm{d}S}{\mathrm{d}x}\right)^2 + p^2 = 0$$

which is eqn 6.3 for S_+. Next consider exp(−i$S_-(x)/\hbar$). Noting that

$$\frac{\mathrm{d}}{\mathrm{d}x}\exp\left(\frac{-\mathrm{i}S}{\hbar}\right) = \frac{-\mathrm{i}}{\hbar}\frac{\mathrm{d}S}{\mathrm{d}x}\exp\left(\frac{-\mathrm{i}S}{\hbar}\right)$$

we obtain upon substitution of exp(−i$S_-(x)/\hbar$) into eqn 6.1:

$$\hbar^2\left\{\frac{-\mathrm{i}}{\hbar}\frac{\mathrm{d}^2S}{\mathrm{d}x^2}\exp\left(\frac{-\mathrm{i}S}{\hbar}\right) + \left(\frac{-\mathrm{i}}{\hbar}\frac{\mathrm{d}S}{\mathrm{d}x}\right)^2\exp\left(\frac{-\mathrm{i}S}{\hbar}\right)\right\} + p^2\exp\left(\frac{-\mathrm{i}S}{\hbar}\right) = 0$$

After factoring out the common term of exp(−i$S_-(x)/\hbar$), we obtain

$$-\mathrm{i}\hbar\frac{\mathrm{d}^2S}{\mathrm{d}x^2} - \left(\frac{\mathrm{d}S}{\mathrm{d}x}\right)^2 + p^2 = 0$$

which is eqn 6.3 for S_-.

6.4 We begin with eqn 6.13 applied to the wavefunction ψ_- and corresponding energy E_-. Therefore, from eqn 6.17a and eqn 6.15,

$$c_1 = \cos\zeta$$

$$c_2 = \sin\zeta$$

$$E = E_- = \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) - \frac{1}{2}d$$
$$d = \left\{\left(E_2^{(0)} - E_1^{(0)}\right)^2 + 4|H_{12}^{(1)}|^2\right\}^{1/2}$$

Substitution into eqn 6.13 yields, with $H_{11} = E_1^{(0)}$, $H_{22} = E_2^{(0)}$, and $H_{12} = H_{21} = |\,H_{12}^{(1)}|\,\mathrm{e}^{\mathrm{i}\varphi}$

$$\frac{1}{2}\cos\zeta\left(E_1^{(0)} - E_2^{(0)} + d\right) + \sin\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} = 0$$

$$\cos\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} + \frac{1}{2}\sin\zeta\left(E_2^{(0)} - E_1^{(0)} + d\right) = 0$$

Multiplication of the first of the equations by sin ζ and the second of the equations by cos ζ produces

$$\frac{1}{2}\cos\zeta\sin\zeta\left(E_1^{(0)} - E_2^{(0)} + d\right) + \sin^2\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} = 0$$

$$\cos^2\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} + \frac{1}{2}\sin\zeta\cos\zeta\left(E_2^{(0)} - E_1^{(0)} + d\right) = 0$$

Subtracting the top equation from the bottom equation and using the trigonometric identities

$$\cos 2\zeta = \cos^2\zeta - \sin^2\zeta$$

$$\sin 2\zeta = 2\sin\zeta\cos\zeta$$

yields

$$\cos 2\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} + \frac{1}{2}\sin 2\zeta\left(E_2^{(0)} - E_1^{(0)}\right) = 0$$

and therefore, since tan $2\zeta = \sin 2\zeta / \cos 2\zeta$,

$$\tan 2\zeta = \frac{-2\left|H_{12}^{(1)}\right|e^{i\varphi}}{E_2^{(0)} - E_1^{(0)}}$$

If we now let $\varphi = \pi$ so that $e^{i\varphi} = -1$, we obtain eqn 6.17b.

6.7 $H = -(\hbar^2/2m)(d^2/dx^2) + mgx$

$H^{(0)} = -(\hbar^2/2m)(d^2/dx^2);\quad H^{(1)} = mgx$

$E^{(1)} = \langle 0|H^{(1)}|0\rangle = mg\,\langle x\rangle = \underline{\tfrac{1}{2}mgL}$

The first-order correction disregards the adjustment of the location of the particle in the gravitational field, so $E^{(1)}$ is the potential energy of a particle at its average height ($\tfrac{1}{2}L$).

For $m = m_e$,

$$E^{(1)}/L = \tfrac{1}{2}mg = \underline{4.47 \times 10^{-30}\ \mathrm{J\ m^{-1}}}$$

6.10 The first-order correction to the energy is given by eqn 6.24:

$$E_0^{(1)} = \langle 0|H^{(1)}|0\rangle$$

where the state $|0\rangle$ is the ground-state harmonic oscillator wavefunction of Section 2.14:

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2} e^{-\alpha^2x^2/2} \qquad \alpha = \left(\frac{mk}{\hbar^2}\right)^{1/4}$$

and the perturbation hamiltonian is

$$H^{(1)} = ax^3 + bx^4$$

The following standard integrals will be useful:

$$\int_0^\infty x^3 \mathrm{e}^{-cx^2}\mathrm{d}x = \frac{1}{2c^2}$$

$$\int_0^\infty x^4 \mathrm{e}^{-cx^2}\mathrm{d}x = \frac{3}{8c^2}\left(\frac{\pi}{c}\right)^{1/2}$$

We also use the result that if the function $f(x)$ in the integrand is an even function of x, then

$$\int_{-\infty}^{0} f(x)\mathrm{d}x = \int_0^\infty f(x)\mathrm{d}x$$

and if the function is odd, then

$$\int_{-\infty}^{0} f(x)\mathrm{d}x = -\int_0^\infty f(x)\mathrm{d}x$$

(a) The anharmonic perturbation is present for all values of x.

$$\begin{aligned} E_0^{(1)} &= \left(\frac{\alpha}{\pi^{1/2}}\right)\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha^2x^2}(ax^3+bx^4)\mathrm{d}x \\ &= \left(\frac{\alpha}{\pi^{1/2}}\right)\left[0+\frac{3b\pi^{1/2}}{4\alpha^5}\right] \\ &= \frac{3b}{4\alpha^4} \end{aligned}$$

(b) The anharmonic perturbation is only present during bond expansion so $H^{(1)}$ vanishes for $x < 0$.

$$E_0^{(1)} = \left(\frac{\alpha}{\pi^{1/2}}\right)\int_0^{\infty} \mathrm{e}^{-\alpha^2x^2}(ax^3 + bx^4)\mathrm{d}x$$

$$= \left(\frac{\alpha}{\pi^{1/2}}\right)\left[\frac{a}{2\alpha^4} + \frac{3b\pi^{1/2}}{8\alpha^5}\right]$$

$$= \frac{a}{2\alpha^3\pi^{1/2}} + \frac{3b}{8\alpha^4}$$

(c) The anharmonic perturbation is only present during bond compression so $H^{(1)}$ vanishes for $x > 0$.

$$E_0^{(1)} = \left(\frac{\alpha}{\pi^{1/2}}\right)\int_{-\infty}^{0} \mathrm{e}^{-\alpha^2x^2}(ax^3 + bx^4)\mathrm{d}x$$

$$= \left(\frac{\alpha}{\pi^{1/2}}\right)\left[-\frac{a}{2\alpha^4} + \frac{3b\pi^{1/2}}{8\alpha^5}\right]$$

$$= -\frac{a}{2\alpha^3\pi^{1/2}} + \frac{3b}{8\alpha^4}$$

Exercise: Repeat the problem for the $v = 1$ harmonic oscillator wavefunction.

6.13 **(a)** $x\psi_0$ spans $B_1 \times A_1 = B_1$ in C_{2v}; hence $\underline{B_1}$ states are admixed.

(b) $l_x\psi_0$ spans $B_2 \times A_1 = B_2$ in C_{2v}; hence $\underline{B_2}$ states are admixed.

Exercise: : The symmetry of the ground state of ClO_2 is $^2B_1$. What symmetry species of excited states are admixed?

6.16 $H^{(1)} = \varepsilon \sin^2\phi$

Form the secular determinant by using

$$H^{(1)}_{m_l'm_l} = (\varepsilon/2\pi)\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}(m_l'-m_l)\phi}(\mathrm{e}^{2\mathrm{i}\phi}+\mathrm{e}^{-2\mathrm{i}\phi}-2)\mathrm{d}\phi/(-4)$$

$$= -(\varepsilon/8\pi)\int_0^{2\pi}\{\mathrm{e}^{\mathrm{i}(2-m_l'+m_l)\phi}+\mathrm{e}^{\mathrm{i}(-2-m_l'+m_l)\phi}-2\mathrm{e}^{-\mathrm{i}(m_l'-m_l)\phi}\}\mathrm{d}\phi$$

$$= -(\varepsilon/4)\{\delta_{m_l',m_l+2}+\delta_{m_l',m_l-2}-2\delta_{m_l',m_l}\}$$

Consequently,

$$H^{(1)}_{1,1} = \tfrac{1}{2}\varepsilon, \quad H^{(1)}_{-1,-1} = \tfrac{1}{2}\varepsilon, \quad H^{(1)}_{1,-1} = -\tfrac{1}{4}\varepsilon, \quad H^{(1)}_{-1,1} = -\tfrac{1}{4}\varepsilon$$

$$S_{1,1} = S_{-1,-1} = 1; \quad S_{1,-1} = S_{-1,1} = 0$$

$$\det|H^{(1)} - SE| = \begin{vmatrix} \tfrac{1}{2}\varepsilon - E & -\tfrac{1}{4}\varepsilon \\ -\tfrac{1}{4}\varepsilon & \tfrac{1}{2}\varepsilon - E \end{vmatrix} = (\tfrac{1}{2}\varepsilon - E)^2 - (-\tfrac{1}{4}\varepsilon)^2 = 0$$

Consequently, $E = \tfrac{1}{2}\varepsilon \pm \tfrac{1}{4}\varepsilon = \tfrac{3}{4}\varepsilon$ and $\tfrac{1}{4}\varepsilon$. Find the coefficients from the secular equations and $|c_1|^2 + |c_2|^2 = 1$ (or by intuition):

$$\left.\begin{aligned}(\tfrac{1}{2}\varepsilon - E)c_1 - \tfrac{1}{4}\varepsilon c_2 &= 0\\ -\tfrac{1}{4}\varepsilon c_1 + (\tfrac{1}{2}\varepsilon - E)c_2 &= 0\end{aligned}\right\}\left\{\begin{aligned}\phi_{\frac{3}{4}} &= (\psi_1 - \psi_{-1})/\sqrt{2}\\ \phi_{\frac{1}{4}} &= (\psi_1 + \psi_{-1})/\sqrt{2}\end{aligned}\right.$$

For the first-order energies we have $E = \tfrac{3}{4}\varepsilon$ and $\tfrac{1}{4}\varepsilon$. If desired, check this as follows:

$$H^{(1)}_{3/4,3/4} = \tfrac{1}{2}(H^{(1)}_{1,1} + H^{(1)}_{-1,-1} - H^{(1)}_{1,-1} - H^{(1)}_{-1,1}) = \tfrac{1}{2}(\varepsilon + \tfrac{1}{2}\varepsilon) = \tfrac{3}{4}\varepsilon$$

$$H^{(1)}_{1/4,1/4} = \tfrac{1}{2}(H^{(1)}_{1,1} + H^{(1)}_{-1,-1} + H^{(1)}_{1,-1} + H^{(1)}_{-1,1}) = \tfrac{1}{2}(\varepsilon - \tfrac{1}{2}\varepsilon) = \tfrac{1}{4}\varepsilon$$

$$H^{(1)}_{3/4,1/4} = \tfrac{1}{2}(H^{(1)}_{1,1} - H^{(1)}_{-1,-1} + H^{(1)}_{1,-1} - H^{(1)}_{-1,1}) = 0$$

This calculation confirms that $H^{(1)}$ is diagonal in the $\phi_{\frac{3}{4}}, \phi_{\frac{1}{4}}$ basis, and that its eigenvalues are $\frac{3}{4}\varepsilon$ and $\frac{1}{4}\varepsilon$.

For the second-order energies we require the following matrix elements:

$$H^{(1)}_{m_l,\frac{3}{4}} = (1/\sqrt{2})\{H^{(1)}_{m_l,1} - H^{(1)}_{m_l,-1}\}$$

$$= \begin{cases} (1/\sqrt{2})H^{(1)}_{3,1} & = -(\varepsilon/4\sqrt{2}) \quad \text{for } m_l = 3 \\ -(1/\sqrt{2})H^{(1)}_{-3,-1} & = +(\varepsilon/4\sqrt{2}) \quad \text{for } m_l = -3, \text{ all others zero} \end{cases}$$

$$H^{(1)}_{m_l,\frac{1}{4}} = (1/\sqrt{2})\{H^{(1)}_{m_l,1} + H^{(1)}_{m_l,-1}\}$$

$$= \begin{cases} (1/\sqrt{2})H^{(1)}_{3,1} & = -(\varepsilon/4\sqrt{2}) \quad \text{for } m_l = 3 \\ (1/\sqrt{2})H^{(1)}_{-3,-1} & = -(\varepsilon/4\sqrt{2}) \quad \text{for } m_l = -3, \text{ all others zero} \end{cases}$$

$$E^{(0)}_{m_l} = m_l^2\hbar^2/2mr^2 = m_l^2 A, \text{ with } A = \hbar^2/2mr^2$$

Both ϕ linear combinations correspond to $|m_l| = 1$, and so for them $E^{(0)} = A$. For the $\phi_{\frac{3}{4}}$ combination:

$$E^{(2)} = \sum_{m_l \neq 0} \left\{ H^{(1)}_{3/4,m_l} H^{(1)}_{m_l,3/4} / (1-m_l^2)A \right\}$$

$$= |H^{(1)}_{3/4,3}|^2/(-8A) + |H^{(1)}_{3/4,-3}|^2/(-8A) = -\varepsilon^2/128A$$

For the $\phi_{1/4}$ combination:

$$E^{(2)} = \sum_{m_l \neq 0} \left\{ H^{(1)}_{1/4,m_l} H^{(1)}_{m_l,1/4} / (1-m_l^2)A \right\}$$

$$= |H^{(1)}_{1/4,3}|^2/(-8A) + |H^{(1)}_{1/4,-3}|^2/(-8A) = -\varepsilon^2/128A$$

[The $m_l = 0$ does not in fact make a contribution to the sum.] The energies to second order are therefore

$$\underline{E_{3/4} = A + \tfrac{3}{4}\varepsilon - \varepsilon^2/128A}, \underline{E_{1/4} = A + \tfrac{1}{4}\varepsilon - \varepsilon^2/128A}$$

Exercise: Find the first- and second-order energy corrections for a particle subject to $H^{(1)} = \varepsilon \sin^4\phi$.

6.19 First, normalize the linear combinations to 1:

$$\int (a_2')^2 \mathrm{d}\tau = \tfrac{1}{2}\int (\mathrm{s_A} + \mathrm{s_C})^2 \mathrm{d}\tau = \tfrac{1}{2}\int (\mathrm{s_A^2} + \mathrm{s_C^2} + 2\mathrm{s_A}\mathrm{s_C})\mathrm{d}\tau$$

$$= 1 + S_{\mathrm{AC}}$$

$$\int (a'')^2 \mathrm{d}\tau = 1 - S_{\mathrm{AC}}$$

Therefore,

$$a_2' = (\mathrm{s_A} + \mathrm{s_C})/\{2(1 + S_{\mathrm{AC}})\}^{1/2}$$

$$a'' = (\mathrm{s_A} - \mathrm{s_C})/\{2(1 - S_{\mathrm{AC}})\}^{1/2}$$

Now construct the matrix elements of H:

$$\int a_1' H a_1' \mathrm{d}\tau = \alpha$$

$$\int a_2' H a_2' \mathrm{d}\tau = \int (\mathrm{s_A} + \mathrm{s_C}) H (\mathrm{s_A} + \mathrm{s_C}) \mathrm{d}\tau / 2(1 + S_{\mathrm{AC}})$$

$$= (\alpha + \gamma)/(1 + S_{\mathrm{AC}})$$

$$\int a'' H a'' \mathrm{d}\tau = (\alpha - \gamma)/(1 - S_{\mathrm{AC}})$$

$$\int a_1' H a_2' \mathrm{d}\tau = \int s_B H(s_A + s_C)\mathrm{d}\tau / \{2(1+S_{AC})\}^{1/2} = \{2/(1+S_{AC})\}^{1/2}\beta$$

$$\int a_1' a_2' \mathrm{d}\tau = \{2/(1+S_{AC})\}^{1/2} S_{AB} \quad [S_{AB} = S_{BC}]$$

Hence, the 2 × 2 secular determinant is

$$\det|H - ES| = \begin{vmatrix} \alpha - E & \frac{(\beta - ES_{AB})\sqrt{2}}{\sqrt{(1+S_{AC})}} \\ \frac{(\beta - ES_{AB})\sqrt{2}}{\sqrt{(1+S_{AC})}} & \left(\frac{\alpha+\gamma}{1+S_{AC}}\right) - E \end{vmatrix}$$

Set $\gamma = (S_{AC}/S_{AB})\beta$; then with $S_{AB} = 0.723$ and $S_{AC} = 0.345$,

$$\det|H - ES| = \begin{vmatrix} \alpha - E & 1.219(\beta - 0.723E) \\ 1.219(\beta - 0.723E) & (\alpha + 0.477\beta)/1.345 - E \end{vmatrix}$$

$$= 0.223E^2 + (1.794\beta - 1.744\alpha)E$$

$$+ (0.355\alpha\beta + 0.744\alpha^2 - 1.486\beta^2)$$

Therefore, we must solve

$$E^2 + (8.045\beta - 7.821\alpha)E + (1.592\alpha\beta + 3.336\alpha^2 - 6.664\beta^2) = 0$$

Write $E/\alpha = \varepsilon$ and $\beta/\alpha = \lambda$; then

$$\varepsilon^2 + (8.045\lambda - 7.821)\varepsilon + (1.592\lambda + 3.336 - 6.664\lambda^2) = 0$$

$$\varepsilon = 3.911 - 4.023\lambda \pm \sqrt{\{22.845\lambda^2 - 33.052\lambda + 11.956\}}$$

which can be plotted as a function of λ, Fig. 6.2. (The result from Problem 6.18, $\varepsilon = 1 \pm \lambda\sqrt{2}$, is also shown.)

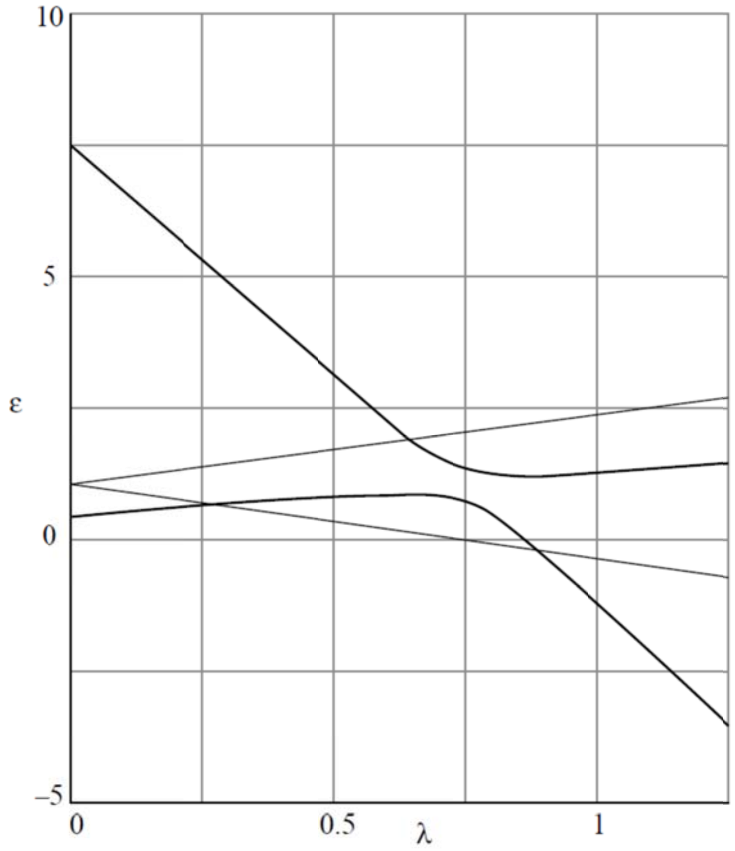


Figure 6.2: The energies calculated in Problem 6.19. The straight lines are the energies calculated in Problem 6.18.

Exercise: Include overlap in the *Exercise* attached to Problem 6.18.

6.22

$$c_f(t) = (1/\mathrm{i}\hbar)\int_0^t H^{(1)}_{\mathrm{fi}}(t)\mathrm{e}^{\mathrm{i}\omega_{\mathrm{fi}}t}\mathrm{d}t \quad [\text{eqn } 6.71]$$

$$c_{2\mathrm{p}}(t) = (1/\mathrm{i}\hbar)\langle 2\mathrm{p}_z|ez|1\mathrm{s}\rangle \int_0^t \mathcal{E}(t)\mathrm{e}^{i\omega_{2\mathrm{p},1s}t}\mathrm{d}t \qquad [H^{(1)}(t) = -\mu_z\mathcal{E}(t) = ez\mathcal{E}(t)]$$

Set $\mathcal{E}(t) = \gamma t$; note that $\omega_{2\text{p},1\text{s}} = \frac{3}{4}hc\mathrm{R}_\mathrm{H}/\hbar = (3\pi/2)c\mathrm{R}_\mathrm{H}$. For simplicity of notation, write $\omega = \omega_{2p,1\text{s}}$

$$c_{2\text{p}}(t) = \gamma(e/\text{i}\hbar)\langle 2\text{p}_z|z|1\text{s}\rangle\int_0^t t\text{e}^{\text{i}\omega t}\text{d}t$$

$$= (e\gamma/\text{i}\hbar)\langle 2\text{p}_z|z|1\text{s}\rangle\{(t/\text{i}\omega)\text{e}^{\text{i}\omega t} + (1/\omega^2)(\text{e}^{\text{i}\omega t} - 1)\}$$

$$|c_{2\text{p}}(t)|^2 = (e\gamma/\hbar)^2\langle 2\text{p}_z|z|1\text{s}\rangle^2(2/\omega^4)\{1 - \cos\omega t - \omega t\sin\omega t + \tfrac{1}{2}\omega^2t^2\}$$

Exercise: Find $|c_{2\text{p}}(t)|^2$ in the case where the perturbation is turned on quadratically ($\mathcal{E} \propto t^2$).

6.25 We use eqn 6.87 for the rate of stimulated emission, taking the value of B from eqn 6.88 and the density of states of the radiation field from eqn 6.92b. The transition dipole moment is calculated by using the hydrogen orbitals $R_{nl}Y_{lm_l}$ where the radial functions are listed in Table 3.4 and the spherical harmonics in Table 3.2; the transition frequency ν is obtained from the energies in eqn 3.66. For the rate of spontaneous emission, use the relation between A and B in eqn 6.93.

First consider the transition dipole moment μ_z for the $3\text{p}_z \to 2\text{s}$ transition.

$$\mu_z = -e\int\psi^*_{3\text{p}_z}z\psi_{2\text{s}}\text{d}\tau = -\frac{3^3\times 2^{10}}{5^6}ea_0$$

$$= -1.769ea_0 = -1.500\times 10^{-29}\ \text{C m}$$

Since the lower (2s) state of the atom is spherically symmetrical, the contributions for 3p_x, 3p_y and 3p_z are identical. Therefore

$$|\mu|^2 = |\mu_x|^2 + |\mu_y|^2 + |\mu_z|^2 = 3\times 3.131e^2a_0^2 = 6.752\times 10^{-58}\ \text{C}^2\ \text{m}^2$$

The Einstein coefficient of stimulated emission is

$$B = \frac{|\mu|^2}{6\varepsilon_0\hbar^2} = 1.143 \times 10^{21}\ \mathrm{J^{-1}\ m^3\ s^{-2}}$$

The frequency of the transition (with R the Rydberg constant) is

$$\nu = \left(\frac{1}{2^2} - \frac{1}{3^2}\right) cR = 4.567 \times 10^{14}\ \mathrm{Hz}$$

and so it follows that

$$A = \frac{8\pi h\nu^3}{c^3} B = 6.728 \times 10^{7}\ \mathrm{s^{-1}}$$

At 1000 K and for the transition frequency,

$$\rho_{\mathrm{rad}} = \frac{8\pi h\nu^3/c^3}{\mathrm{e}^{h\nu/kT} - 1} = 1.782 \times 10^{-23}\ \mathrm{J\ Hz^{-1}\ m^{-3}}$$

It then follows that the rate of stimulated emission is $B\rho_{\mathrm{rad}} = 2.036 \times 10^{-2}\ \mathrm{s^{-1}}$ whereas that of spontaneous emission is $A = 6.728 \times 10^{7}\ \mathrm{s^{-1}}$.

Exercise: Find the dependence on atomic number of the rates of stimulated and spontaneous emission for the 3p → 2s transition in hydrogenic atoms at 1000 K.

6.28 We use eqn 6.97 to estimate the lifetime τ from the full width at half maximum, which we denote Δ. The latter is converted from a wavenumber to an energy in joules by multiplication by hc; the full width as an energy in joules is then identified with δE.

$$\tau = \frac{\hbar}{(\delta E)} = \frac{1}{2\pi c\Delta}$$

(a) $\tau = (2\pi \times 2.9979 \times 10^{10}\ \mathrm{cm\ s^{-1}} \times 0.010\ \mathrm{cm^{-1}})^{-1} = 5.3 \times 10^{-10}\ \mathrm{s} = \underline{530\ \mathrm{ps}}$

(b) $\tau = (2\pi \times 2.9979 \times 10^{10}\ \mathrm{cm\ s^{-1}} \times 1.5\ \mathrm{cm^{-1}})^{-1} = 3.5 \times 10^{-12}\ \mathrm{s} = \underline{3.5\ \mathrm{ps}}$

(c) $\tau = (2\pi \times 2.9979 \times 10^{10}\ \mathrm{cm\ s^{-1}} \times 40\ \mathrm{cm^{-1}})^{-1} = 13 \times 10^{-14}\ \mathrm{s} = \underline{130\ \mathrm{fs}}$

Exercise: What is the full width of the spectral peak if the lifetime of the upper state is 1.0 μs?

Chapter 7

Atomic spectra and atomic structure

Exercises

7.1 The Rydberg constant R_∞ replaces the μ in eqn 7.2 for R_H by m_e:

$$R_\infty = \frac{m_e e^4}{8h^3 c\varepsilon_0^2} = \frac{1}{2}\left(\frac{e^2}{2hc\varepsilon_0}\right)^2 \times \left(\frac{m_e c}{h}\right) = \frac{\alpha^2}{2\lambda_C}$$

7.2 $\tilde{\nu} = \mathrm{R}_{\mathrm{He}^+} \times \{(1/n_1^2) - (1/n_2^2)\}$ [eqn 7.3]

$\mathrm{R}_{\mathrm{He}^+} = Z^2(\mu_{\mathrm{He}^+}/m_e)\mathrm{R}_\infty$ [eqn 7.31b]

$\mu_{\mathrm{He}^+} = mm_e/(m + m_e)$, $m = m(\mathrm{He}^{2+})$; $\mathrm{R}_\infty = 109\ 737.31\ \mathrm{cm}^{-1}$

$$m(\mathrm{He}^{2+}) = m({}^4_2\mathrm{He}) - 2m_e$$

$$= 4.0026 \times (1.660\ 54 \times 10^{-27}\ \mathrm{kg}) - 2(9.109\ 38 \times 10^{-31}\ \mathrm{kg})$$

$$= 6.6447 \times 10^{-27}\ \mathrm{kg}$$

$$\mathrm{R}_{\mathrm{He}^+} = 4\mathrm{R}_\infty/(1.000\ 14) = 4.3889 \times 10^5\ \mathrm{cm}^{-1}$$

Therefore, the transitions are predicted to lie at

$$\tilde{\nu}/\mathrm{cm}^{-1} = 4.3889 \times 10^5\{\tfrac{1}{4} - (1/n^2)\},\ n = 3, 4, \ldots$$

$$= 6.0957 \times 10^4,\ 8.2292 \times 10^4,\ 9.2167 \times 10^4, \ldots\ 1.0972 \times 10^5$$

Exercise: Find the positions of the corresponding lines in Li^{2+}.

7.3 The wavenumber of the transition $n_2 \rightarrow n_1$ in atomic hydrogen is given by eqn 7.3; we will replace μ by m_e and use the value of the Rydberg constant given in the inside front cover. The longest possible wavelength (smallest wavenumber) for a series will be the transition from $n_1 + 1 \rightarrow n_1$ where n_1 for each series is given in Section 7.1. The shortest possible wavelength (the series limit) will be given by $n_2 = \infty \rightarrow n_1$; in this case, the transition wavenumber simplifies to $\mathcal{R}_H \times (1/n_1^2)$.

(a) For the Lyman series, $n_1 = 1$. The smallest wavenumber is

$$\tilde{\nu} = \left(\frac{1}{1^2} - \frac{1}{2^2}\right) \times 1.097\,37 \times 10^5 \text{ cm}^{-1} = 82\,303 \text{ cm}^{-1}$$

and the longest possible wavelength is

$$\lambda = 1/\ \tilde{\nu}\ = 1.2150 \times 10^{-5} \text{ cm} = \underline{121.50 \text{ nm}}$$

The series limit is

$$\tilde{\nu} = \frac{\mathcal{R}}{1^2} = 109\,737 \text{ cm}^{-1}$$

and the shortest possible wavelength is

$$\lambda = 1/\tilde{\nu}\ = 9.1127 \times 10^{-6} \text{ cm} = \underline{91.127 \text{ nm}}$$

(b) For the Balmer series, $n_1 = 2$. The smallest wavenumber is

$$\tilde{\nu} = \left(\frac{1}{2^2} - \frac{1}{3^2}\right) \times 1.097\,37 \times 10^5 \text{ cm}^{-1} = 15\,241 \text{ cm}^{-1}$$

and the longest possible wavelength is

$$\lambda = 1/\ \tilde{\nu} = 6.5612 \times 10^{-5}\ \text{cm} = \underline{656.12\ \text{nm}}$$

The series limit is

$$\tilde{\nu}\ = \frac{\mathsf{R}}{2^2} = 27\ 434\ \text{cm}^{-1}$$

and the shortest possible wavelength is

$$\lambda = 1/\ \tilde{\nu} = 3.6451 \times 10^{-5}\ \text{cm} = \underline{364.51\ \text{nm}}$$

(c) For the Paschen series, $n_1 = 3$. The smallest wavenumber is

$$\tilde{\nu}\ = \left(\frac{1}{3^2} - \frac{1}{4^2}\right) \times 1.097\ 37 \times 10^5\ \text{cm}^{-1} = 5334.5\ \text{cm}^{-1}$$

and the longest possible wavelength is

$$\lambda = 1/\ \tilde{\nu} = 1.8746 \times 10^{-4}\ \text{cm} = \underline{1874.6\ \text{nm}}$$

The series limit is

$$\tilde{\nu} = \frac{\mathsf{R}}{3^2} = 12\ 193\ \text{cm}^{-1}$$

and the shortest possible wavelength is

$$\lambda = 1/\tilde{\nu} = 8.2014 \times 10^{-5}\ \text{cm} = \underline{820.14\ \text{nm}}$$

(d) For the Brackett series, $n_1 = 4$. The smallest wavenumber is

$$\tilde{\nu} = \left(\frac{1}{4^2} - \frac{1}{5^2}\right) \times 1.097\ 37 \times 10^5\ \text{cm}^{-1} = 2469.1\ \text{cm}^{-1}$$

and the longest possible wavelength is

$$\lambda = 1/\tilde{\nu} = 4.0501 \times 10^{-4}\ \text{cm} = \underline{4050.1\ \text{nm}}$$

The series limit is

$$\tilde{\nu} = \frac{\mathcal{R}}{4^2} = 6858.6\ \text{cm}^{-1}$$

and the shortest possible wavelength is

$$\lambda = 1/\tilde{\nu} = 1.4580 \times 10^{-4}\ \text{cm} = \underline{1458.0\ \text{nm}}$$

Exercise: Repeat the problem for the spectrum of He^+.

7.4 $\mu/m_e = 1/(1 + m_e/m_\mu) = 1/(1 + 1/207) = 0.995$

$$\tilde{\nu} = \mathcal{R}_\mu\{(1/n_1^2) - (1/n_2^2)\} = 0.995\mathcal{R}_\infty\{(1/n_1^2) - (1/n_2^2)\}$$

$$= \underline{(1.092 \times 10^5\ \text{cm}^{-1}) \times \{(1/n_1^2) - (1/n_2^2)\}}$$

with $n_1 = 1, 2, \ldots$ and $n_2 = n_1 + 1, n_1 + 2, \ldots$. The ionization limit (for $n_1 = 1$) lies at $1.092 \times 10^5\ \text{cm}^{-1}$($\lambda = 91.58$ nm).

Exercise: Predict the form of the spectrum of positronium (e^+, e^-).

7.5 Draw on $\Delta l = \pm 1$. Then the allowed transitions are

$$\underline{1s \rightarrow 2p,\ 2p \rightarrow 3d,\ \text{and}\ 3s \rightarrow 5p}$$

Exercise: Which of the following are electric-dipole allowed: 5s → 2p, 5s → 3d, 5s → 5f, 5s → 5p?

7.6 $E_n = -\mathcal{R}/n^2$. For convenience, take the energy minimum as $E_1 \equiv 0$;

$$E_n = \mathcal{R}\{1 - 1/n^2\} = 0,\ \tfrac{3}{4}\mathcal{R},\ \tfrac{8}{9}\mathcal{R},\ \tfrac{15}{16}\mathcal{R},\ldots$$

The data fit this sequence with

$$\mathcal{R}/\text{cm}^{-1} = 2\ 743\ 963,\ 2\ 744\ 051,\ 2\ 744\ 067$$

and mean value 2 744 027. Write $\mathcal{R} = Z^2\mathcal{R}_\infty$ [ignore mass correction]; then $Z = 5.00$. The ion is therefore $\underline{\text{B}^{4+}}$.

The ionization energy is given by the series limit ($n = \infty$), which lies at $\mathcal{R}$ = 2 744 027 cm^{-1}. Hence $I = hc\mathcal{R} = 5.450\ 87 \times 10^{-17}$ J, corresponding to 3.283×10^4 kJ mol^{-1} and 340.2 eV.

Exercise: Identify the one-electron ion giving rise to a spectrum showing that its np-orbitals were at 0, 6 666 000 cm^{-1}, 7 901 000 cm^{-1}, . . . Predict its ionization energy (in kJ mol^{-1} and eV).

7.7 The electric dipole transition moment is given by $< 3\text{p}_z \mid \mu_z \mid 1\text{s} >$ where

$$\mu_z = -er\cos\theta$$

$$\psi_{1\text{s}} = \left(\frac{1}{\pi}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{3/2}\text{e}^{-Zr/a_0}$$

$$\psi_{3\text{p}_z} = \left(\frac{1}{648\pi}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{3/2}\left(4-\frac{2Zr}{3a_0}\right)\left(\frac{2Zr}{3a_0}\right)\text{e}^{-Zr/3a_0}\cos\theta$$

Therefore, the transition dipole moment is

$$\begin{aligned}\langle 3\text{p}_z|\mu_z|1\text{s}\rangle &\\ &= -e\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\int_{r=0}^{\infty}\left(\frac{1}{648\pi^2}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{3}\\ &\times\left(4-\frac{2Zr}{3a_0}\right)\left(\frac{2Zr}{3a_0}\right)\text{e}^{-4Zr/3a_0}r^3\cos^2\theta\sin\theta\,\text{d}\theta\,\text{d}\varphi\,\text{d}r\end{aligned}$$

The integration over φ yields 2π and that over θ yields 2/3. The integration over r, which can be done using mathematical software or standard integration tables, yields $(1/648\pi^2)^{1/2}(a_0/Z)\times(-2187/16)$. The net result is

$$\langle 3\mathrm{p}_z|\mu_z|1\mathrm{s}\rangle = \frac{729}{4\sqrt{648}}\frac{ea_0}{Z}$$

7.8 The spin-orbit coupling constant ζ for a hydrogenic atom is given by eqn 7.20; here $Z = 3$ (Li^{2+}). Using the values of α and R_∞ given in the inside front cover, we find (a) $n = 2$, $l = 1$, $\zeta = 19.72\ \mathrm{cm}^{-1}$; (b) $n = 3$, $l = 2$, $\zeta = 1.17\ \mathrm{cm}^{-1}$.

7.9 Li : $1s^22s^1$, ${}^2S_{1/2}$

Be : $1s^22s^2$, ${}^1S_0$

B : $1s^22s^22p^1$, ${}^2P_{1/2}$, ${}^2P_{3/2}$ with $E({}^2P_{1/2}) < E({}^2P_{3/2})$

C : $1s^22s^22p^2$, ${}^1D_2$; ${}^3P_2$, ${}^3P_1$, ${}^3P_0$; ${}^1S_0$

with $E({}^3P_0) < E({}^3P_1) < E({}^3P_2) < E({}^1D_2) < E({}^1S_0)$

N : $1s^22s^22p^3$; $(l = 1) \times (l = 1) = (L = 2, 1, 0)$

$$(l = 1) \times (L = 2, 1, 0) = (L = 3, 2, 1 \text{ and } 2, 1, 0 \text{ and } 1)$$

Hence, $2p^3$ gives rise to F, 2D, 3P, S terms. Three spin-$\frac{1}{2}$ species can give rise to $S = (\frac{1}{2}\times\frac{1}{2})\times\frac{1}{2} = (1+0)\times\frac{1}{2} = \frac{3}{2}+\frac{1}{2}+\frac{1}{2}$, or to one quartet and two doublets. Three *equivalent* p-electrons are constrained by the Pauli principle, and can give rise only to ${}^4S$, ${}^2D$, ${}^2P$. Therefore, for N we predict ${}^4S < {}^2D < {}^2P$ (as observed).

O : $1s^22s^22p^4 \equiv 1s^22s^22p^62p^{-2}$ [particle-hole formalism]; this configuration gives rise to ${}^1D_2$; ${}^3P_2$, ${}^3P_1$, ${}^3P_0$; ${}^1S_0$ with ${}^3P_2 < {}^3P_1 < {}^3P_0 < {}^1D_2 < {}^1S_0$

F : $1s^22s^22p^5 \equiv 1s^22s^22p^62p^{-1}$; ${}^2P_{1/2}$, ${}^2P_{3/2}$ with ${}^2P_{3/2} < {}^2P_{1/2}$.

Ne : $1s^22s^22p^6$, $^1S_0$.

Exercise: Establish the terms for the atoms Na to Cl.

7.10

$$H = -(\hbar^2/2m_e)(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - (3e^2/4\pi\varepsilon_0)\{(1/r_1) + (1/r_2) + (1/r_3)\}$$

$$+ (e^2/4\pi\varepsilon_0)\{(1/r_{12}) + (1/r_{23}) + (1/r_{13})\}$$

$$= H^{(0)} + H^{(1)}; \qquad H^{(0)} = H_1 + H_2 + H_3$$

$$H_i = -(\hbar^2/2m_e)\nabla_i^2 - (3e^2/4\pi\varepsilon_0)(1/r_i) \quad i = 1, 2, 3$$

$$H^{(1)} = (e^2/4\pi\varepsilon_0)\{(1/r_{12}) + (1/r_{23}) + (1/r_{13})\}$$

$$H^{(0)}\psi(1)\psi(2)\psi(3) = (H_1 + H_2 + H_3)\psi(1)\psi(2)\psi(3)$$

$$= \{H_1\psi(1)\}\psi(2)\psi(3) + \psi(1)\{H_2\psi(2)\}\psi(3) + \psi(1)\psi(2)\{H_3\psi(3)\}$$

$$= (E_1 + E_2 + E_3)\psi(1)\psi(2)\psi(3) = E^{(0)}\psi(1)\psi(2)\psi(3)$$

Exercise: Write the general form of the hamiltonian for a Z-electron neutral atom, and show that $H^{(0)}\psi(1, \ldots, Z) = E^{(0)}\psi(1, \ldots, Z)$, with $\psi(1, \ldots, Z)$ a product of one-electron orbitals.

7.11 We use the notation introduced in Section 7.11 for the spinorbital, a joint spin-space state of the electron. The Slater determinant (eqn 7.42a) corresponding to the ground state of atomic lithium, taking the spin state of the 2s electron to be α, is

$$\psi(1, 2, 3) = (1/3!)^{1/2}\begin{vmatrix} \psi_{1s}^{\alpha}(1) & \psi_{1s}^{\beta}(1) & \psi_{2s}^{\alpha}(1) \\ \psi_{1s}^{\alpha}(2) & \psi_{1s}^{\beta}(2) & \psi_{2s}^{\alpha}(2) \\ \psi_{1s}^{\alpha}(3) & \psi_{1s}^{\beta}(3) & \psi_{2s}^{\alpha}(3) \end{vmatrix}$$

We demonstrate here the antisymmetry of $\psi(1, 2, 3)$ upon interchange of the labels of electrons 1 and 2. Explicitly expanding the above determinant, we find

$$\begin{aligned}\psi(1,2,3) = (1/6)^{1/2} \quad & [\psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{2s}^{\alpha}(3) + \psi_{1s}^{\beta}(1)\psi_{2s}^{\alpha}(2)\psi_{1s}^{\alpha}(3) + \\ & \psi_{2s}^{\alpha}(1)\psi_{1s}^{\alpha}(2)\psi_{1s}^{\beta}(3) - \psi_{2s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(3) - \\ & \psi_{1s}^{\alpha}(1)\psi_{2s}^{\alpha}(2)\psi_{1s}^{\beta}(3) - \psi_{1s}^{\beta}(1)\psi_{1s}^{\alpha}(2)\psi_{2s}^{\alpha}(3)]\end{aligned}$$

while interchange of labels 1 and 2 yields

$$\begin{aligned}\psi(1,2,3) = (1/6)^{1/2} \quad & [\psi_{1s}^{\alpha}(2)\psi_{1s}^{\beta}(1)\psi_{2s}^{\alpha}(3) + \psi_{1s}^{\beta}(2)\psi_{2s}^{\alpha}(1)\psi_{1s}^{\alpha}(3) + \\ & \psi_{2s}^{\alpha}(2)\psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(3) - \psi_{2s}^{\alpha}(2)\psi_{1s}^{\beta}(1)\psi_{1s}^{\alpha}(3) - \\ & \psi_{1s}^{\alpha}(2)\psi_{2s}^{\alpha}(1)\psi_{1s}^{\beta}(3) - \psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(1)\psi_{2s}^{\alpha}(3)] \\ & = -\psi(1,2,3)\end{aligned}$$

as required.

Exercise: Write the Slater determinant for the configuration $1s^2 2s^1$ of a lithium atom in which both of the 1s electrons have the same spin state; show that this determinant is identically zero.

7.12 To confirm the radial integration in Example 7.2, we need to show

$$\int_0^{\infty}\left\{\int_0^{r_2}\frac{r_1^2 \mathrm{e}^{-2Zr_1/a_0}}{r_2}\,\mathrm{d}r_1 + \int_{r_2}^{\infty}\frac{r_1^2 \mathrm{e}^{-2Zr_1/a_0}}{r_1}\,\mathrm{d}r_1\right\} r_2^2 \mathrm{e}^{-2Zr_2/a_0}\,\mathrm{d}r_2 = \frac{5}{2^7}\left(\frac{a_0}{Z}\right)^5$$

We use the following results:

$$\int_0^{r_2} \frac{r_1^2 \mathrm{e}^{-2Zr_1/a_0}}{r_2}\mathrm{d}r_1$$

$$= \frac{1}{r_2}\int_0^{r_2} r_1^2 \mathrm{e}^{-2Zr_1/a_0}\mathrm{d}r_1 = \text{-}\mathrm{e}^{-2Zr_2/a_0}\left(\frac{a_0 r_2}{2Z} + \frac{a_0^2}{2Z^2}\right)$$

$$+ \left(-\mathrm{e}^{-2Zr_2/a_0} + 1\right)\frac{a_0^3}{4Z^3 r_2}$$

$$\int_{r_2}^{\infty} \frac{r_1^2 \mathrm{e}^{-2Zr_1/a_0}}{r_1}\mathrm{d}r_1 = \frac{a_0^2 \mathrm{e}^{-2Zr_2/a_0}}{4Z^2}\left(\frac{2Zr_2}{a_0} + 1\right)$$

Substitution of the above two integrals then produces

$$\int_0^{\infty}\left\{\int_0^{r_2} \frac{r_1^2 \mathrm{e}^{-\frac{2Zr_1}{a_0}}}{r_2}\mathrm{d}r_1 + \int_{r_2}^{\infty} \frac{r_1^2 \mathrm{e}^{-\frac{2Zr_1}{a_0}}}{r_1}\mathrm{d}r_1\right\} r_2^2 \mathrm{e}^{-\frac{2Zr_2}{a_0}}\mathrm{d}r_2$$

$$= \int_0^{\infty}\left\{\text{-}\mathrm{e}^{-4Zr_2/a_0}\left(\frac{a_0 r_2^3}{2Z} + \frac{r_2^2 a_0^2}{2Z^2}\right)\right.$$

$$\left. + \left(-\mathrm{e}^{-4Zr_2/a_0} + \mathrm{e}^{-2Zr_2/a_0}\right)\frac{a_0^3 r_2}{4Z^3} + \frac{a_0^2 \mathrm{e}^{-4Zr_2/a_0}}{4Z^2}\left(\frac{2Zr_2^3}{a_0} + r_2^2\right)\right\}\mathrm{d}r_2$$

$$= \int_0^{\infty}\left\{\text{-}\mathrm{e}^{-4Zr_2/a_0}\left(\frac{r_2^2 a_0^2}{4Z^2}\right) + \left(-\mathrm{e}^{-4Zr_2/a_0} + \mathrm{e}^{-2Zr_2/a_0}\right)\frac{a_0^3 r_2}{4Z^3}\right\}\mathrm{d}r_2$$

Using the standard integral

$$\int_0^{\infty} r^n \mathrm{e}^{-ar}\mathrm{d}r = \frac{n!}{a^{n+1}}$$

we obtain

$$\int_0^\infty \left\{ \int_0^{r_2} \frac{r_1^2 \mathrm{e}^{-\frac{2Zr_1}{a_0}}}{r_2} \mathrm{d}r_1 + \int_{r_2}^\infty \frac{r_1^2 \mathrm{e}^{-\frac{2Zr_1}{a_0}}}{r_1} \mathrm{d}r_1 \right\} r_2^2 \mathrm{e}^{-\frac{2Zr_2}{a_0}} \mathrm{d}r_2$$

$$= \left\{ \frac{-2a_0^2}{4Z^2\left(\frac{4Z}{a_0}\right)^3} + \frac{-a_0^3}{4Z^3\left(\frac{4Z}{a_0}\right)^2} + \frac{a_0^3}{4Z^3\left(\frac{2Z}{a_0}\right)^2} \right\} = \left(\frac{a_0}{Z}\right)^5 \left\{ \frac{-1}{2^7} + \frac{-2}{2^7} + \frac{2^3}{2^7} \right\}$$

$$= \frac{5}{2^7}\left(\frac{a_0}{Z}\right)^5$$

as in Example 7.2.

7.13 A 3p Slater orbital of effective nuclear charge Z_{eff} is given by (see 7.41, $n_{\text{eff}} = 3$)

$$\psi = Nr^2 \mathrm{e}^{-Z_{\text{eff}}r/3a_0} Y_{1,m_l}$$

We first determine the normalization constant N using the standard integral given in the solution above to Exercise 7.12. Since the spherical harmonic Y is normalized, we only need to be concerned with the radial integral.

$$1 = \int_0^\infty N^2 r^4 \mathrm{e}^{-2Z_{\text{eff}}r/3a_0} r^2 \,\mathrm{d}r = N^2 \frac{6!\, a_0^7}{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}$$

and therefore

$$N = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^{7/2}}{720^{1/2} a_0^{7/2}}$$

To find the expectation values of r^n, we only need be concerned with the radial integral since the spherical harmonic is normalized. We again make use of the standard integral

$$\int_0^\infty r^n \mathrm{e}^{-ar} \mathrm{d}r = \frac{n!}{a^{n+1}}$$

(a)

$$\langle r\rangle = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}rr^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}r^2\mathrm{d}r = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^7\mathrm{e}^{-2Z_{\text{eff}}r/3a_0}\mathrm{d}r$$

$$= \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\times\frac{7!}{\left(\frac{2Z_{\text{eff}}}{3a_0}\right)^8} = \frac{21a_0}{2Z_{\text{eff}}}$$

(b)

$$\langle 1/r\rangle = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^2\mathrm{e}^{-\frac{Z_{\text{eff}}r}{3a_0}}(1/r)r^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}r^2\mathrm{d}r = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^5\mathrm{e}^{-2Z_{\text{eff}}r/3a_0}\mathrm{d}r$$

$$= \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\times\frac{5!}{\left(\frac{2Z_{\text{eff}}}{3a_0}\right)^6} = \frac{Z_{\text{eff}}}{9a_0}$$

(c)

$$\langle 1/r^3\rangle = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^2\mathrm{e}^{-\frac{Z_{\text{eff}}r}{3a_0}}(1/r^3)r^2\mathrm{e}^{-Z_{\text{eff}}r/3a_0}r^2\mathrm{d}r = \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\int_0^\infty r^3\mathrm{e}^{-2Z_{\text{eff}}r/3a_0}\mathrm{d}r$$

$$= \frac{\left(\frac{2Z_{\text{eff}}}{3}\right)^7}{720a_0^7}\times\frac{3!}{\left(\frac{2Z_{\text{eff}}}{3a_0}\right)^4} = \frac{Z_{\text{eff}}^3}{405a_0^3}$$

7.14 Consider the four-electron Be atom with electron configuration $1s^22s^2$. From eqn 7.49,

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} - (2J_{1s1s} - K_{1s1s} + 2J_{1s2s} - K_{1s2s} + 2J_{2s1s} - K_{2s1s} + 2J_{2s2s} - K_{2s2s})$$

Since, $J_{1s1s} = K_{1s1s}$, $J_{2s2s} = K_{2s2s}$, $J_{1s2s} = J_{2s1s}$, and $K_{1s2s} = K_{2s1s}$, this simplifies to

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} - (J_{1s1s} + 4J_{1s2s} - 2K_{1s2s} + J_{2s2s})$$

From eqn 7.48a,

$$\varepsilon_{1s} = E_{1s} + 2J_{1s1s} + 2J_{2s1s} - K_{1s1s} - K_{2s1s}$$

$$\varepsilon_{2s} = E_{2s} + 2J_{1s2s} + 2J_{2s2s} - K_{1s2s} - K_{2s2s}$$

Therefore, substituting the above expressions for ε into the equation for E and again noting that $J_{1s1s} = K_{1s1s}$, $J_{2s2s} = K_{2s2s}$, $J_{1s2s} = J_{2s1s}$, and $K_{1s2s} = K_{2s1s}$, we obtain

$$E = 2E_{1s} + 2E_{2s} + J_{1s1s} + J_{2s2s} - 2K_{1s2s} + 4J_{1s2s}$$

This is the expression formally found in Problem 7.19.

7.15 $^1\mathrm{S}: J = (0 \times 0) = 0$; hence $\underline{^1\mathrm{S}_0}$

$^2\mathrm{P}: J = (\tfrac{1}{2} \times 1) = \tfrac{3}{2} + \tfrac{1}{2}$; hence $\underline{^2\mathrm{P}_{3/2}, {}^2\mathrm{P}_{1/2}}$

$^3\mathrm{P}: J = (1 \times 1) = 2 + 1 + 0$; hence $\underline{^3\mathrm{P}_2, {}^3\mathrm{P}_1, {}^3\mathrm{P}_0}$

$^3\mathrm{D}: J = (1 \times 2) = 3 + 2 + 1$; hence $\underline{^3\mathrm{D}_3, {}^3\mathrm{D}_2, {}^3\mathrm{D}_1}$

$^2\mathrm{D}: J = (\tfrac{1}{2} \times 2) = \tfrac{5}{2} + \tfrac{3}{2}$; hence $\underline{^2\mathrm{D}_{5/2}, {}^2\mathrm{D}_{3/2}}$

$^1\mathrm{D}: J = (0 \times 2) = 2$; hence $\underline{^1\mathrm{D}_2}$

$^4\mathrm{D}: J = (\tfrac{3}{2} \times 2) = \tfrac{7}{2} + \tfrac{5}{2} + \tfrac{3}{2} + \tfrac{1}{2}$;

hence $\underline{^4\mathrm{D}_{7/2}, {}^4\mathrm{D}_{5/2}, {}^4\mathrm{D}_{3/2}, {}^4\mathrm{D}_{1/2}}$

Exercise: What levels may arise from the terms ^{4}F, ^{4}D, ^{4}P?

7.16 $1s^1 2p^1: L = 1; S = 0, 1$; hence ^{1}P, ^{3}P with levels $^1\mathrm{P}_1$, $^3\mathrm{P}_2$, $^3\mathrm{P}_1$, $^3\mathrm{P}_0$.

Energies: $\underline{^3\mathrm{P}_0 < {}^3\mathrm{P}_1 < {}^3\mathrm{P}_2 < {}^1\mathrm{P}_1}$ [Hund rules]

$2p^1 3p^1: L = 2, 1, 0; S = 0,1$; hence ^{3}D, ^{1}D, ^{3}P, ^{1}P, ^{3}S, ^{1}S.

Energies: $\underline{^3\mathrm{D}_1 < {}^3\mathrm{D}_2 < {}^3\mathrm{D}_3 < {}^3\mathrm{P}_0 < {}^3\mathrm{P}_1 < {}^3\mathrm{P}_2}$

$\underline{< {}^3\mathrm{S}_1 < {}^1\mathrm{D}_2 < {}^1\mathrm{P}_1 < {}^1\mathrm{S}_0}$

$3p^1 3d^1: L = 3, 2, 1; S = 0,1$; hence ^{3}F, ^{1}F, ^{3}D, ^{1}D, ^{3}P, ^{1}P.

Energies: $\underline{^3\mathrm{F}_2 < {}^3\mathrm{F}_3 < {}^3\mathrm{F}_4 < {}^3\mathrm{D}_1 < {}^3\mathrm{D}_2 < {}^3\mathrm{D}_3}$

$\underline{< {}^3\mathrm{P}_0 < {}^3\mathrm{P}_1 < {}^3\mathrm{P}_2 < {}^1\mathrm{F}_3 < {}^1\mathrm{D}_2 < {}^1\mathrm{P}_1}$

Exercise: Arrange in order of increasing energy the levels and terms arising from $1s^1 3p^1$, $3p^2$, $2s^1 4f^1$, $5g^2$.

7.17 **(a)** d^2 : $L = (2 \times 2) = 4 + 3 + 2 + 1 + 0$; $S = 1, 0$ but the Pauli principle forbids ^3G (and alternate triplets). Hence $\underline{^1G, {}^3F, {}^1D, {}^3P, {}^1S}$ arise.

(b) f^2 : $L = (3 \times 3) = 6 + 5 + \ldots + 0$; $S = 1, 0$. Pauli forbids ^3I etc.; hence $\underline{^1I, {}^3H, {}^1G, {}^3F, {}^1D, {}^3P, {}^1S}$ arise.

Exercise: What terms may arise from the general $(nl)^2$ configuration?

7.18 Using group theoretical arguments (as in eqn 7.70), we find:

(a) For d^2: $\Gamma^{(2)} \times \Gamma^{(2)} = \Gamma^{(4)} + [\,\Gamma^{(3)}\,] + \Gamma^{(2)} + [\,\Gamma^{(1)}\,] + \Gamma^{(0)}$

$$\Gamma^{(1/2)} \times \Gamma^{(1/2)} = \Gamma^{(1)} + [\,\Gamma^{(0)}\,]$$

Since $[\,\Gamma^{(0)}\,]$ is associated with the antisymmetric singlet spin state and the overall wavefunction must be antisymmetric, we conclude that (symmetric) $\Gamma^{(4)}$ (a G state) must be a singlet state. Similarly, symmetric $\Gamma^{(2)}$ (a D state) and symmetric $\Gamma^{(0)}$ (an S state) must be singlets. The antisymmetric $[\,\Gamma^{(3)}\,]$ (an F state) and antisymmetric $[\,\Gamma^{(1)}]$ (a P state) must be triplets.

(b) For f^2: $\Gamma^{(3)} \times \Gamma^{(3)} = = \Gamma^{(6)} + [\,\Gamma^{(5)}\,] + \Gamma^{(4)} + [\,\Gamma^{(3)}\,] + \Gamma^{(2)} + [\,\Gamma^{(1)}\,] + \Gamma^{(0)}$

$$\Gamma^{(1/2)} \times \Gamma^{(1/2)} = \Gamma^{(1)} + [\,\Gamma^{(0)}\,]$$

By the same arguments an in part **(a)**, $\Gamma^{(6,4,2,0)}$ (I, G, D, S states) must be singlet states and $[\,\Gamma^{(5,3,1)}\,]$ (H, F, P states) must be triplet states.

7.19 $E^{(1)} = \mu_B \mathcal{B} M_L$ [eqn 7.72]

$\Delta E^{(1)} = \mu_B \mathcal{B}$; $\Delta\tilde{\nu} = (\mu_B/hc)\mathcal{B}$

Therefore, $\mathcal{B} = hc\Delta\tilde{\nu}/\mu_B = \underline{2.14\ \text{T}}$ when $\tilde{\nu} = 1\ \text{cm}^{-1}$.

Exercise: Calculate the magnetic field required to produce a splitting of $1\ \text{cm}^{-1}$ between the states of a $^1D_2$ level.

7.20

$$g_J = 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \quad \text{[eqn 7.76]}$$

(a) $J_{\max} = L + S$,

$$g_{L+S} = 1+\frac{(L+S)(L+S+1)+S(S+1)-L(L+1)}{2(L+S)(L+S+1)}$$

$$= \underline{1 + S/(L + S)}$$

(b) $J_{\min} = L - S$ (for $S \le L$)

$$g_{L-S} = 1+\frac{(L-S)(L-S+1)+S(S+1)-L(L+1)}{2(L-S)(L-S+1)}$$

$$= \underline{1 - S/(L - S + 1)}$$

Exercise: Calculate the g-factor for a level in which J has its minimum value, but for which $L \le S$. Evaluate $\sum_J J(J+1)g_J$ for a given S, L.

7.21 Since ${}^1\text{F} \rightarrow {}^1\text{D}$ is a transition between singlets, the normal Zeeman effect will be observed: the transition splits into three lines with separation $\Delta\tilde{\nu} = (\mu_B/hc)\mathcal{B} =$ 1.87 cm^{-1} for $\mathcal{B} = 4.0$ T [use first part of Problem 7.19].

Exercise: How many lines will be observed in a magnetic field of 4.0 T for a ${}^1\text{F} \rightarrow {}^1\text{P}$ transition?

7.22 For the ${}^3\text{P} \rightarrow {}^3\text{S}$ transition we must distinguish the levels and calculate their respective g-factors:

$$g_J(L = S) = 1+\left\{\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right\}_{L=S}$$

$$= 1+\tfrac{1}{2} = \tfrac{3}{2}$$

Therefore, $g_J(^3\mathrm{P}) = \frac{3}{2}$ for $J = 0, 1, 2$.

$$g_J(^3\mathrm{S}_1) = 1 + \left\{\frac{J(J+1)+S(S+1)}{2J(J+1)}\right\}_{J=S} = 1+1=2$$

At $\mathcal{B} = 4$ T,

$$\Delta\tilde{\nu} = g_J\mu_\mathrm{B}\mathcal{B}/hc = g_J \times (1.87\ \mathrm{cm}^{-1}) = \begin{cases} 2.80\ \mathrm{cm}^{-1} & \text{for } g_J = \frac{3}{2} \\ 3.74\ \mathrm{cm}^{-1} & \text{for } g_J = 2 \end{cases}$$

Construct the diagram in Fig. 7.1. The transitions are those for which $\Delta J = 0, \pm 1$ and $\Delta M_J = 0, \pm 1$.

Exercise: Construct the form of the Zeeman effect on a $^4\mathrm{F} \rightarrow {}^4\mathrm{D}$ transition.

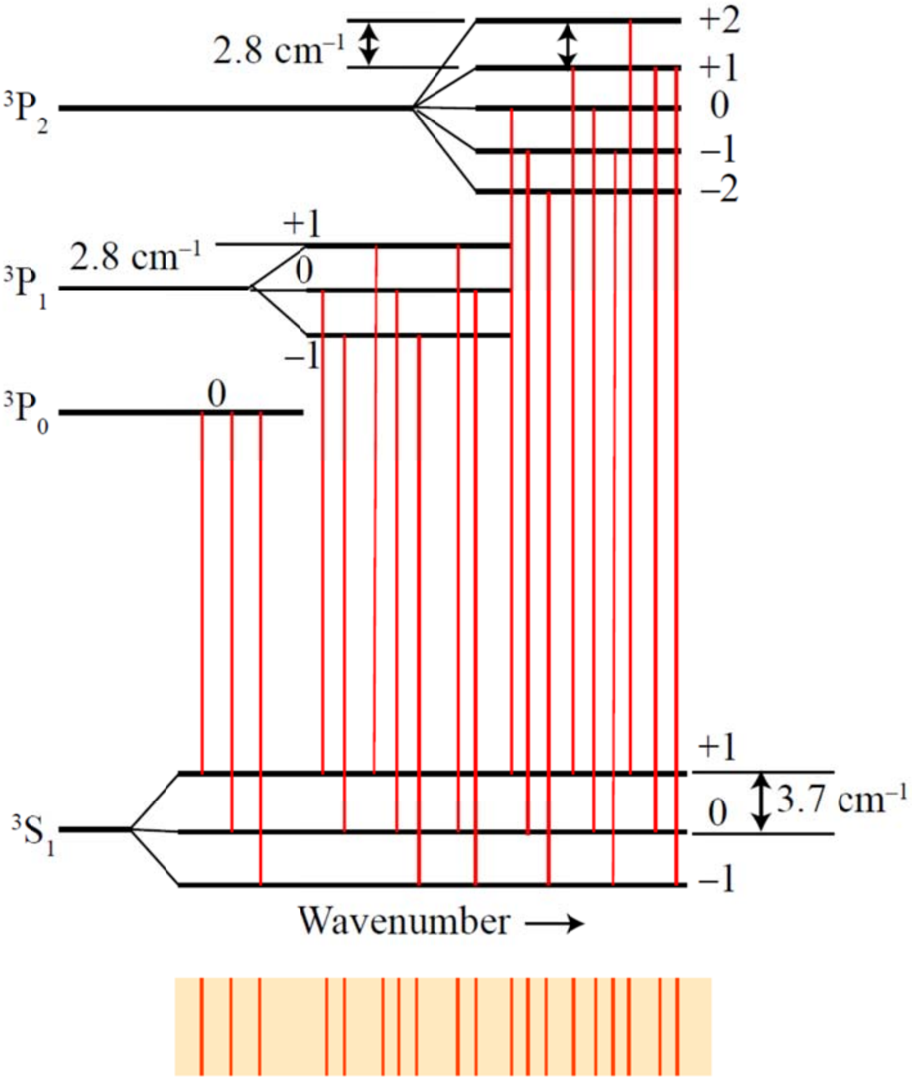


Figure 7.1: The energy levels, transitions, and resulting spectrum of the atom treated in Problem 7.22.

7.23 We seek a solution to eqn 7.98 for the function χ:

$$\frac{\mathrm{d}^2\chi}{\mathrm{d}x^2} = \frac{\chi^{3/2}}{x^{1/2}}$$

where

$$x = \alpha r$$

with

$$\alpha = 2(4)^{2/3}Z^{1/3}/(3\pi)^{2/3}$$

The density ρ is given in terms of the function χ by eqn 7.62. To proceed, assume far from the nucleus that χ is proportional to x^m. Taking,

$$\frac{\mathrm{d}^2\chi}{\mathrm{d}x^2} = am(m-1)x^{m-2}$$

$$\frac{\chi^{3/2}}{x^{1/2}} = a^{3/2}x^{\frac{3m}{2}-\frac{1}{2}}$$

Equating the above two expressions yields:

$$m-2 = \frac{3m}{2} - \frac{1}{2} \quad \text{so} \quad m = -3$$

and

$$am(m-1) = a^{3/2} = 12a \quad \text{so} \quad a = 144$$

Substitution of $\chi = 144x^{-3}$ into eqn 7.62 yields

$$\rho = \frac{32Z^2}{9\pi^3}\left(\frac{\chi}{x}\right)^{3/2} = \frac{32Z^2}{9\pi^3}\left(\frac{1728}{x^6}\right) = \frac{6144Z^2}{\alpha^6\pi^3} \times \frac{1}{r^6}$$

The density is therefore proportional to $1/r^6$ and the constant of proportionality is

$$\frac{6144Z^2}{\alpha^6\pi^3} = \frac{6144Z^2(3\pi)^4}{\pi^3 2^6 4^4 Z^2} = \frac{497664\pi}{16384} = 30.375\pi$$

Problems

7.1 $\langle n'l'm_l'|\mu_m|nlm_l\rangle \propto \int R_{n'l'}Y^*_{l'm_l'}rY_{1m}R_{nl}Y_{lm_l}r^2\mathrm{d}r\sin\theta\mathrm{d}\theta\mathrm{d}\phi$

[The proportionality factor is irrelevant; but because $z = 2(\pi/3)^{1/2}rY_{10}$ and $x \pm \mathrm{i}y = \mp$ $2(2\pi/3)^{1/2}rY_{1,\pm1}$, with $\mu_0 = \mu_z$ and $\mu_{\pm1} = \mp(\mu_x \pm \mathrm{i}\mu_y)/\sqrt{2}$, it is equal to $-2(\pi/3)^{1/2}e$.] Then

$$\langle n'l'm_l'|\mu_m|nlm_l\rangle \propto \int_0^\infty R_{n'l'}R_{nl}r^3\mathrm{d}r\int Y_{l'm_l'}^{*}Y_{1m}Y_{lm_l}\sin\theta\mathrm{d}\theta\mathrm{d}\phi$$

Because

$$Y_{l'm_l'}^{*}Y_{1m}Y_{lm_l} \propto \exp\{\mathrm{i}(m_l+m-m_l')\phi\}$$

the integral vanishes unless $m_l' = m_l + m$; therefore $\Delta m_l = m = 0, \pm1$. Since the spherical harmonics are bases for $\Gamma^{(l')}$, $\Gamma^{(1)}$, and $\Gamma^{(l)}$ in R_3, their product is a basis for the totally symmetric irreducible representation only if $(l', 1, l)$ satisfies the triangle condition. Hence $l' = l, l \pm 1$. The parity of Y_{1m} under inversion is -1. Therefore $Y_{l'm_l'}$ and Y_{lm_l} must be of mutually opposite parity. Consequently $l' = l$ is excluded, and we conclude that $\Delta l = \pm1$. There is no symmetry constraint on the r-integration, and the radial integral is nonzero for all values of $n' - n$. [There are symmetry properties of radial integrals—recall the high, hidden symmetry of the Coulomb potential: see M.J. Englefield, *Group theory and the Coulomb problem*, Wiley-Interscience (1972).]

Exercise: Establish the selection rules for the electric quadrupole transitions of atoms. [The transition operators are proportional to the quadratic forms xx, xy, etc., which themselves are proportional to the Y_{2m}.]

7.4

$$hc\zeta_{nl} = \hbar^2\int_0^\infty \xi(r)R_{nl}^2(r)r^2\mathrm{d}r \quad \text{[eqn 7.15]}$$

$$= (Ze^2\hbar^2/8\pi\varepsilon_0 m_\mathrm{e}^2c^2)\int_0^\infty (1/r)R_{nl}^2(r)\mathrm{d}r \quad \text{[eqn 7.16]}$$

$$= (Ze^2\hbar^2/8\pi\varepsilon_0 m_\mathrm{e}^2c^2)\{Z^3/a_0^3n^3l(l+\tfrac{1}{2})(l+1)\}$$

[Use the values of $\langle 1/r^3\rangle$ quoted in the solution of Exercise 3.19.]

Exercise: Find a relation between $\langle 1/r^3\rangle$ and $1/\langle r\rangle^3$ for an electron in a hydrogenic orbital.

7.7

$$E_{\mathrm{so}}(j) - E_{\mathrm{so}}(j-1) = \tfrac{1}{2}hc\zeta_{nl}\{j(j+1) - (j-1)j\}$$

$$= jhc\zeta_{nl}$$

Exercise: Show that the difference of the squares of neighbouring level energies is proportional to j^3.

7.10 $\langle nlm_l|H^{(1)}|nlm_l\rangle = -(1/2\mu c^2)\langle nlm_l|(E_{nlm_l} - V)^2|nlm_l\rangle$

$$= -(1/2\mu c^2)\langle nlm_l|\,E^2_{nlm_l} + V^2 - 2VE_{nlm_l}|nlm_l\rangle$$

$$= -(1/2\mu c^2)\,\{E^2_{nlm_l} + \langle nlm_l|V^2|nlm_l\rangle - 2\langle nlm_l|V|nlm_l\rangle E_{nlm_l}\}$$

From the virial theorem

$$\langle E\rangle = \langle T\rangle + \langle V\rangle = (\tfrac{1}{2}s + 1)\langle V\rangle = \tfrac{1}{2}\langle V\rangle \quad [s = -1 \text{ for } V \propto 1/r]$$

Consequently

$$\langle nlm_l|H^{(1)}|nlm_l\rangle = -(1/2\mu c^2)\{\langle nlm_l|V^2|nlm_l\rangle - 3E^2_{nlm_l}\}$$

$$V^2 = (e^2/4\pi\varepsilon_0)^2(1/r^2);\; E^2_{nlm_l} = (hc\mathcal{R}_{\mathrm{H}})^2/n^4$$

$$\langle nlm_l|(1/r^2)|nlm_l\rangle = (1/a^2)\{1/(l + \tfrac{1}{2})\,n^3)\}$$

[See L. Pauling and E.B. Wilson, *Introduction to quantum mechanics*, McGraw-Hill (1935), p.145, for values of $\langle 1/r^p\rangle$.]

$$\langle nlm_l|H^{(1)}|nlm_l\rangle = -(1/2\mu c^2)\left\{\frac{(e^2/4\pi\varepsilon_0 a)^2}{(l+\frac{1}{2})n^3} - \frac{3(hc\mathrm{R}_\mathrm{H})^2}{n^4}\right\}$$

$$= -\tfrac{1}{2}\,\alpha^4\mu c^2\left\{\frac{1}{(l+\frac{1}{2})n^3} - \frac{3}{4n^4}\right\}$$

For the ground state ($n = 1$, $l = 0$):

$$E^{(1)} = \langle 100|H^{(1)}|100\rangle = -\tfrac{5}{8}\,\alpha^4\mu c^2 = \underline{-1.450\times 10^{-22}\ \mathrm{J}}\ (-7.299\ \mathrm{cm}^{-1})$$

Exercise: Find the first-order relativistic correction to the energy of a harmonic oscillator.

7.13 Consider a two-electron system involving two orthonormal spinorbitals φ_a and φ_b; for simplicity of notation, these will be denoted a and b. Explicit expansion of the Slater determinant (eqn 7.42a) yields

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\{a(1)b(2) - a(2)b(1)\}$$

Now consider the one- and two-electron operators in eqn 7.43. To confirm the Condon-Slater rules given in eqns 7.44 and 7.45, keep in mind that

$$\langle a(1)|a(1)\rangle = \langle a(2)|a(2)\rangle = \langle b(1)|b(1)\rangle = \langle b(2)|b(2)\rangle = 1$$

$$\langle a(1)|b(1)\rangle = \langle a(2)|b(2)\rangle = \langle b(1)|a(1)\rangle = \langle b(2)|a(2)\rangle = 0$$

First, consider the one-electron operator $\Omega_1 = \Omega(1) + \Omega(2)$.

$$\begin{aligned}\langle\Psi|\Omega_1|\Psi\rangle &= \frac{1}{2}\langle a(1)b(2)-a(2)b(1)|\Omega(1)+\Omega(2)|a(1)b(2)-a(2)b(1)\rangle \\ &= \frac{1}{2}\{\langle a(1)|\Omega(1)|a(1)\rangle+\langle a(2)|\Omega(2)|a(2)\rangle+\langle b(1)|\Omega(1)|b(1)\rangle \\ &+\langle b(2)|\Omega(2)|b(2)\rangle\} = \langle a(1)|\Omega(1)|a(1)\rangle+\langle b(1)|\Omega(1)|b(1)\rangle\end{aligned}$$

which is eqn 7.44a. The last line above follows from the indistinguishability of electrons 1 and 2 so that, for example,

$$\langle a(1)|\Omega(1)|a(1)\rangle = \langle a(2)|\Omega(2)|a(2)\rangle$$

For the two-electron operator $\Omega_2 = \Omega(1,2)$:

$$\begin{aligned}\langle\Psi|\Omega_2|\Psi\rangle &= \frac{1}{2}\langle a(1)b(2)-a(2)b(1)|\Omega(1,2)|a(1)b(2)-a(2)b(1)\rangle \\ &= \frac{1}{2}\{\langle a(1)b(2)|\Omega(1,2)|a(1)b(2)\rangle+\langle a(2)b(1)|\Omega(1,2)|a(2)b(1)\rangle \\ &-\langle a(1)b(2)|\Omega(1,2)|a(2)b(1)\rangle-\langle a(2)b(1)|\Omega(1,2)|a(1)b(2)\rangle\}\end{aligned}$$

which is eqn 7.45a. The other Condon-Slater rules involve one-electron and two-electron-excited state wavefunctions. Consider first the one-electron-excited state wavefunction:

$$\Psi_b^c(1,2) = \frac{1}{\sqrt{2}}\{a(1)c(2)-a(2)c(1)\}$$

The one-electron integral is (recalling the orthonormality of all spinorbitals)

$$\begin{aligned}\langle\Psi|\Omega_1|\Psi_b^c\rangle &= \frac{1}{2}\langle a(1)b(2)-a(2)b(1)|\Omega(1)+\Omega(2)|a(1)c(2)-a(2)c(1)\rangle \\ &= \frac{1}{2}\{\langle b(2)|\Omega(2)|c(2)\rangle+\langle b(1)|\Omega(1)|c(1)\rangle = \langle b(1)|\Omega(1)|c(1)\rangle\end{aligned}$$

which is eqn 7.44b. The two-electron integral is

$$\begin{aligned}\langle\Psi|\Omega_2|\Psi_b^c\rangle &= \frac{1}{2}\langle a(1)b(2)-a(2)b(1)|\Omega(1,2)|a(1)c(2)-a(2)c(1)\rangle \\ &= \frac{1}{2}\{\langle a(1)b(2)|\Omega(1,2)|a(1)c(2)\rangle+\langle a(2)b(1)|\Omega(1,2)|a(2)c(1)\rangle \\ &-\langle a(1)b(2)|\Omega(1,2)|a(2)c(1)\rangle-\langle a(2)b(1)|\Omega(1,2)|a(1)c(2)\rangle\} \\ &= \langle a(2)b(1)|\Omega(1,2)|a(2)c(1)\rangle-\langle a(2)b(1)|\Omega(1,2)|a(1)c(2)\rangle\end{aligned}$$

which is eqn 7.45b, the last line following from the indistinguishability of electrons 1 and 2. The last of the Condon-Slater rules involves the two-electron-excited state wavefunction

$$\Psi_{ab}^{cd}(1,2) = \frac{1}{\sqrt{2}}\{c(1)d(2) - c(2)d(1)\}$$

The two-electron integral is

$$\begin{aligned}\langle\Psi|\Omega_2|\Psi_{ab}^{cd}\rangle &= \frac{1}{2}\langle a(1)b(2) - a(2)b(1)|\Omega(1,2)|c(1)d(2) - c(2)d(1)\rangle \\ &= \frac{1}{2}\{\langle a(1)b(2)|\Omega(1,2)|c(1)d(2)\rangle + \langle a(2)b(1)|\Omega(1,2)|c(2)d(1)\rangle \\ &- \langle a(1)b(2)|\Omega(1,2)|c(2)d(1)\rangle - \langle a(2)b(1)|\Omega(1,2)|c(1)d(2)\rangle\} \\ &= \langle a(1)b(2)|\Omega(1,2)|c(1)d(2)\rangle - \langle a(1)b(2)|\Omega(1,2)|c(2)d(1)\rangle\end{aligned}$$

which is eqn 7.45c.

7.16 ${}^1E - {}^3E = (E_a + E_b + J + K) - (E_a + E_b + J - K) = 2K$ [eqn 7.37]

$$\{{}^1E(1s^12s^1) - {}^3E(1s^12s^1)\}/hc = (166\,272 - 159\,850)\ \text{cm}^{-1} = 6422\ \text{cm}^{-1}$$

Therefore,

$$K_{1s^12s^1}/hc = \underline{3211\ \text{cm}^{-1}} \quad (0.3981\ \text{eV})$$

$$\{{}^1E(1s^13s^1) - {}^3E(1s^13s^1)\}/hc = (184\,859 - 183\,231)\ \text{cm}^{-1} = 1628\ \text{cm}^{-1}$$

Therefore,

$$K_{1s^13s^1}/hc = \underline{814\ \text{cm}^{-1}}(0.1009\ \text{eV})$$

Exercise: The terms of Li^+ lie at 491 361 cm^{-1}($1s^1\ 2s^1\ {}^1S$), 476 046 cm^{-1} ($1s^12s^1\ {}^3S$), 554 761 cm^{-1}($1s^1\ 3s^1\ {}^3S$), and 558 779 cm^{-1}($1s^13s^1\ {}^1S$). Find $K_{1s^12s^1}$ and $K_{1s^13s^1}$ and suggest reasons why they differ from those for He.

7.19

$$\psi = (1/4!)^{1/2}\begin{vmatrix} 1\mathrm{s}(1) & 1\bar{\mathrm{s}}(1) & 2\mathrm{s}(1) & 2\bar{\mathrm{s}}(1) \\ 1\mathrm{s}(2) & 1\bar{\mathrm{s}}(2) & 2\mathrm{s}(2) & 2\bar{\mathrm{s}}(2) \\ 1\mathrm{s}(3) & 1\bar{\mathrm{s}}(3) & 2\mathrm{s}(3) & 2\bar{\mathrm{s}}(3) \\ 1\mathrm{s}(4) & 1\bar{\mathrm{s}}(4) & 2\mathrm{s}(4) & 2\bar{\mathrm{s}}(4) \end{vmatrix}$$

where 1s and 2s denote α spin-orbitals and $1\,\bar{\mathrm{s}}$ and $2\,\bar{\mathrm{s}}$ denote β spin-orbitals.

$$\langle \| 1\mathrm{s}(1) \ldots 2\,\bar{\mathrm{s}}\,(4) \| | H | \| 1s(1) \ldots 2\,\bar{\mathrm{s}}\,(4) \| \rangle$$

$$= (1/4!)^{1/2}\langle [1\mathrm{s}(1)1\,\bar{\mathrm{s}}\,(2)2\mathrm{s}(3)2\,\bar{\mathrm{s}}\,(4)] - [1\mathrm{s}(1)1\,\bar{\mathrm{s}}\,(2)2\,\bar{\mathrm{s}}\,(3)2\mathrm{s}(4)]$$

$$- [1\mathrm{s}(1)2\mathrm{s}(2)1\,\bar{\mathrm{s}}\,(3)2\,\bar{\mathrm{s}}\,(4)] + [1\mathrm{s}(1)2\mathrm{s}(2)2\,\bar{\mathrm{s}}\,(3)1\,\bar{\mathrm{s}}\,(4)]$$

$$+ [1\mathrm{s}(1)2\,\bar{\mathrm{s}}\,(2)1\,\bar{\mathrm{s}}\,(3)2\mathrm{s}(4)] - [1\mathrm{s}(1)2\,\bar{\mathrm{s}}\,(2)2\mathrm{s}(3)1\,\bar{\mathrm{s}}\,(4)]$$

$$- [1\,\bar{\mathrm{s}}\,(1)1\mathrm{s}(2)2\mathrm{s}(3)2\,\bar{\mathrm{s}}\,(4)] + [1\,\bar{\mathrm{s}}\,(1)1\mathrm{s}(2)2\,\bar{\mathrm{s}}\,(3)2\mathrm{s}(4)]$$

$$+ [1\,\bar{\mathrm{s}}\,(1)2\mathrm{s}(2)1\mathrm{s}(3)2\,\bar{\mathrm{s}}\,(4)] - [1\,\bar{\mathrm{s}}\,(1)2\mathrm{s}(2)2\,\bar{\mathrm{s}}\,(3)1\mathrm{s}(4)]$$

$$- [1\,\bar{\mathrm{s}}\,(1)2\,\bar{\mathrm{s}}\,(2)1\mathrm{s}(3)2\mathrm{s}(4)] + [1\,\bar{\mathrm{s}}\,(1)2\,\bar{\mathrm{s}}\,(2)2\mathrm{s}(3)1\mathrm{s}(4)]$$

$$+ [2\mathrm{s}(1)1\mathrm{s}(2)1\,\bar{\mathrm{s}}\,(3)2\,\bar{\mathrm{s}}\,(4)] - [2\mathrm{s}(1)1\mathrm{s}(2)2\,\bar{\mathrm{s}}\,(3)1\,\bar{\mathrm{s}}\,(4)]$$

$$- [2\mathrm{s}(1)1\,\bar{\mathrm{s}}\,(2)1\mathrm{s}(3)2\,\bar{\mathrm{s}}\,(4)] + [2\mathrm{s}(1)1\,\bar{\mathrm{s}}\,(2)2\,\bar{\mathrm{s}}\,(3)1\mathrm{s}(4)]$$

$$+ [2\mathrm{s}(1)2\,\bar{\mathrm{s}}\,(2)1\mathrm{s}(3)1\,\bar{\mathrm{s}}\,(4)] - [2\mathrm{s}(1)2\,\bar{\mathrm{s}}\,(2)1\,\bar{\mathrm{s}}\,(3)1\mathrm{s}(4)]$$

$$- [2\,\bar{\mathrm{s}}\,(1)1\mathrm{s}(2)1\,\bar{\mathrm{s}}\,(3)2\mathrm{s}(4)] + [2\,\bar{\mathrm{s}}\,(1)1\mathrm{s}(2)2\mathrm{s}(3)1\,\bar{\mathrm{s}}\,(4)]$$

$$+ [2\,\bar{\mathrm{s}}\,(1)1\,\bar{\mathrm{s}}\,(2)1\mathrm{s}(3)2\mathrm{s}(4)] - [2\,\bar{\mathrm{s}}\,(1)1\,\bar{\mathrm{s}}\,(2)2\mathrm{s}(3)1\mathrm{s}(4)]$$

$$- [2\,\bar{\mathrm{s}}\,(1)2\mathrm{s}(2)1\mathrm{s}(3)1\,\bar{\mathrm{s}}\,(4)] + [2\,\bar{\mathrm{s}}\,(1)2\mathrm{s}(2)1\,\bar{\mathrm{s}}\,(3)1\mathrm{s}(4)]$$

$$\times [T_1 + T_2 + T_3 + T_4 + V_1 + V_2 + V_3 + V_4 + V_{12} + V_{13} + V_{14} + V_{23} + V_{24} + V_{34}]$$

$$\times \det |1s(1) \ldots 2\bar{s}(4)|\rangle$$

$$= \underline{2E_{1s} + 2E_{2s} + \langle 1s(1)1s(2)\,|V_{12}|\,1s(1)1s(2)\rangle}$$

$$\underline{+4\langle 1s(1)2s(2)\,|V_{12}|\,1s(1)2s(2)\rangle}$$

$$\underline{+\langle 2s(1)2s(2)\,|V_{12}|\,2s(1)2s(2)\rangle}$$

$$\underline{-2\langle 1s(1)2s(2)\,|V_{12}|\,2s(1)1s(2)\rangle}$$

[many terms are identical in value], with

$$\langle 1s(1)1s(2)|V_{12}|1s(1)1s(2)\rangle = j_0 \int \psi_{1s}^2(1)(1/r_{12})\psi_{1s}^2(2)\,d\tau_1 d\tau_2$$

$$[j_0 = +e^2/4\pi\varepsilon_0]$$

$$\langle 1s(1)2s(2)|V_{12}|1s(1)2s(2)\rangle = j_0 \int \psi_{1s}^2(1)(1/r_{12})\psi_{2s}^2(2)\,d\tau_1 d\tau_2$$

$$\langle 2s(1)2s(2)|V_{12}|2s(1)2s(2)\rangle = j_0 \int \psi_{2s}^2(1)(1/r_{12})\psi_{2s}^2(2)\,d\tau_1 d\tau_2$$

$$\langle 1s(1)2s(2)|V_{12}|2s(1)1s(2)\rangle = j_0 \int \psi_{1s}(1)\psi_{2s}(1)(1/r_{12})\psi_{1s}(2)\psi_{2s}(2)\,d\tau_1 d\tau_2$$

In terms of the Hartree–Fock expressions [eqn 7.49]:

$$E = 2E_{1s} + 2E_{2s} + \{(2J_{1s1s} - K_{1s1s}) + (2J_{2s2s} - K_{2s2s})$$

$$+ (2J_{1s2s} - K_{1s2s}) + (2J_{2s1s} - K_{2s1s})\}$$

$$= 2E_{1s} + 2E_{2s} + \{J_{1s1s} + J_{2s2s} + 4J_{1s2s} - 2K_{1s2s}\}$$

$$= \underline{2E_{1s} + 2E_{2s}}$$

$$+\ \underline{\langle 1s(1)1s(2)\,|V_{12}|\,1s(1)1s(2)\rangle + \langle 2s(1)2s(2)\,|V_{12}|\,2s(1)2s(2)\rangle}$$

$$+\ \underline{4\langle 1s(1)2s(2)\,|V_{12}|\,1s(1)2s(2)\rangle - 2\langle 1s(1)2s(2)\,|V_{12}|\,2s(1)1s(2)\rangle}$$

as before.

Exercise: Find an expression for the (Hartree–Fock) energy of Ne and for its first ionization energy.

7.22 In the Thomas-Fermi method (see eqns 7.58-59),

$$\mu = \frac{5}{3}C\rho(\boldsymbol{r})^{2/3} - j_0\frac{Z}{r} + j_0\int \frac{\rho(\boldsymbol{r}_1)}{|\boldsymbol{r}-\boldsymbol{r}_1|}\mathrm{d}\boldsymbol{r}_1$$

To impose the additional constraint

$$j_0\int \mathrm{e}^{-2kr}\nabla^2\,\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \, < \, \infty$$

we introduce a Lagrange multiplier λ for the additional constraint, producing

$$\mu = \frac{5}{3}C\rho(\boldsymbol{r})^{2/3} - j_0\frac{Z}{r} + j_0\int \frac{\rho(\boldsymbol{r}_1)}{|\boldsymbol{r}-\boldsymbol{r}_1|}\mathrm{d}\boldsymbol{r}_1 - \lambda j_0\nabla^2\,(\mathrm{e}^{-2kr})$$

Since (see *Further information* 14.1 and the steps leading to eqn 14.112)

$$\nabla^2(\mathrm{e}^{-2kr}) = 4k^2\mathrm{e}^{-2kr} - \frac{4k\mathrm{e}^{-2kr}}{r}$$

we find, by setting $4k\lambda = Z$,

$$\begin{aligned}\mu = \frac{5}{3}C\rho(\boldsymbol{r})^{2/3} - j_0\frac{Z}{r}&\\ &+ j_0\int \frac{\rho(\boldsymbol{r}_1)}{|\boldsymbol{r}-\boldsymbol{r}_1|}\mathrm{d}\boldsymbol{r}_1 - \frac{Zj_0}{4k}\left(4k^2\mathrm{e}^{-2kr} - \frac{4k\mathrm{e}^{-2kr}}{r}\right)\\ &= \frac{5}{3}C\rho(\boldsymbol{r})^{2/3} - j_0\frac{Z}{r}(1-\mathrm{e}^{-2kr}) + j_0\int \frac{\rho(\boldsymbol{r}_1)}{|\boldsymbol{r}-\boldsymbol{r}_1|}\mathrm{d}\boldsymbol{r}_1 - Zj_0k\,\mathrm{e}^{-2kr}\end{aligned}$$

The presence of the term $(1 - \mathrm{e}^{-2kr})$ removes the singularity at $r = 0$.

Chapter 8

An introduction to molecular structure

Exercises

8.1 Substitution of the trial wavefunction $\psi\psi_{\mathrm{N}}$ into eqn 8.2, and using eqn 8.1b, yields

$$(T_{\mathrm{e}} + T_{\mathrm{N}} + V)\psi\psi_{\mathrm{N}} = E\psi\psi_{\mathrm{N}}$$

Since the nuclear wavefunction does not depend on electronic coordinates whereas the electronic wavefunction depends (parametrically) on nuclear coordinates, we can write

$$(\psi_{\mathrm{N}}T_{\mathrm{e}}\psi + T_{\mathrm{N}}\psi\psi_{\mathrm{N}} + V\psi\psi_{\mathrm{N}}) = E\psi\psi_{\mathrm{N}}$$

Consider the term $T_{\mathrm{N}}\psi\psi_{\mathrm{N}}$.

$$\begin{aligned} T_{\mathrm{N}}\psi\psi_{\mathrm{N}} &= -\sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\frac{\partial}{\partial Z_I}\frac{\partial}{\partial Z_I}\psi\psi_{\mathrm{N}} = -\sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\frac{\partial}{\partial Z_I}\psi\frac{\partial\psi_{\mathrm{N}}}{\partial Z_I} - \sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\frac{\partial}{\partial Z_I}\psi_{\mathrm{N}}\frac{\partial\psi}{\partial Z_I} \\ &= -2\sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\frac{\partial\psi}{\partial Z_I}\frac{\partial\psi_{\mathrm{N}}}{\partial Z_I} - \sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\psi\frac{\partial^2\psi_{\mathrm{N}}}{\partial Z_I^2} - \sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\psi_{\mathrm{N}}\frac{\partial^2\psi}{\partial Z_I^2} \\ &= W + \psi T_{\mathrm{N}}\psi_{\mathrm{N}} \end{aligned}$$

where we have used the definition of W in the equation following eqn 8.4. We therefore obtain

$$(\psi_{\mathrm{N}}T_{\mathrm{e}}\psi + W + \psi T_{\mathrm{N}}\psi_{\mathrm{N}} + V\psi\psi_{\mathrm{N}}) = E\psi\psi_{\mathrm{N}}$$

which is eqn 8.4.

8.2 The Schrödinger equation for the total wavefunction Ψ of the hydrogen molecule-ion is

$$-\frac{\hbar^2}{2m_e}\nabla_e^2\Psi - \sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\nabla_I^2\Psi + V\Psi = E\Psi$$

where the laplacian in the first (second) term is with respect to electronic (nuclear) coordinates and the potential energy V is given by

$$V = \frac{e^2}{4\pi\varepsilon_0|\boldsymbol{R}_1 - \boldsymbol{R}_2|} - \sum_{I=1}^{2}\frac{e^2}{4\pi\varepsilon_0|\boldsymbol{r}_e - \boldsymbol{R}_I|}$$

The Schrödinger equation for the electronic wavefunction ψ, within the Born-Oppenheimer approximation, is

$$-\frac{\hbar^2}{2m_e}\nabla_e^2\psi + V\psi = E_e\psi$$

and that for the nuclear wavefunction ψ_N is

$$-\sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\nabla_I^2\psi_N + E_e\psi_N = E\psi_N$$

8.3 The secular determinant is given in Section 8.3(a), immediately preceding eqn 8.16. Expanding the determinant yields

$$(\alpha - E)(\alpha - E) - (\beta - ES)(\beta - ES) = 0$$

Therefore

$$(\alpha - E)^2 = (\beta - ES)^2$$

with roots

$$\alpha - E = \beta - ES \quad \Rightarrow \quad E_- = \frac{\alpha - \beta}{(1-S)}$$

$$\alpha - E = -(\beta - ES) \quad \Rightarrow \quad E_+ = \frac{\alpha + \beta}{(1+S)}$$

To find the coefficients c_A and c_B, we use eqn 8.14. For energy E_-,

$$c_A(\alpha - E_-) + c_B(\beta - E_- S) = 0$$

$$c_A\left(\frac{\alpha - \alpha S}{(1-S)} - \frac{\alpha - \beta}{(1-S)}\right) + c_B\left(\frac{\beta - \beta S}{(1-S)} - \frac{\alpha S - \beta S}{(1-S)}\right) = 0$$

$$c_A(\beta - \alpha S) + c_B(\beta - \alpha S) = 0$$

$$c_A = -c_B$$

and requiring that the wavefunction $c_A(\chi_A - \chi_B)$ be normalized yields:

$$\int c_A^2(\chi_A^2 - 2\chi_A\chi_B + \chi_B^2)\mathrm{d}\tau = 1$$

$$c_A^2(1 - 2S + 1) = 1$$

$$c_A = \frac{1}{\sqrt{2(1-S)}}$$

Similarly for energy E_+,

$$c_A(\alpha - E_+) + c_B(\beta - E_+ S) = 0$$

$$c_A\left(\frac{\alpha + \alpha S}{(1+S)} - \frac{\alpha + \beta}{(1+S)}\right) + c_B\left(\frac{\beta + \beta S}{(1+S)} - \frac{\alpha S + \beta S}{(1+S)}\right) = 0$$

$$c_A(\alpha S - \beta) + c_B(\beta - \alpha S) = 0$$

$$c_A = c_B$$

and requiring that the wavefunction $c_A(\chi_A + \chi_B)$ be normalized yields:

$$\int c_A^2(\chi_A^2 + 2\chi_A\chi_B + \chi_B^2)\mathrm{d}\tau = 1$$

$$c_A^2(1 + 2S + 1) = 1$$

$$c_A = \frac{1}{\sqrt{2(1+S)}}$$

8.4 First, since each electron is in a σ-orbital, $\lambda_1 = \lambda_2 = 0$, so $\Lambda = 0$, corresponding to a Σ term.

Second, with regard to the overall parity of the state, since g × u = u, the term must be u parity.

Third, if the two electrons have opposite spins, the term has $S = 0$ and is a singlet (multiplicity of 1); if the two electrons have the same spins, the term has $S = 0$ and is

a triplet (multiplicity of 3).

Finally, each σ-orbital has a character of +1 under reflection in a plane that contains the internuclear axis and since (+1) × (+1) = +1, the term includes a right superscript of +.

As a result, the terms that arise are ${}^1\Sigma_u^+$ and ${}^3\Sigma_u^+$.

8.5

$$\Psi\left(1,2;{}^1\Sigma_u^+\right) = \left(\tfrac{1}{2}\right)^{1/2}\{\psi_+(1)\psi_-(2) + \psi_+(2)\psi_-(1)\}\sigma_-(1,2)$$
$$\Psi\left(1,2;{}^3\Sigma_u^+\right) = \left(\tfrac{1}{2}\right)^{1/2}\{\psi_+(1)\psi_-(2) - \psi_+(2)\psi_-(1)\}\sigma_+(1,2)$$

where ψ_+ and ψ_- are defined in eqns 8.24(a) and 8.24(b) and the spin states σ_- and σ_+ are defined in Section 7.11. Note that there are three possible σ_+ states corresponding to values of M_S of +1, 0 or −1.

8.6 The question refers to the orbital part of $c_1\Psi_1 + c_3\Psi_3$ which we denote ψ. Noting, and therefore ignoring, the spin factors that are common to Ψ_1 and Ψ_3, we obtain, denoting $a = \chi_A$, $b = \chi_B$, and $1\sigma = (a+b)/\sqrt{2}$, $2\sigma = (a-b)/\sqrt{2}$]

$$\psi = c_1 1\sigma(1)1\sigma(2) + c_3 2\sigma(1)2\sigma(2)$$
$$= \tfrac{1}{2}c_1\{a(1)+b(1)\}\{a(2)+b(2)\} + \tfrac{1}{2}c_3\{a(1)-b(1)\}\{a(2)-b(2)\}$$

$$= \tfrac{1}{2}c_1\{a(1)a(2) + b(1)b(2) + a(1)b(2) + b(1)a(2)\}$$

$$+ \tfrac{1}{2}c_3\{a(1)a(2) + b(1)b(2) - a(1)b(2) - b(1)a(2)\}$$

$$= \tfrac{1}{2}(c_1 + c_3)\{a(1)a(2) + b(1)b(2)\} + \tfrac{1}{2}(c_1 - c_3)\{a(1)b(2) + b(1)a(2)\}$$

as in eqn 8.30.

8.7 Expansion of the secular determinant in eqn 8.32 and setting the overlap S to zero yields

$$(\alpha_A - E)(\alpha_B - E) - \beta^2 = 0$$

which produces the following quadratic energy for the energy:

$$E^2 + E(-\alpha_A - \alpha_B) + (\alpha_A\alpha_B - \beta^2) = 0$$

The roots to the above equation are

$$E = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\sqrt{(\alpha_A + \alpha_B)^2 - 4(\alpha_A\alpha_B - \beta^2)}$$

$$= \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2}$$

$$= \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\sqrt{(\alpha_A - \alpha_B)^2\left\{1 + \frac{4\beta^2}{(\alpha_A - \alpha_B)^2}\right\}}$$

$$= \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}|\alpha_A - \alpha_B|\sqrt{1 + 4\beta^2/(\alpha_A - \alpha_B)^2}$$

When the two orbitals have greatly differing energies, $|\alpha_A - \alpha_B| >> \beta$, and using the approximation $(1 + x)^{1/2} = 1 + \frac{1}{2}x$, we obtain

$$E = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}|\alpha_A - \alpha_B|\left\{1 + \frac{2\beta^2}{(\alpha_A - \alpha_B)^2}\right\}$$

$$= \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}|\alpha_A - \alpha_B| \pm \frac{\beta^2}{|\alpha_A - \alpha_B|}$$

With α_B greater than α_A, we have the roots

$$E_+ = \alpha_B + \frac{\beta^2}{|\alpha_A - \alpha_B|}$$

$$E_- = \alpha_A - \frac{\beta^2}{|\alpha_A - \alpha_B|}$$

as in eqn 8.33.

8.8 Refer to Fig. 8.18 of the text.

(a) $C_2 : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4,\ {}^1\Sigma_g^+$

(b) $C_2^+ : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^3,\ {}^2\Pi_u$

(c) $C_2^- : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^1,\ {}^2\Sigma_g^+$

(d) $N_2^+ : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^1,\ {}^2\Sigma_g^+$

(e) $N_2^- : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2 1\pi_g^{*1},\ {}^2\Pi_g$

(f) $F_2^+ : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2 1\pi_g^{*3},\ {}^2\Pi_g$

(g) $Ne_2^+ : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2 1\pi_g^{*4} 2\sigma_u^{*1},\ {}^2\Sigma_u^+$

where the superscript * indicates an antibonding molecular orbital.

Exercise: Predict the ground configurations of Na_2, S_2 and HCl and decide which terms lie lowest.

8.9 We use the results of Exercise 8.8; only the molecular orbitals formed from the $n = 2$ atomic orbitals need be considered since the lower energy molecular orbitals (from $n = 1$ atomic orbitals) are completely filled and thus have equal number of bonding and antibonding electrons. In Exercise 8.8, the antibonding molecular orbitals are designated with a * superscript.

(a) C_2: bond order $= \frac{1}{2}(6 - 2) = 2$ HOMO $= 1\pi_u$; LUMO $= 2\sigma_g$

(b) C_2^+ : bond order = $\frac{1}{2}(5 - 2) = 1.5$ HOMO = $1\pi_u$; LUMO = $2\sigma_g$

(c) C_2^- : bond order = $\frac{1}{2}(7 - 2) = 2.5$ HOMO = $2\sigma_g$; LUMO = $1\pi_g$

(d) N_2^+ : bond order = $\frac{1}{2}(7 - 2) = 2.5$ HOMO = $2\sigma_g$; LUMO = $1\pi_g$

(e) N_2^- : bond order = $\frac{1}{2}(8 - 3) = 2.5$ HOMO = $1\pi_g$; LUMO = $2\sigma_u$

(f) F_2^+ : bond order = $\frac{1}{2}(8 - 5) = 1.5$ HOMO = $1\pi_g$; LUMO = $2\sigma_u$

(g) Ne_2^+ : bond order = $\frac{1}{2}(8 - 7) = 0.5$ HOMO = $2\sigma_u$; LUMO = $3\sigma_g$

Exercise: Find the bond orders of the dications C_2^{2+} and F_2^{2+} as well as the dianions C_2^{2-} and F_2^{2-}.

8.10 The secular determinant for the cyclopropenyl radical is

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$

Expanding the determinant results in the following cubic equation:

$$(\alpha - E)^3 - 3(\alpha - E)\beta^2 + 2\beta^3 = 0$$

which, with $x = \alpha - E$, can be written as

$$x^3 - 3\beta^2 x + 2\beta^3 = 0$$

$$(x - \beta)^2(x + 2\beta) = 0$$

Therefore, roots are $x = \beta, \beta, -2\beta$. The energy levels are $E = \alpha - \beta, \alpha - \beta, \alpha + 2\beta$. The total π-electron energy is $2(\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta$ and the delocalization energy is

$$E_{\text{deloc}} = 3\alpha + 3\beta - 3(\alpha + \beta) = 0$$

and the radical is not predicted to be stable.

8.11 The Hückel molecular orbital energy level diagram for benzene is shown in Fig. 8.30 of the text. Whereas benzene has six π-electrons, its cation has five and its dianion has eight. To compute the delocalization energy, recall that each π-electron in an *unconjugated* system contributes an energy of $\alpha + \beta$.

(a) The benzene cation has a ground-state electron configuration

$a_{2u}^2 e_{1g}^3$ and a total π-electron energy of $2(\alpha + 2\beta) + 3(\alpha + \beta) = 5\alpha + 7\beta$. Therefore the delocalization energy is

$$5\alpha + 7\beta - 5(\alpha + \beta) = \underline{2\beta}$$

(b) The benzene dianion has a ground-state electron configuration

$a_{2u}^2 e_{1g}^4 e_{2u}^2$ and a total π-electron energy of $2(\alpha + 2\beta) + 4(\alpha + \beta) + 2(\alpha - \beta) = 8\alpha + 6\beta$.

Therefore the delocalization energy is

$$8\alpha + 6\beta - 8(\alpha + \beta) = \underline{-2\beta}$$

and the dianion is predicted to be unstable.

Exercise: Repeat the problem for $C_4H_4^+$ and $C_4H_4^{2-}$.

8.12

Complex	Number unpaired electrons	S_{TOT}	Multiplicity
d^4	2	1	3
d^5	1	½	2
d^6	0	0	1
d^7	1	½	2

8.13

Complex	Number unpaired electrons	S_{TOT}	Multiplicity
d^4	4	2	5
d^5	5	5/2	6

8.14 **(a)** In a tetrahedral environment (symmetry group T_d), the d-orbitals span E(d_{z^2}, $d_{x^2-y^2}$) and T_2(d_{xy}, d_{xz}, d_{yz}). [Refer to the T_d character table; $d_{xy} \propto xy$ etc.]

Exercise: Determine which symmetry species are spanned by the f-orbitals in a tetrahedral complex.

(b) See Problem 5.16(b) in Chapter 5. The symmetry species spanned by f-orbitals in the rotational subgroup T are A + 2T.

8.15 From Section 8.11, we have the following two equations:

(a) $u_k(x) = A\mathrm{e}^{\mathrm{i}(\alpha-k)x} + B\mathrm{e}^{-\mathrm{i}(\alpha+k)x}$

(b) $u_k(x) = C\mathrm{e}^{(\beta-\mathrm{i}k)x} + D\mathrm{e}^{-(\beta+\mathrm{i}k)x}$

Differentiation of the above equatioins produces

(a) $u'_k(x) = \mathrm{i}A(\alpha-k)\mathrm{e}^{\mathrm{i}(\alpha-k)x} - \mathrm{i}B(\alpha+k)\mathrm{e}^{-\mathrm{i}(\alpha+k)x}$

(b) $u'_k(x) = C(\beta-\mathrm{i}k)\mathrm{e}^{(\beta-\mathrm{i}k)x} - D(\beta+\mathrm{i}k)\mathrm{e}^{-(\beta+\mathrm{i}k)x}$

The conditions $u_k(a) = u_k(-b)$ and $u'_k(a) = u'_k(-b)$ then lead to the four statements in Section 8.11 of the text, and hence to the determinant in eqn 8.44. For the equivalence to eqn 8.45, use symbolic algebra software.

Problems

8.1

$$j'/j_0 = (1/R)\,\{1-(1+s)\mathrm{e}^{-2s}\}, \quad s = R/a_0,\ j_0 = e^2/4\pi\varepsilon_0$$

$$k'/j_0 = (1/a_0)\{1+s\}\mathrm{e}^{-s}, \quad S = \{1+s+\tfrac{1}{3}s^2\}\mathrm{e}^{-s}$$

$$E_+ - E_{1s} = j_0/R - (j' + k')/(1 + S) \quad \text{[eqn 8.23a]}$$

$$E_- - E_{1s} = j_0/R + (j' - k')/(1 - S) \quad \text{[eqn 8.23b]}$$

$$(E_+ - E_{1s})/j_0 = (1/R) - \left\{\frac{(1/R)[1-(1+s)\mathrm{e}^{-2s}] + (1/a_0)[1+s]\mathrm{e}^{-s}}{1+[1+s+\frac{1}{3}s^2]\mathrm{e}^{-s}}\right\}$$

$$= \left\{\frac{(1-\frac{2}{3}s^2)+(1+s)\mathrm{e}^{-s}}{1+(1+s+\frac{1}{3}s^2)\mathrm{e}^{-s}}\right\}\left(\frac{\mathrm{e}^{-s}}{R}\right)$$

$$(E_+ - E_{1s})(a_0/j_0) = \left\{\frac{(1-\frac{2}{3}s^2)+(1+s)\mathrm{e}^{-s}}{1+(1+s+\frac{1}{3}s^2)\mathrm{e}^{-s}}\right\}\left(\frac{\mathrm{e}^{-s}}{s}\right)$$

$$(E_- - E_{1s})(a_0/j_0) = \left\{\frac{2-[(1-2s-\frac{4}{3}s^2)+(1+s)\mathrm{e}^{-s}]\mathrm{e}^{-s}}{1-(1+s+\frac{1}{3}s^2)\mathrm{e}^{-s}}\right\}\left(\frac{1}{s}\right)$$

$$(\alpha - E_{1s})(a_0/j_0) = [-j' + (j_0/R)](a_0/j_0) \quad \text{[eqn 8.20]}$$

$$= (1 + s)(\mathrm{e}^{-2s}/s)$$

$$(\beta - E_{1s}S)(a_0/j_0) = [-k' + (j_0S/R)](a_0/j_0) \quad \text{[eqn 8.21a]}$$

$$= (1 - \frac{2}{3}s^2)(\mathrm{e}^{-s}/s)$$

The $E_\pm - E_{1s}$ values are plotted in Fig. 8.1; the α and β integrals are plotted in Fig. 8.2. The E_+ curve has a minimum (the equilibium bond length) at $R \approx 130$ pm ($s \approx 2.5$) corresponding to $E_+ - E_{1s} = -1.22 \times 10^{-3}\, j_0$ pm^{-1}. Because $j_0 = 2.31 \times 10^{-28}$ J m, we have

$$\underline{E_+ - E_{1s} = -2.81\times10^{-19}\ \text{J (1.76 eV, 170 kJ mol}^{-1}\text{)}}$$

Therefore the dissociation energy (neglecting the zero-point vibrational energy) is 170 kJ mol^{-1}.

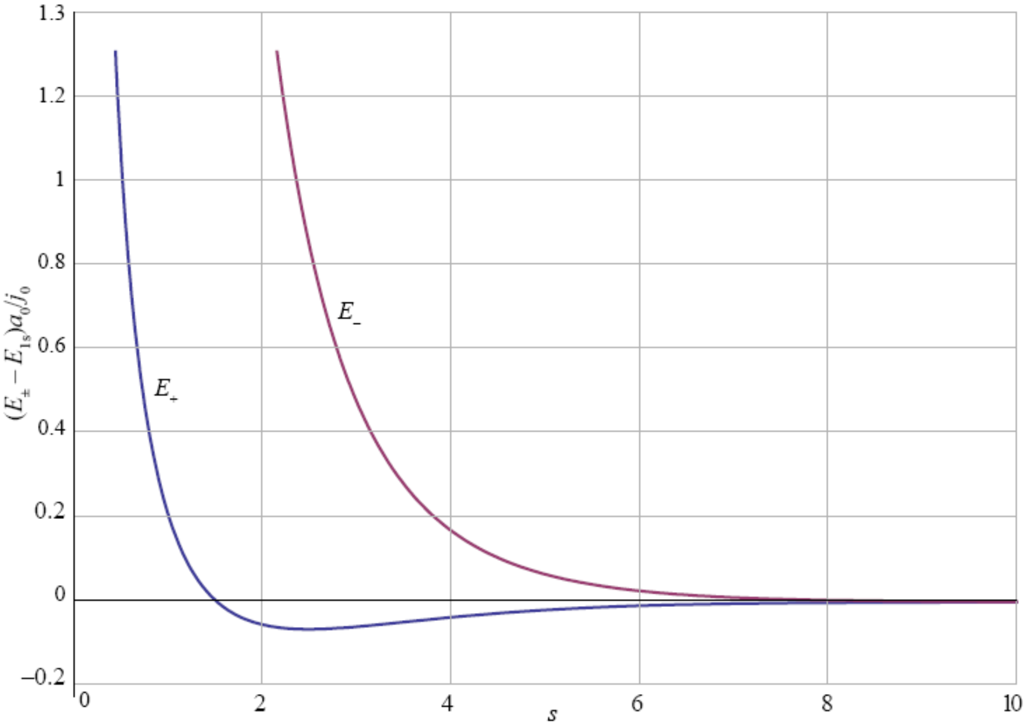


Figure 8.1: The values of $E_\pm - E_{1s}$ calculated in Problem 8.1.

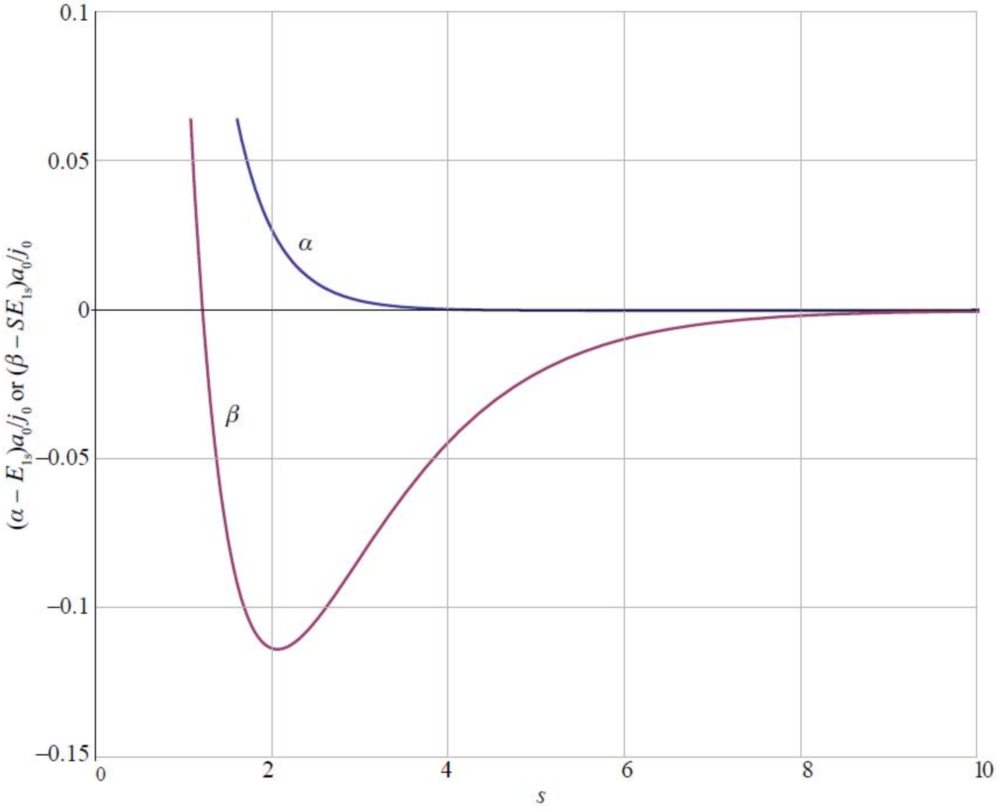


Figure 8.2: The dependence of the integrals α and β with distance ($s = R/a_0$).

Exercise: Plot the molecular potential energy curves for He_2^{3+} and estimate its bond length and dissociation energy if you find it to be stable. [$s \to ZR/a_0$]

8.4

$$k_f = (d^2E/dR^2)_0 = (1/a_0^2)(d^2E/dx^2)_0 \quad [x = R/a_0]$$

The 0 indicates the minimum of the curve, which occurs at close to $x = 2.5$ [Section 8.3, Fig. 8.12 of the text].

$$E = E_{1s} + j_0/xa_0 - \left(\frac{j' + \dot{k}'}{1+S}\right) \quad \text{[eqn 8.23a]}$$

$$= E_{1s} + j_0/xa_0 - \frac{(j_0/xa_0)\{1-(1+x)e^{-2x}\} + (j_0/a_0)(1+x)e^{-x}}{1+(1+x+\frac{1}{3}x^2)e^{-x}}$$

$$= E_{1s} + \frac{j_0}{a_0}\left\{\frac{1}{x} - \frac{(1/x)\{1-(1+x)e^{-2x}\} + (1+x)e^{-x}}{1+(1+x+\frac{1}{3}x^2)e^{-x}}\right\}$$

$$k_f = \left(\frac{j_0}{a_0^3}\right)\frac{d^2}{dx^2}\ \{\ldots\}\ \text{evaluated at } x = 2.5$$

$$= 0.061\,884 j_0/a_0^3 \quad \text{[mathematical software second derivative evaluator]}$$

The vibrational frequency is therefore

$$\omega = \left(\frac{2k_f}{m_H}\right)^{1/2} = \left(\frac{0.061\,884e^2}{2\pi\varepsilon_0 m_H a_0^3}\right)^{1/2}$$

$$= \left(\frac{2\times 0.061\,884\hbar^2}{m_e m_H a_0^4}\right)^{1/2} [a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2] = \frac{0.35181\hbar}{(m_e m_H)^{1/2}a_0^2}$$

$$= \underline{3.41\times 10^{14}\ s^{-1}}\ (\nu = 54.3\ \text{THz})$$

8.7 The Hamiltonian for the hydrogen molecule is given in eqn 8.25a and can be written as

$$H = \Omega_0 + \Omega_1 + \Omega_2$$

where

$$\Omega_0 = \frac{j_0}{R}$$

$$\Omega_1 = \Omega_1(1) + \Omega_1(2),\ \Omega_1(i) = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{j_0}{r_{Ai}} - \frac{j_0}{r_{Bi}}$$

$$\Omega_2 = \frac{j_0}{r_{12}}$$

The ground-state energy is given by $<\Psi(1,2)\,|\,H\,|\,\Psi(1,2)>$ where Ψ is the two-electron Slater determinant (eqn 7.42a) composed of the spinorbitals

$$\varphi_1(i) = N\{A(i) + B(i)\}\alpha(i)$$

$$\varphi_2(i) = N\{\mathrm{A}(i) + \mathrm{B}(i)\}\beta(i)$$

where (see eqn 8.24a) $\mathrm{A}(i) = \chi_{\mathrm{A}}(i)$, $\mathrm{B}(i) = \chi_{\mathrm{B}}(i)$, $N = \{2(1 + S\}^{-1/2}$, and $S = <\mathrm{A} \mid \mathrm{B}>$.

The Slater-Condon rules appear in eqns 7.44 and 7.45.

$$\begin{aligned}\langle\Psi|H|\Psi\rangle = \Omega_0 &+ \sum_i \langle\varphi_i(1)|\Omega_1(1)|\varphi_i(1)\rangle \\ &+ \frac{1}{2}\sum_{i \neq j}\{\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_i(1)\varphi_j(2)\rangle - \langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_j(1)\varphi_i(2)\rangle\}\end{aligned}$$

where the first term (Ω_0) results because Ψ is normalized and independent of R. The second term develops as follows since the spin states α and β are normalized:

$$\begin{aligned}\sum_i \langle\varphi_i(1)|\Omega_1(1)|\varphi_i(1)\rangle &= 2\langle\varphi_1(1)|\Omega_1(1)|\varphi_1(1)\rangle \\ &= 2N^2\langle\mathrm{A}(1) + \mathrm{B}(1)|\Omega_1(1)|\mathrm{A}(1) + \mathrm{B}(1)\rangle \\ &= 2N^2\{2\langle\mathrm{A}(1)|\Omega_1(1)|\mathrm{A}(1)\rangle + 2\langle\mathrm{A}(1)|\Omega_1(1)|\mathrm{B}(1)\rangle\}\ \text{(by symmetry)} \\ &= 4N^2\left\{E_{1s} - j_0\left\langle\mathrm{A}(1)\left|\frac{1}{r_{\mathrm{B}1}}\right|\mathrm{A}(1)\right\rangle - j_0\left\langle\mathrm{A}(1)\left|\frac{1}{r_{\mathrm{A}1}}\right|\mathrm{B}(1)\right\rangle + E_{1s}\langle\mathrm{A}(1)|\mathrm{B}(1)\rangle\right\} \\ &= 4N^2E_{1s}(1+S) - 4N^2(j' + k') = 2E_{1s} - 2(j' + k')/(1+S)\end{aligned}$$

Similarly, the third term develops as follows:

$$\begin{aligned}\frac{1}{2}\sum_{i \neq j}\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_i(1)\varphi_j(2)\rangle &= \langle\varphi_1(1)\varphi_2(2)|\Omega_2|\varphi_1(1)\varphi_2(2)\rangle \\ &= N^4\langle\{\mathrm{A}(1) + \mathrm{B}(1)\}\{\mathrm{A}(2) + \mathrm{B}(2)\}|\Omega_2|\{\mathrm{A}(1) + \mathrm{B}(1)\}\{\mathrm{A}(2) + \mathrm{B}(2)\}\rangle \\ &= N^4\{\langle\mathrm{A}(1)\mathrm{A}(2)|\Omega_2|\mathrm{A}(1)\mathrm{A}(2)\rangle + \langle\mathrm{A}(1)\mathrm{A}(2)|\Omega_2|\mathrm{A}(1)\mathrm{B}(2)\rangle \\ &+ \langle\mathrm{A}(1)\mathrm{A}(2)|\Omega_2|\mathrm{B}(1)\mathrm{A}(2)\rangle + \langle\mathrm{A}(1)\mathrm{A}(2)|\Omega_2|\mathrm{B}(1)\mathrm{B}(2)\rangle \\ &+ \langle\mathrm{A}(1)\mathrm{B}(2)|\Omega_2|\mathrm{A}(1)\mathrm{A}(2)\rangle + \langle\mathrm{A}(1)\mathrm{B}(2)|\Omega_2|\mathrm{A}(1)\mathrm{B}(2)\rangle \\ &+ \langle\mathrm{A}(1)\mathrm{B}(2)|\Omega_2|\mathrm{B}(1)\mathrm{A}(2)\rangle + \langle\mathrm{A}(1)\mathrm{B}(2)|\Omega_2|\mathrm{B}(1)\mathrm{B}(2)\rangle \\ &+ \langle\mathrm{B}(1)\mathrm{A}(2)|\Omega_2|\mathrm{A}(1)\mathrm{A}(2)\rangle + \langle\mathrm{B}(1)\mathrm{A}(2)|\Omega_2|\mathrm{A}(1)\mathrm{B}(2)\rangle \\ &+ \langle\mathrm{B}(1)\mathrm{A}(2)|\Omega_2|\mathrm{B}(1)\mathrm{A}(2)\rangle + \langle\mathrm{B}(1)\mathrm{A}(2)|\Omega_2|\mathrm{B}(1)\mathrm{B}(2)\rangle \\ &+ \langle\mathrm{B}(1)\mathrm{B}(2)|\Omega_2|\mathrm{A}(1)\mathrm{A}(2)\rangle + \langle\mathrm{B}(1)\mathrm{B}(2)|\Omega_2|\mathrm{A}(1)\mathrm{B}(2)\rangle \\ &+ \langle\mathrm{B}(1)\mathrm{B}(2)|\Omega_2|\mathrm{B}(1)\mathrm{A}(2)\rangle + \langle\mathrm{B}(1)\mathrm{B}(2)|\Omega_2|\mathrm{B}(1)\mathrm{B}(2)\rangle\}\end{aligned}$$

Recognizing that many of the matrix elements are equal by symmetry, we obtain:

$$\frac{1}{2}\sum_{i\neq j}\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_i(1)\varphi_j(2)\rangle$$

$$= N^4\{2\langle \mathrm{A}(1)\mathrm{A}(2)|\Omega_2|\mathrm{A}(1)\mathrm{A}(2)\rangle + 8\langle \mathrm{A}(1)\mathrm{A}(2)|\Omega_2|\mathrm{A}(1)\mathrm{B}(2)\rangle + 2\langle \mathrm{A}(1)\mathrm{B}(2)|\Omega_2|\mathrm{A}(1)\mathrm{B}(2)\rangle + 4\langle \mathrm{A}(1)\mathrm{A}(2)|\Omega_2|\mathrm{B}(1)\mathrm{B}(2)\rangle\}$$

Using the definitions in eqns 8.28a-d, we obtain

$$\frac{1}{2}\sum_{i\neq j}\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_i(1)\varphi_j(2)\rangle = 2N^4\{m + 4l + j + 2k\} = \frac{m + 4l + j + 2k}{2(1+S)^2}$$

We now explore the final term and show that it vanishes:

$$-\frac{1}{2}\sum_{i\neq j}\{\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_j(1)\varphi_i(2)\rangle\} =$$

$$-\frac{1}{2}\{\langle\varphi_1(1)\varphi_2(2)|\Omega_2|\varphi_2(1)\varphi_1(2)\rangle + \langle\varphi_2(1)\varphi_1(2)|\Omega_2|\varphi_1(1)\varphi_2(2)\rangle\}$$

The first term on the right is proportional to < α(1) | β(1) > and the second term is proportional to < β(1) | α(1) > and since both of these vanish due to orthogonality of the spin states, the final term is zero. Therefore, upon collecting all terms:

$$E = \langle\Psi|H|\Psi\rangle = \frac{j_0}{R} + 2E_{1s} - \frac{2(j' + k')}{1+S} + \frac{m + 4l + j + 2k}{2(1+S)^2}$$

which is eqn 8.27.

8.10 **(a)** CO : $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$, $^1\Sigma^+$ [isoelectronic with N_2]

Bond order = (8 − 2)/2 = 3 HOMO = 3σ; LUMO = 2π

(b) NO : . . . $1\pi^4 3\sigma^2 2\pi^{*1}$, $^2\Pi$ [isoelectronic with O_2^+]

Bond order = (6 – 1)/2 = 2.5 HOMO = 2π; LUMO = 4σ

where the * superscript indicates an antibonding molecular orbital.

Exercise: Predict the ground configurations of (a) O_2, (b) O_2^+, and (c) O_2^-.

8.13 To construct the symmetry-adapted linear combinations (SALCs) for methane, we identify the four hydrogen atoms as equivalent atoms in the molecule and proceed to form linear combinations of the atomic orbitals that belong to a specific symmetry species. In the case of a minimal basis set, we consider only 1s orbitals on the hydrogen atoms, denoting them s_A, s_B, s_C, s_D. We then follow the method set out in Example 5.9. The effect of the operations of the group T_d (the point group for methane, $h = 24$) on the basis set of four hydrogen atomic orbitals is given in the following table:

Operation in T_d	s_A	s_B	s_C	s_D
E	s_A	s_B	s_C	s_D
C_3^+ (one of 4 C_3 axes)	s_A	s_C	s_D	s_B
C_3^- (one of 4 C_3 axes)	s_A	s_D	s_B	s_C
C_3^+ (second)	s_D	s_B	s_A	s_C
C_3^- (second)	s_C	s_B	s_D	s_A
C_3^+ (third)	s_B	s_D	s_C	s_A
C_3^- (third)	s_D	s_A	s_C	s_B
C_3^+ (fourth)	s_C	s_A	s_B	s_D
C_3^- (fourth)	s_B	s_C	s_A	s_D
C_2 (one of 3 C_2 axes)	s_B	s_A	s_D	s_C
C_2 (second)	s_C	s_D	s_A	s_B
C_2 (third)	s_D	s_C	s_B	s_A
σ_d (one of six planes)	s_A	s_B	s_D	s_C
σ_d (second)	s_A	s_D	s_C	s_B
σ_d (third)	s_A	s_C	s_B	s_D
σ_d (fourth)	s_D	s_B	s_C	s_A
σ_d (fifth)	s_C	s_B	s_A	s_D
σ_d (sixth)	s_B	s_A	s_C	s_D

S_4^+ (one of 3 S_4 axes)	s_C	s_D	s_B	s_A
S_4^- (one of 3 S_4 axes)	s_D	s_C	s_A	s_B
S_4^+ (second)	s_B	s_D	s_A	s_C
S_4^- (second)	s_C	s_A	s_D	s_B
S_4^+ (third)	s_D	s_A	s_B	s_C
S_4^- (third)	s_B	s_C	s_D	s_A

For the irreducible representation of symmetry species A_1 (see the character table), $d = 1$ and all $\chi(R) = 1$. The first column therefore gives

$$1/24\ (6s_A + 6s_B + 6s_C + 6s_D) = 1/4\ (s_A + s_B + s_C + s_D)$$

and all three other columns gives the same result. For the irreducible representation of symmetry species T_2 (see the character table), $d = 3$ and the characters are (3, 0, −1, 1, −1). The first column therefore gives

$3/24\ (3s_A + 0 - s_B - s_C - s_D + s_A + s_A + s_A + s_D + s_C + s_B - s_C - s_D - s_B - s_C - s_D - s_B) =$
$3/24\ (6s_A - 2s_B - 2s_C - 2s_D)$.

The second column gives

$3/24\ (3s_B + 0 - s_A - s_D - s_C + s_B + s_D + s_C + s_B + s_B + s_A - s_D - s_C - s_D - s_A - s_A - s_C) =$
$3/24\ (6s_B - 2s_A - 2s_C - 2s_D)$.

The third column gives

$3/24\ (3s_C + 0 - s_D - s_A - s_B + s_D + s_C + s_B + s_C + s_A + s_C - s_B - s_A - s_A - s_D - s_B - s_D) =$
$3/24\ (6s_C - 2s_A - 2s_B - 2s_D)$.

The fourth column gives

$3/24\ (3s_D + 0 - s_C - s_B - s_A + s_C + s_B + s_D + s_A + s_D + s_D - s_A - s_B - s_C - s_B - s_C - s_A) =$
$3/24\ (6s_D - 2s_A - 2s_B - 2s_C)$.

The four linear combinations are not linearly independent (the sum of all four is zero) but we can form three linear independent combinations using
(result from columns 1 + 2),
(result from columns 2 + 3),
(result from columns 3 + 4).
We therefore have the following SALCs, indicating also the atomic orbitals on the carbon atom (2s, $2p_x$, $2p_y$, $2p_z$) that have the correct symmetry to form molecular orbitals with the SALCs:

A_1: SALC = $s_A + s_B + s_C + s_D$; can overlap with C 2s

T_2: SALCS = (i) $s_A + s_B - s_C - s_D$, (ii) $s_B + s_C - s_A - s_D$, (iii) $s_C + s_D - s_A - s_B$;

Each can overlap with carbon $2p_x$, $2p_y$, $2p_z$.

Note that we can show that for all other irreducible representations (that is, A_2, E, T_1), no columns survive.

8.16 In the allyl radical, each carbon atom contributes one p-orbital and one p-electron to the π-electron framework. We follow the procedure of Example 8.4; the secular equation to solve is

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

This expands to

$$(\alpha - E)^3 - 2\beta^2(\alpha - E) = 0$$

or

$$(\alpha - E)[(\alpha - E)^2 - 2\beta^2] = 0$$

which has the following three roots:

$$E = \alpha \quad E = \alpha + \sqrt{2}\beta \quad E = \alpha - \sqrt{2}\beta$$

For the allyl radical, two electrons are in the lowest energy molecular orbital (of energy $\alpha + \sqrt{2}\beta)$ and one electron is in the molecular orbital of energy α. The total π-electron energy using the Hückel approximation is therefore

$$2(\alpha + \sqrt{2}\beta) + \alpha = \underline{3\alpha + 2\sqrt{2}\beta}$$

Exercise: Estimate the delocalization energy for the allyl radical. Comment on its predicted stability.

8.19 The basis p_1, p_2, p_3, $p_4 \equiv p_N$, p_5, p_6 transforms as follows in C_{2v} (write the C_2 axis cutting through p_1 and p_N):

	p_1	p_2	p_3	p_N	p_5	p_6	χ
E	p_1	p_2	p_3	p_N	p_5	p_6	6
C_2	$-p_1$	$-p_6$	$-p_5$	$-p_N$	$-p_3$	$-p_2$	-2
σ'_v	$-p_1$	$-p_2$	$-p_3$	$-p_N$	$-p_5$	$-p_6$	-6
σ_v	p_1	p_6	p_5	p_N	p_3	p_2	2

The characters 6, –2, –6, 2 span $2A_2 + 4B_1$. The unnormalized symmetry-adapted linear combinations are

$$\pi(A_2) = p_{A_2}p_2 = p_2 - p_6; \quad (p_2 - p_6)/\sqrt{2} \text{ when normalized}$$

$$\pi(A_2) = p_{A_2}p_3 = p_3 - p_5; \quad (p_3 - p_5)/\sqrt{2} \text{ when normalized}$$

$$\pi(B_1) = p_{B_1}p_1 = p_1;$$

$$\pi(B_1) = p_{B_1}p_2 = p_2 + p_6; \quad (p_2 + p_6)/\sqrt{2} \text{ when normalized}$$

$$\pi(B_1) = p_{B_1}p_3 = p_3 + p_5; \quad (p_3 + p_5)/\sqrt{2} \text{ when normalized}$$

$$\pi(B_1) = p_{B_1}p_N = p_N$$

The A_2 determinant in the Hückel approximation involves the matrix elements

$$\tfrac{1}{2}\langle p_2 - p_6|H|p_2 - p_6\rangle = \tfrac{1}{2}\langle p_3 - p_5|H|p_3 - p_5\rangle = \alpha_C \equiv \alpha$$

$$\tfrac{1}{2}\langle p_2 - p_6|H|p_3 - p_5\rangle = \tfrac{1}{2}\{\langle p_2|H|p_3\rangle + \langle p_6|H|p_5\rangle - \langle p_6|H|p_3\rangle - \langle p_2|H|p_5\rangle\}$$

$$= \tfrac{1}{2}\{\beta + \beta - 0 - 0\} = \beta$$

The A_2 secular determinant is therefore

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0; \quad \text{consequently } \underline{E = \alpha \pm \beta}$$

The B_1 determinant involves

$$\langle p_1|H|p_1\rangle = \alpha$$

$$\tfrac{1}{2}\langle p_2 + p_6|H|p_2 + p_6\rangle = \alpha = \tfrac{1}{2}\langle p_3 + p_5|H|p_3 + p_5\rangle$$

$$\langle p_N|H|p_N\rangle = \alpha_N \approx \alpha + \tfrac{1}{2}\beta$$

$$\langle p_1|H|p_2 + p_6\rangle/\surd 2 = (\beta + \beta)/\surd 2 = \beta\surd 2$$

$$\langle p_1|H|\text{all others}\rangle = 0$$

$$\tfrac{1}{2}\langle p_2 + p_6|H|p_3 + p_5\rangle = \tfrac{1}{2}(\beta + \beta) = \beta$$

$$\langle p_2 + p_6|H|p_N\rangle/\surd 2 = 0$$

$$\langle p_3 + p_5|H|p_N\rangle/\surd 2 = \beta_{CN}\surd 2 \approx \beta\surd 2$$

The determinant itself is therefore

$$\begin{vmatrix} \alpha - E & \beta\surd 2 & 0 & 0 \\ \beta\surd 2 & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta\surd 2 \\ 0 & 0 & \beta\surd 2 & \alpha + \tfrac{1}{2}\beta - E \end{vmatrix}$$

$$= (\alpha - E)^3(\alpha + \tfrac{1}{2}\beta - E) - 2(\alpha - E)^2\beta^2 - (\alpha - E)(\alpha + \tfrac{1}{2}\beta - E)\beta^2$$

$$- 2\beta^2(\alpha - E)(\alpha + \tfrac{1}{2}\beta - E) + 4\beta^4 = 0$$

Write $(\alpha - E)/\beta = x$; then solve

$$x^3(x+\tfrac{1}{2}) - 2x^2 - x(x+\tfrac{1}{2}) - 2x(x+\tfrac{1}{2}) + 4 = 0$$

or

$$x^4 + \tfrac{1}{2}x^3 - 5x^2 - \tfrac{3}{2}x + 4 = 0$$

The roots of this equation (determined numerically) are

$$x = 0.8410, \quad 1.9337, \quad -1.1672, \quad -2.1074$$

so, in this approximation, the energies of the B_1 orbitals lie at

$$\underline{E = \alpha - 1.9337\beta,\ \alpha - 0.8410\beta,\ \alpha + 1.1672\beta,\ \alpha + 2.1074\beta}$$

The π-electron energy is therefore

$$E_\pi = 2(\alpha + 2.1074\beta) + 2(\alpha + \beta) + 2(\alpha + 1.1672\beta) = \underline{6\alpha + 8.5492\beta}$$

The delocalization energy is

$$E_{\text{deloc}} = 6\alpha_C + 8.5492\beta - \{5\alpha_C + \alpha_N + 6\beta\} = 2.0492\beta$$

Exercise: Find the Hückel molecular orbitals energies of pyrazine using the same set of approximations.

8.22 The Clebsch–Gordan series for $f^2 (l = 3)$ is

$$3 \times 3 = 6 + 5 + \cdots + 0$$

so $f^2 \rightarrow$ I, H, G, F, D, P, S. As the orbitals are equivalent, I must be ^{1}I [Pauli principle], and so the permitted terms for the free ion are

$$\underline{^1\text{I},\ ^3\text{H},\ ^1\text{G},\ ^3\text{F},\ ^1\text{D},\ ^3\text{P},\ ^1\text{S}}$$

[either note that terms alternate in general, or else evaluate the symmetrized and anti-symmetrized direct products].

For the second part, use eqn 5.47b:

$$\chi(C_\alpha) = \frac{\sin[(L+\frac{1}{2})\alpha]}{\sin\frac{1}{2}\alpha}$$

with $\alpha = 0(E)$, $2\pi/3(C_3)$, $\pi(C_2)$, $\pi/2(C_4)$, $\pi(C_2')$. Draw up the following Table:

Term	E	C_3	C_2	C_4	C_2'	Decomposition
I	13	1	1	–1	1	$A_1 + A_2 + E + T_1 + 2T_2$
H	11	–1	–1	1	–1	$E + 2T_1 + T_2$
G	9	0	1	1	1	$A_1 + E + T_1 + T_2$
F	7	1	–1	–1	–1	$A_2 + T_1 + T_2$
D	5	–1	1	–1	1	$E + T_2$
P	3	0	–1	1	–1	T_1
S	1	1	1	1	1	A_1

For the decompositions use

$$a_l = (1/h)\sum_c g(c)\chi^{(l)}(c)\chi(c) \quad \text{[eqn 5.23]}$$

$$= (1/24)\ \{\chi^{(l)}(E)\chi(E) + 8\chi^{(l)}(C_3)\chi(C_3) + 3\chi^{(l)}(C_2)\chi(C_2)$$

$$+ 6\chi^{(l)}(C_4)\chi(C_4) + 6\chi^{(l)}(C_2')\chi(C_2')\}$$

in conjuction with the *O* character table. The multiplicities carry over. Therefore:

$$^1\mathrm{I} \rightarrow \underline{{}^1\mathrm{A}_1 + {}^1\mathrm{A}_2 + {}^1\mathrm{E} + {}^1\mathrm{T}_1 + 2\,{}^1\mathrm{T}_2}$$

$$^3H \rightarrow \underline{^3E + 2\,^3T_1 + {}^3T_2}$$

$$^1G \rightarrow \underline{^1A_1 + {}^1E + {}^1T_1 + {}^1T_2}$$

$$^3F \rightarrow \underline{^3A_2 + {}^3T_1 + {}^3T_2}$$

$$^1D \rightarrow \underline{^1E + {}^1T_2}$$

$$^3P \rightarrow \underline{^3T_1}$$

$$^1S \rightarrow \underline{^1A_1}$$

Exercise: What terms does a g^2 configuration give rise to **(a)** in a free atom, **(b)** an octahedral complex?

8.25 Once again, it is helpful to have a model of the tetrahedral system labelled with the orbitals. Use the same cube as in Problem 8.24, but labelled as in Fig. 8.11.

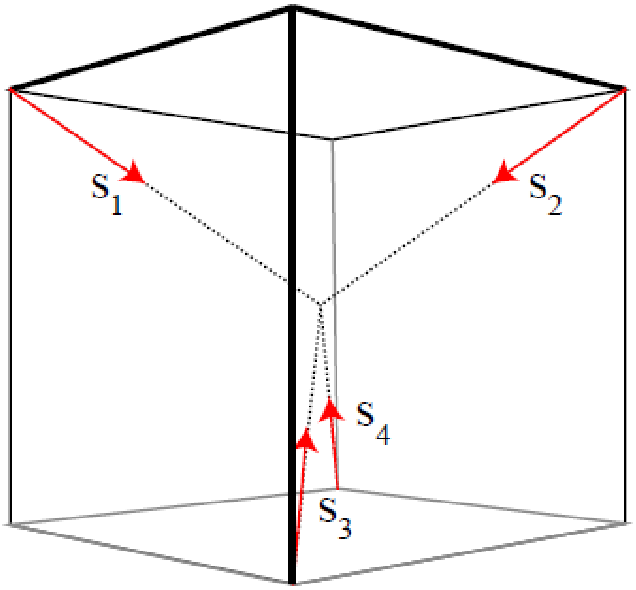


Figure 8.11: A representation of the s-orbital basis in a tetrahedral complex.

The s-orbital linear combinations can be constructed as follows. Consider s_1; under the operations of the group (Fig. 8.12) it transforms as follows:

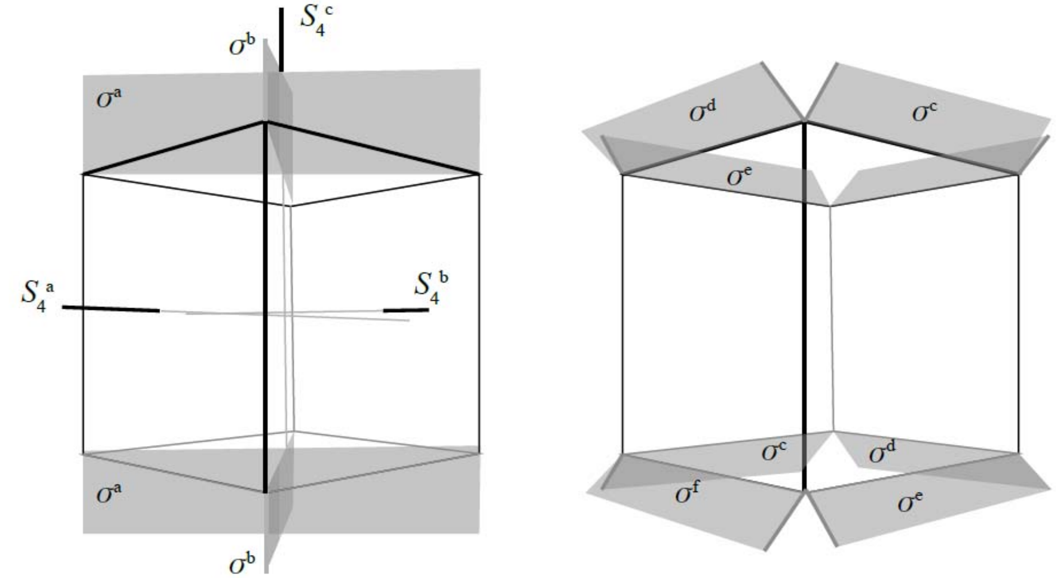


Figure 8.12: The operations of the group T_d.

R	E	C_3^{+a}	C_3^{+b}	C_3^{+c}	C_3^{+d}	C_3^{-a}	C_3^{-b}	C_3^{-c}	C_3^{-d}	C_2^a	C_2^b	C_2^c
Rs_1	s_1	s_3	s_2	s_1	s_3	s_4	s_4	s_1	s_2	s_3	s_4	s_2
R	σ_d^a	σ_d^b	σ_d^c	σ_d^d	σ_d^e	σ_d^f	S_4^a	S_4^b	S_4^c	S_4^{-a}	S_4^{-b}	S_4^{-c}
Rs_1	s_1	s_2	s_4	s_1	s_1	s_3	s_4	s_3	s_3	s_2	s_2	s_4

Application of the projection operators to s_1 then leads to:

$$p_{A_1}s_1 = (1/24)\{s_1 + s_3 + s_2 + \cdots + s_3 + s_2 + s_4\}$$

$= (1/4)\{s_1 + s_2 + s_3 + s_4\}$

$p_{T_2}s_1 = (1/4)\{3s_1 - s_2 - s_3 - s_4\}$

$p_{T_2}s_2 = (1/4)\{3s_2 - s_3 - s_4 - s_1\}$ [by symmetry]

$p_{T_2}s_3 = (1/4)\{3s_3 - s_4 - s_1 - s_2\}$

$p_{T_2}s_4 = (1/4)\{3s_4 - s_1 - s_2 - s_3\}$

Ignoring normalization, we take the following linear combinations (chosen, Fig. 8.13, so as to have the symmetries of p_x, p_y, p_z):

$$\left.\begin{aligned} p_{T_2}s_1 + p_{T_2}s_2 &= s_1 + s_2 - s_3 - s_4 \\ p_{T_2}s_2 + p_{T_2}s_3 &= s_2 + s_3 - s_4 - s_1 \\ p_{T_2}s_1 + p_{T_2}s_3 &= s_1 + s_3 - s_2 - s_4 \end{aligned}\right\} T_2$$

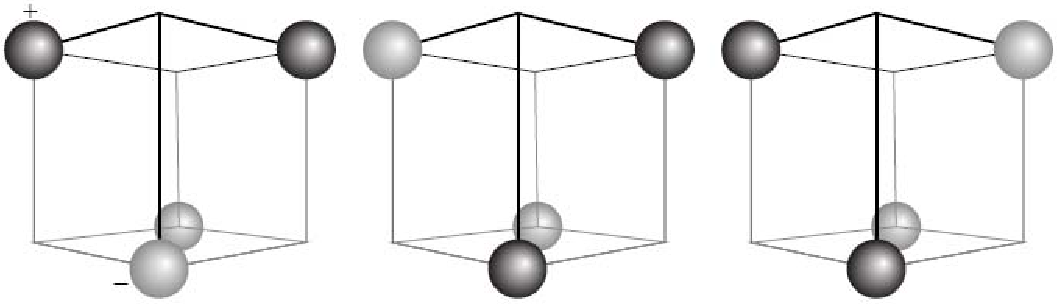


Figure 8.13: The symmetry-adapted linear combinations of s-orbitals of T_2 symmetry.

The p-orbital basis (Fig. 8.14) transforms under the operations of the group (*T*) as illustrated by the following behaviour of p_1:

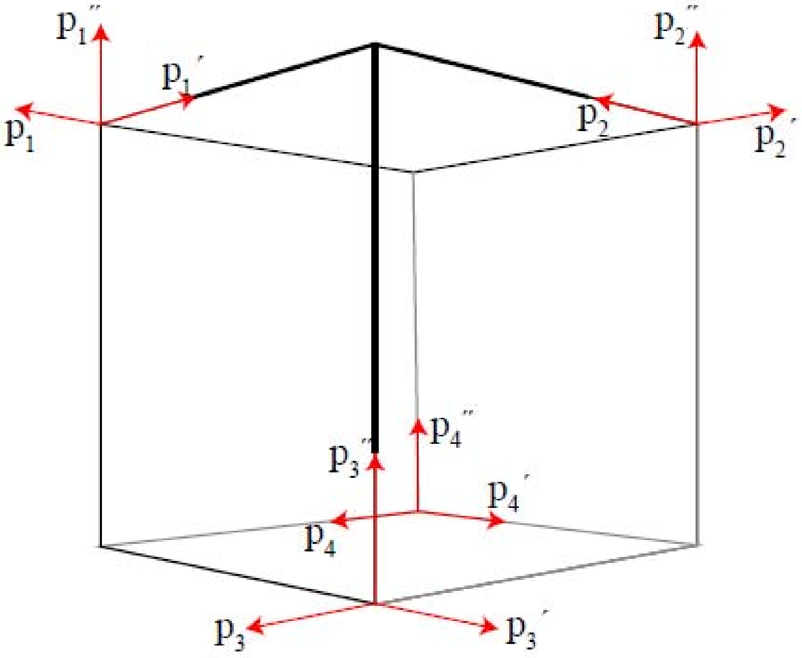


Figure 8.14: The p-orbital basis in a tetrahedral molecule.

R	E	C_3^a	C_3^b	C_3^c	C_3^d	C_3^{-a}	C_3^{-b}	C_3^{-c}	C_3^{-d}	C_2^a	C_2^b	C_2^c
Rp_1	p_1	$-p_3''$	p_2'	p_1''	p_3'	$-p_4'$	$-p_4''$	$-p_1'$	p_2''	p_3	$-p_4$	$-p_2$

R	σ_d^a	σ_d^b	σ_d^c	σ_d^d	σ_d^e	σ_d^f	S_4^a	S_4^b	S_4^c	S_4^{-a}	S_4^{-b}	S_4^{-c}
Rp_1	$-p_1'$	p_2'	$-p_4''$	p_1	p_1''	p_3	$-p_4$	$-p_3''$	$-p_4'$	$-p_2$	p_2''	p_3'

Since we have taken the p-orbital basis, which spans $A_1 + E + 2T_2$, there will be $A_1 + T_2$ components (corresponding to the s-basis, as in the first part of the Problem) as well as

E + T_1 + T_2 components. We shall construct only the E p-orbital combinations. The projection operator gives

$$p_E p_1 = (2/24)\{2p_1 + p''_3 - p'_2 - p''_1 - p'_3 + p'_4 + p''_4 + p'_1 - p''_2 + 2p_3 - 2p_4 - 2p_2\}$$

The remaining $p_E p_j$ may be constructed similarly.

Exercise: Find the remaining E, T_1, and T_2 symmetry-adapted combinations.

8.28 The plots corresponding to Fig. 8.43 of the text but with (a) $\gamma = \underline{\pi}$, (b) $\gamma = 2\pi$ are shown in Fig. 8.16. The allowed solutions lie within the tinted band. Evaluate the function for a range of values of γ, $0 < \gamma < \frac{1}{2}\pi$.

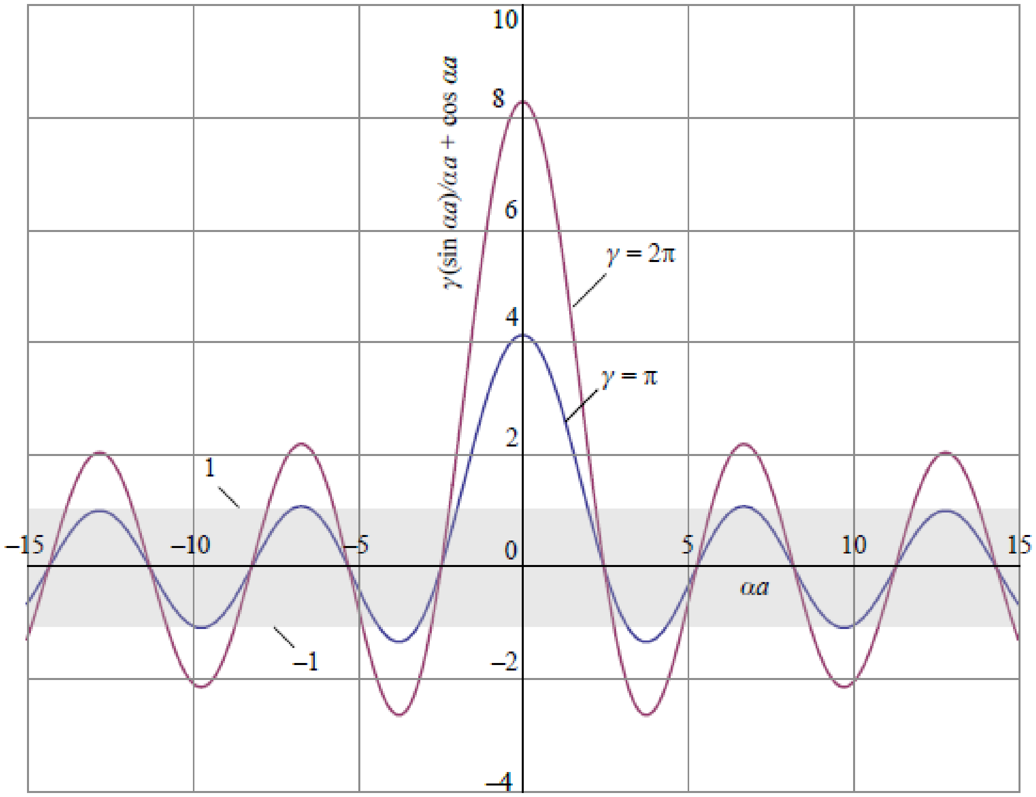


Figure 8.16: The determination of the bands of allowed energies for $\gamma = \pi$ and $\gamma = 2\pi$.

Chapter 9

The calculation of electronic structure

Exercises

9.1 $\Psi^0 = \psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_\mathrm{e})$

$$H^0 = \sum_{i=1}^{N_\mathrm{e}} h_i$$

$$H^0\Psi^0 = \sum_{i=1}^{N_\mathrm{e}} h_i\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_\mathrm{e})$$

$$= (h_1 + h_2 + \cdots + h_{N_\mathrm{e}})(\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_\mathrm{e}))$$

$$= [h_1\psi_a^0(1)]\psi_b^0(2)\ldots\psi_z^0(N_\mathrm{e}) + \psi_a^0(1)[h_2\psi_b^0(2)]\ldots\psi_z^0(N_\mathrm{e})$$

$$+\cdots+\psi_a^0(1)\psi_b^0(2)\ldots[h_{N_\mathrm{e}}\psi_z^0(N_\mathrm{e})]$$

$$= E_a^0\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_\mathrm{e}) + E_b^0\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_\mathrm{e})$$

$$+\cdots+E_z^0\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_\mathrm{e})$$

$$= [E_a^0 + E_b^0 + \cdots + E_z^0]\psi^0$$

Eigenvalue = $\underline{E_a^0 + E_b^0 + \cdots + E_z^0}$

Exercise: Confirm that $\det|\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_\mathrm{e})|$ is an eigenfunction of H^0 and determine its corresponding eigenvalue.

9.2 $\Psi = (6)^{-1/2}\det|\psi_{1\mathrm{s}}^{\alpha}(1)\psi_{1\mathrm{s}}^{\beta}(2)\psi_{1\mathrm{s}}^{\alpha}(3)|$

$$= (6)^{-1/2}\begin{vmatrix} \psi_{1s}^{\alpha}(1) & \psi_{1s}^{\beta}(1) & \psi_{1s}^{\alpha}(1) \\ \psi_{1s}^{\alpha}(2) & \psi_{1s}^{\beta}(2) & \psi_{1s}^{\alpha}(2) \\ \psi_{1s}^{\alpha}(3) & \psi_{1s}^{\beta}(3) & \psi_{1s}^{\alpha}(3) \end{vmatrix}$$

$$= (6)^{-1/2}\left\{\begin{matrix} \psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(3) \\ +\psi_{1s}^{\alpha}(2)\psi_{1s}^{\beta}(3)\psi_{1s}^{\alpha}(1) \\ +\psi_{1s}^{\beta}(1)\psi_{1s}^{\alpha}(2)\psi_{1s}^{\alpha}(3) \\ -\psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(3) \\ -\psi_{1s}^{\alpha}(2)\psi_{1s}^{\beta}(3)\psi_{1s}^{\alpha}(1) \\ -\psi_{1s}^{\beta}(1)\psi_{1s}^{\alpha}(2)\psi_{1s}^{\alpha}(3) \end{matrix}\right\} = (6)^{-1/2} \times 0 = \underline{0}$$

Exercise: Write the HF ground-state wavefunction Ψ_0 for the He$^-$ ion and give examples of singly excited, doubly excited, and triply excited Slater determinants.

9.3 In the first *brief illustration* in Section 9.3, the Roothaan equations are presented in matrix form and one line of the resulting expansion is given. The remaining three lines of the expansion are

$$F_{AA}c_{A\sigma'} + F_{AB}c_{B\sigma'} = \varepsilon_{\sigma}S_{AA}c_{A\sigma'} + \varepsilon_{\sigma}S_{AB}c_{B\sigma'}$$

$$F_{BA}c_{A\sigma} + F_{BB}c_{B\sigma} = \varepsilon_{\sigma'}S_{BA}c_{A\sigma} + \varepsilon_{\sigma'}S_{BB}c_{B\sigma}$$

$$F_{BA}c_{A\sigma'} + F_{BB}c_{B\sigma'} = \varepsilon_{\sigma'}S_{BA}c_{A\sigma'} + \varepsilon_{\sigma'}S_{BB}c_{B\sigma'}$$

9.4 Proceed as in the *brief illustration* development for F_{AB}.

$$\begin{aligned} F_{AA} = h_{AA} &+ P_{AA}\left\{(AA|AA) - \tfrac{1}{2}(AA|AA)\right\} + P_{AB}\left\{(AA|AB) - \tfrac{1}{2}(AA|BA)\right\} \\ &+ P_{BA}\left\{(AB|AA) - \tfrac{1}{2}(AB|AA)\right\} + P_{BB}\left\{(AB|AB) - \tfrac{1}{2}(AB|BA)\right\} \\ &= h_{AA} + P_{AA}\left\{\tfrac{1}{2}(AA|AA) + \tfrac{1}{2}(AB|AB)\right\} + P_{AB}\left\{\tfrac{1}{2}(AA|AB) + \tfrac{1}{2}(AB|AA)\right\} \end{aligned}$$

$$\begin{aligned} F_{BA} = h_{BA} &+ P_{AA}\left\{(BA|AA) - \tfrac{1}{2}(BA|AA)\right\} + P_{AB}\left\{(BA|AB) - \tfrac{1}{2}(BA|BA)\right\} \\ &+ P_{BA}\left\{(BB|AA) - \tfrac{1}{2}(BB|AA)\right\} + P_{BB}\left\{(BB|AB) - \tfrac{1}{2}(BB|BA)\right\} \\ &= h_{BA} + P_{AA}\{(BA|AA)\} + P_{AB}\{(BB|AA)\} \end{aligned}$$

$$
\begin{aligned}
F_{\mathrm{BB}} = h_{\mathrm{BB}} &+ P_{\mathrm{AA}}\left\{(\mathrm{BA}|\mathrm{BA}) - \tfrac{1}{2}(\mathrm{BA}|\mathrm{AB})\right\} + P_{\mathrm{AB}}\left\{(\mathrm{BA}|\mathrm{BB}) - \tfrac{1}{2}(\mathrm{BA}|\mathrm{BB})\right\} \\
&+ P_{\mathrm{BA}}\left\{(\mathrm{BB}|\mathrm{BA}) - \tfrac{1}{2}(\mathrm{BB}|\mathrm{AB})\right\} + P_{\mathrm{BB}}\left\{(\mathrm{BB}|\mathrm{BB}) - \tfrac{1}{2}(\mathrm{BB}|\mathrm{BB})\right\} \\
&= h_{\mathrm{BB}} + P_{\mathrm{AA}}\left\{\tfrac{1}{2}(\mathrm{BA}|\mathrm{BA}) + \tfrac{1}{2}(\mathrm{BB}|\mathrm{BB})\right\} + P_{\mathrm{AB}}\left\{\tfrac{1}{2}(\mathrm{BA}|\mathrm{BB}) + \tfrac{1}{2}(\mathrm{BB}|\mathrm{BA})\right\}
\end{aligned}
$$

9.5 An Al atom has 13 electrons, so the normalization factor

$$N = (13!)^{-1/2} = 1.267\ldots \times 10^{-5}$$

A restricted HF wave function is

$$
\begin{aligned}
N \det\Big|&\psi_{1\mathrm{s}}^{\alpha}(1)\psi_{1\mathrm{s}}^{\beta}(2)\psi_{2\mathrm{s}}^{\alpha}(3)\psi_{2\mathrm{s}}^{\beta}(4)\psi_{2\mathrm{p}_{+1}}^{\alpha}(5)\psi_{2\mathrm{p}_{+1}}^{\beta}(6)\psi_{2\mathrm{p}_{0}}^{\alpha}(7) \\
&\psi_{2\mathrm{p}_{0}}^{\beta}(8)\psi_{2\mathrm{p}_{-1}}^{\alpha}(9)\psi_{2\mathrm{p}_{-1}}^{\beta}(10)\psi_{3\mathrm{s}}^{\alpha}(11)\psi_{3\mathrm{s}}^{\beta}(12)\psi_{3\mathrm{p}_{+1}}^{\alpha}(13)\Big|
\end{aligned}
$$

An unrestricted HF wavefunction is

$$
\begin{aligned}
N \det\Big|&\psi_{1\mathrm{s}}^{\alpha}(1)\psi_{1\mathrm{s}}^{\beta}(2)\psi_{2\mathrm{s}}^{\alpha}(3)\psi_{2\mathrm{s}}^{\beta}(4)\psi_{2\mathrm{p}_{+1}}^{\alpha}(5)\psi_{2\mathrm{p}_{+1}}^{\beta}(6)\psi_{2\mathrm{p}_{0}}^{\alpha}(7) \\
&\psi_{2\mathrm{p}_{0}}^{\beta}(8)\psi_{2\mathrm{p}_{-1}}^{\alpha}(9)\psi_{2\mathrm{p}_{-1}}^{\beta}(10)\psi_{3\mathrm{s}}^{\alpha}(11)\psi_{3\mathrm{s}}^{\beta}(12)\psi_{3\mathrm{p}_{+1}}^{\alpha}(13)\Big|
\end{aligned}
$$

Exercise: Give an example of a restricted and an unrestricted Hartree–Fock wavefunction for a sodium atom. Show that the RHF wavefunction is an eigenfunction of S^2 and evaluate its eigenvalue.

9.6 A calculation using 20 (spatial) basis functions yields 40 different Hartree–Fock SCF spinorbitals. As a chlorine atom has 17 electrons, there will be 17 occupied and $\underline{23}$ virtual orbitals.

Exercise: In a Hartree–Fock SCF calculation on the chloride ion Cl^- using 25 (spatial) basis functions, how many virtual orbitals are determined?

9.7 An f-type Gaussian orbital is one for which $i + j + k = 3$ for the integers (i, j, k) of eqn

9.20. There are therefore 10 f-type Gaussian orbitals with possibilities (0,0,3), (0,3,0), (3,0,0), (2,1,0), (2,0,1), (0,2,1), (1,2,0), (1,0,2), (0,1,2), (1,1,1).

9.8 Using the notation of eqn (9.17) for the two-electron integral for the basis functions, we have

$$(\mathrm{AA}|\mathrm{BB}) = j_0 \int \mathrm{A}^*(1)\mathrm{A}^*(2)\frac{1}{r_{12}}\mathrm{B}(1)\mathrm{B}(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2$$

With an s-type Gaussian orbital of the form

$$g(\boldsymbol{r}_i) = N\mathrm{e}^{-\alpha r_{\mathrm{A}i}^2}$$

for electron *i* on atomic nucleus A and a similar expression for atomic nucleus B, we then have

$$(\mathrm{AA}|\mathrm{BB}) = j_0 N^4 \int \mathrm{e}^{-\alpha r_{\mathrm{A}1}^2}\mathrm{e}^{-\alpha r_{\mathrm{A}2}^2}\frac{1}{r_{12}}\mathrm{e}^{-\alpha r_{\mathrm{B}1}^2}\mathrm{e}^{-\alpha r_{\mathrm{B}2}^2}\,\mathrm{d}\tau_1\mathrm{d}\tau_2$$

9.9 **(a)** For NH_3:

A minimal basis set uses one basis function to represent each hydrogen 1s-orbital, and one basis function each for the nitrogen 1s, 2s, $2p_x$, $2p_y$, $2p_z$. The total number of basis functions is 8.

(b) For CH_3Cl:

A minimal basis set uses one basis function to represent each hydrogen 1s-orbital, one basis function for carbon 1s, one basis function for carbon 2s, three basis functions for the three carbon 2p-orbitals, one basis function for chlorine 1s, one basis function for chlorine 2s, three basis functions for chlorine 2p, one basis function for chlorine 3s, and three basis functions for chlorine 3p. The total number of basis functions is 3 × 1 + 5 + 9 = 17.

9.10 **(a)** A split-valence basis set uses two basis functions for each valence atomic orbital and one basis function for each inner-shell atomic orbital. Therefore the total number of basis functions is 6 (for the three H 1s) + 1 (for the N 1s) + 2 (for the N 2s) + 6 (for the three N 2p) = 15.

(b) A double-zeta (DZ) basis set replaces each basis set function in the minimal basis set by two basis function. Therefore, 8 (see Exercise 9.9a) is replaced by 16. In addition, for a DZP basis set, a set of three 2p-functions is added to each H atom (giving 9 more basis functions) and a set of six 3d-functions is added to the N atom. Therefore the total number of DZP basis set functions is 16 + 9 + 6 = 31.

9.11 Ethanol has two carbon, six hydrogen and one oxygen atom. We draw up the following tables showing the number of primitives comprising each contracted Gaussian function and the atomic orbital being represented.

(i) 6-31G

Number of primitives comprising contracted Gaussian function	Atomic orbital
3	H1s
1	H1s
6	C1s
3	C2s
1	C2s
3 × 3	3 C2p
3 × 1	3 C2p
6	O1s
3	O2s
1	O2s
3 × 3	3 O2p

3 × 1	3 O2p

The total number of basis functions (contracted Gaussians) is

$$6(1 + 1) + 2(1 + 1 + 1 + 3 + 3) + 1(1 + 1 + 1 + 3 + 3) = \underline{39}$$

The total number of primitives is

$$6(3 + 1) + 2(6 + 3 + 1 + 3 \times 3 + 3 \times 1) + 1(6 + 3 + 1 + 3 \times 3 + 3 \times 1) = \underline{90}$$

(ii) 6-31G*

To the 6-31G basis, we add six d-type polarization functions to each of the three non-hydrogen atoms.

$$\text{Total number of basis functions} = 39 + 3 \times 6 = \underline{57}$$

$$\text{Total number of primitives} = 90 + 3 \times 6 = \underline{108}$$

(iii) 6-31G**

To the 6-31G* basis, we add three p-type polarization functions to each of the six hydrogen atoms.

$$\text{Total number of basis functions} = 57 + 6 \times 3 = \underline{75}$$

$$\text{Total number of primitives} = 108 + 6 \times 3 = \underline{126}$$

Exercise: Repeat the determination of the number of basis set functions in electronic structure calculations on 1,4-dibromobenzene, $C_6H_4Br_2$.

9.12 In a 6-31G** calculation on ethanol, we see from Problem 9.11 that there are 75 basis set functions. In addition, there are $N_e = 6 \times 1 + 2 \times 6 + 1 \times 8 = 26$ electrons. The total number of different Slater determinants is therefore

$$\binom{2M}{N_{\mathrm{e}}} = \binom{150}{26} = \frac{150!}{26!1224!} = \underline{9.406\ldots \times 10^{28}}$$

Exercise: Determine the total number of different Slater determinants that can be formed in a 6-31G** calculation on 1,4-dibromobenzene, $C_6H_4Br_2$.

9.13 Slater determinants **(a)**, **(b)**, **(d)**, and **(e)** can all contribute to a wavefunction of ^{2}S symmetry. Determinant (c) is of P symmetry and determinant (f) is of ^{4}S symmetry.

Exercise: Give examples of Slater determinants that can contribute to the ground-state wavefunction of magnesium. Be sure to include determinants that use 3p- and 3d-orbitals.

9.14 Slater determinants **(a)**, **(d)**, and **(e)** can contribute. Determinants (b) and (c) are of Π symmetry and (f) is of gerade symmetry.

Exercise: Give examples of Slater determinants that can contribute to the $^3\Sigma_{\mathrm{g}}^-$ ground-state wavefunction of molecular oxygen. Include determinants that involve 3p- and 3d-orbitals.

9.15 The unwritten integrals arise from expansion of the integrand (the *brief illustration in Section* 9.9) [A(1) – B(1)][A(2) – B(2)]1/r_{12}) [A(1) + B(1)][A(2) + B(2)] and therefore the complete set of two-electron integrals is

(AA|AA) **+** (AA|AB) + (AA|BA) + (AA|BB) – (AB|BA) – (AB|AA) – (AB|AB) – (AB|BB) – (BA|BA) – (BA|AB) – (BA|AA) – (BA|BB) + (BB|AA) **+** (BB|AB) + (BB|BA) + (BB|BB).

9.16 In the *brief illustration* in Section 9.9, we showed that when MP2 is applied to molecular hydrogen in the minimal basis of two H1s orbitals, the (second-order) estimate of the correlation energy is

$$E_0^{(2)} = \frac{\{(\mathrm{AA}|\mathrm{AA}) - (\mathrm{AB}|\mathrm{AB})\}^2}{4\{E(1\sigma_{\mathrm{g}}1\sigma_{\mathrm{g}}) - E(1\sigma_{\mathrm{u}}1\sigma_{\mathrm{u}})\}}$$

If we define Q and ΔE as in the *brief illustration* in Section 9.10, we can write the above as

$$E_0^{(2)} = -\frac{Q^2}{\Delta E}$$

It should also be noted that in MPPT as discussed in Section 9.9, the HF energy is the sum of the zero-order energy and first order correction. As a result,

$$E_0^{(2)} = E - \left(E_0^{(0)} + E_0^{(1)}\right) = E - \ E_{\mathrm{HF}}$$

In the coupled-cluster CCD method (see eqn 9.33),

$$E - E_{\mathrm{HF}} = \ \langle \Psi_0 | HC_2 | \Psi_0 \rangle = \left\langle \Psi_0 \middle| H \middle| \Psi_{1\sigma_{\mathrm{g}}1\sigma_{\mathrm{g}}}^{1\sigma_{\mathrm{u}}1\sigma_{\mathrm{u}}} \right\rangle t = Qt$$

The equation for t is

$$Qt^2 - \Delta Et - Q = 0$$

with roots of

$$t = \frac{\Delta E \pm \sqrt{(\Delta E)^2 + 4Q^2}}{2\mathrm{Q}} = \frac{\Delta E \pm \Delta E\sqrt{1 + 4(Q/\Delta E)^2}}{2\mathrm{Q}}$$

If $Q << \Delta E$, we can use the approximation $(1 + x)^{1/2} = 1 + x/2$ which yields, taking the negative choice of the plus/minus,

$$t = \frac{\Delta E - \Delta E\left(1 + \frac{2Q^2}{\{\Delta E\}^2}\right)}{2Q} = -\frac{Q}{\Delta E}$$

and therefore

$$E - E_{HF} = Qt = -Q^2/\Delta E$$

This matches the result from MP2.

9.17 Equation 7.65 gives the expression for the 'one-point' electron density:

$$\rho(\boldsymbol{r}) = 2\sum_m \psi_m^*(\boldsymbol{r})\psi_m(\boldsymbol{r})$$

If we use the molecular orbital $\psi_A + \psi_B$ for ψ_m, then the density is given by

$$\begin{aligned}\rho(\boldsymbol{r}) &= 2\{\psi_A^*(\boldsymbol{r}) + \psi_B^*(\boldsymbol{r})\}\{\psi_A(\boldsymbol{r}) + \psi_B(\boldsymbol{r})\}\\ &= 2\{|\psi_A(\boldsymbol{r})|^2 + |\psi_B(\boldsymbol{r})|^2 + \psi_A^*(\boldsymbol{r})\psi_B(\boldsymbol{r}) + \psi_A(\boldsymbol{r})\psi_B^*(\boldsymbol{r})\}\end{aligned}$$

If the basis set functions are real, this becomes

$$\rho(\boldsymbol{r}) = 2\{\psi_A^2(\boldsymbol{r}) + \psi_B^2(\boldsymbol{r}) + 2\psi_A(\boldsymbol{r})\psi_B(\boldsymbol{r})\}$$

9.18 To compute the Hessian matrix, we need the second derivatives of the function.

$$f = \sin ax \cos by$$

$$\frac{\partial f}{\partial x} = a\cos ax \cos by$$

$$\frac{\partial^2 f}{\partial x^2} = -a^2 \sin ax \cos by$$

$$\frac{\partial^2 f}{\partial x \partial y} = -ab\cos ax \sin by = \frac{\partial^2 f}{\partial y \partial x}$$

$$\frac{\partial f}{\partial y} = -b \sin ax \sin by$$

$$\frac{\partial^2 f}{\partial y^2} = -b^2 \sin ax \cos by$$

Therefore, the Hessian matrix is

$$\boldsymbol{H} = \begin{pmatrix} -a^2 \sin ax \cos by & -ab\cos ax \sin by \\ -ab \cos ax \sin by & -b^2 \sin ax \cos by \end{pmatrix}$$

9.19 **(a)** MPPT and CC are not variational so (iv), (v) and (vi) can yield energies below the exact ground-state energy.

(b) Of the methods discussed in Chapter 9, full CI, MPPT, and CC are size-consistent. Therefore, (i), (iii), and (vii) are not assured of being size-consistent.

Exercise: Discuss which of the two features, being variational or being size-consistent, is a more important characteristic of an electronic structure calculation.

9.20 A p-type GTO is given by

$$g_{100} = Nx\mathrm{e}^{-\alpha r^2}$$

$$\frac{\partial g_{100}}{\partial x} = N\mathrm{e}^{-\alpha r^2} - 2\alpha N x^2 \mathrm{e}^{-\alpha r^2}$$

$$= \underline{g_{000} - 2\alpha g_{200}}$$

Exercise: Consider a general Cartesian Gaussian g_{ijk}. Find expressions for both the first and second derivatives of g_{ijk} with respect to x in terms of other Gaussian functions.

9.21 In the ZDO approximation, all two-electron integrals (ab|cd) vanish except those for which a = c and b = d. Therefore, the following integrals that appear in the solution of Exercise 9.4 vanish in the ZDO approximation:

(AA|BB) = (AA|AB) = (AB|AA) = (BA|AA) = (BB|AA) = (BA|BB) = (BB|BA) = 0

9.22 We begin with equation 9.58c and specifically consider a *cis* conformation of the quartet of atoms, for which the convention is the dihedral angle $\tau = 0$. For small torsional displacements φ, $\cos(-\varphi) = \cos\varphi = 1 - \varphi^2/2$. Therefore,

$$E_{\mathrm{tor}} = \sum A[1+\cos(n\tau-\varphi)] = \sum A[1+\cos(-\varphi)] = \sum A[1+\cos(\varphi)]$$
$$= \sum A[1+1-\tfrac{1}{2}\varphi^2] = \sum 2A - \sum \tfrac{1}{2}A\varphi^2$$

The presence of the term of the form ½ $A\varphi^2$ indicates harmonic oscillation.

Problems

9.1 We write the single Slater determinant as

$$N \det|\phi_a(1)\phi_b(2)\ldots\phi_z(N_e)|$$

and show that $N = (N_e!)^{-1/2}$ is the normalization factor.

When we expand the Slater determinant, we get

$$N\begin{vmatrix} \phi_a(1) & \phi_b(1) & \dots & \phi_z(1) \\ \phi_a(2) & \phi_b(2) & \dots & \phi_z(2) \\ \vdots & \vdots & & \vdots \\ \phi_a(N_e) & \phi_b(N_e) & \dots & \phi_z(N_e) \end{vmatrix} = N\sum_P \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)$$

where P allows for all permutations of electrons among the spinorbitals and ε_P is either +1 or −1, depending on whether the number of electron interchanges is even or odd. We require a normalized Slater determinant, so

$$1 = \int |N|^2 \left[\sum_P \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)\right]^*$$

$$\times \left[\sum_P \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)\right]\mathrm{d}\tau$$

$$= |N|^2 \int \left[\sum_P \varepsilon_P P\phi_a^*(1)\phi_b^*(2)\dots\phi_z^*(N_e)\right]$$

$$\times \left[\sum_P \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)\right]\mathrm{d}\tau$$

Each permutation operator P will give rise to a sum of N_e ! products of spinorbitals. However, because the spinorbitals are orthonormal, we only have contributions to the integral when the permutation arising from $[\Sigma_P\ \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)]^*$ is exactly the same permutation that arises from $[\Sigma_P\ \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)]$. Therefore, there are $N_e!$ contributions to the integral. In addition, because the spinorbitals are normalized, each of the $N_e!$ contributions is exactly 1. (Note that $\varepsilon_P^2 = 1$.) For example, one of the $N_e!$ contributions is

$$\int \phi_a^*(1)\phi_b^*(2)\ldots\phi_z^*(N_\mathrm{e})\phi_a(1)\phi_b(2)\ldots\phi_z(N_\mathrm{e})\mathrm{d}\tau$$

$$= \int \phi_a^*(1)\phi_a(1)\mathrm{d}\tau_1 \int \phi_b^*(2)\phi_b(2)\mathrm{d}\tau_2 \ldots \int \phi_z^*(N_\mathrm{e})\phi_z(N_\mathrm{e})\mathrm{d}\tau_n$$

$$= 1 \times 1 \times \cdots \times 1 = 1$$

Thus,

$$1 = |N|^2 \times N_\mathrm{e}!$$

Choosing N as positive and real, we have

$$\underline{N = (N_\mathrm{e}!)^{-1/2}}$$

Exercise: Show that the HF wavefunction Ψ_0 and a singly excited Slater determinant are orthonormal.

9.4 In a (4s)/[2s] contraction scheme, the most diffuse s-type primitive is left uncontracted. Therefore, the s-type Gaussian with exponent $\alpha = 0.123\,317$ is a single basis function. The remaining three primitives are used to form a single contracted Gaussian basis function of the form

$$\chi = N\begin{Bmatrix} 0.474\,49\ g\ (\alpha = 0.453\,757) + \\ 0.134\,24\ g\ (\alpha = 2.013\,30) + \\ 0.019\,06\ g\ (\alpha = 13.3615) \end{Bmatrix}$$

where N is a constant so that χ is properly normalized.

Exercise: Determine the constant N such that the contracted basis function χ is normalized.

9.7 We need to show that

$$\langle \Phi_0 |H| \Phi_a^p \rangle = 0$$

where Φ_0 is the HF ground-state wavefunction

$$\Phi_0 = (N_e!)^{-1/2} \det |\phi_1\phi_2 \dots \phi_a\phi_b \dots \phi_{N_e}|$$

and Φ_a^p is a singly excited determinant

$$\Phi_a^p = (N_e!)^{-1/2} \det |\phi_1\phi_2 \dots \phi_p\phi_b \dots \phi_{N_e}|$$

Using the Slater–Condon rule for two Slater determinants differing by only one spinorbital (see Problem 9.8), we have

$$\langle \Phi_0 |H| \Phi_a^p \rangle = \langle \phi_a(1) |h_1| \phi_p(1) \rangle + \sum_i \{[\phi_a\phi_i][\phi_p\phi_i] - [\phi_a\phi_i][\phi_i\phi_p]\}$$

We now show that $\langle \phi_a(1)|f_1|\phi_p(1)\rangle$ and $\langle \Phi_0|H|\Phi_a^p\rangle$ are equal, and we subsequently show that $\langle \phi_a(1)|f_1|\phi_p(1)\rangle = 0$.

$$f_1\phi_p(1) = \varepsilon_p\phi_p(1) \quad \text{[eqn 7.89]}$$

$$= h_1\phi_p(1) + \sum_i \{J_i(1) - K_i(1)\}\phi_p(1) \quad \text{[eqn 7.88b]}$$

$$= h_1\phi_p(1) + \sum_i \left\{\int \phi_i^*(2)\left(\frac{j_0}{r_{12}}\right)\phi_i(2)\mathrm{d}\boldsymbol{x}_2\right\}\phi_p(1)$$

$$- \sum_i \left\{\int \phi_i^*(2)\left(\frac{j_0}{r_{12}}\right)\phi_p(2)\mathrm{d}\boldsymbol{x}_2\right\}\phi_i(1)$$

Multiplication by $\phi_a^*(1)$ and integration over $\boldsymbol{x}_1$ yields

$$\langle \phi_a(1)|f_1|\phi_p(1)\rangle = \langle \phi_a(1)|h_1|\phi_p(1)\rangle + \sum_i \{[\phi_a\phi_i|\phi_p\phi_i] - [\phi_a\phi_i|\phi_i\phi_p]\}$$

where we have used the notation of *Further information* 7.1 and Problem 9.8. We therefore have shown

$$\langle \Phi_0|H|\Phi_a^p\rangle = \langle \phi_a(1)|f_1|\phi_p(1)\rangle$$

In addition since

$$f_1\phi_p(1) = \varepsilon_p\phi_p(1)$$

we see that

$$\begin{aligned}\langle \phi_a(1)|f_1|\phi_p(1)\rangle &= \langle \phi_a(1)|\varepsilon_p|\phi_p(1)\rangle \\ &= \varepsilon_p\langle \phi_a(1)|\phi_p(1)\rangle \\ &= 0\end{aligned}$$

because the spinorbitals are orthogonal. Therefore

$$\underline{\langle \Phi_0\,|H|\,\Phi_a^p\rangle = 0}$$

as was to be proved.

Exercise: Show that hamiltonian matrix elements between Φ_0 and triply excited determinants are identically zero.

9.10 **(a)** The ground-state electron configuration of the diatomic molecule C_2 is (Section 8.6)

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$$

where $1\sigma_g$ and $1\sigma_u$ arise from carbon 1s atomic orbitals and $2\sigma_g$, $2\sigma_u$, and $1\pi_u$ arise from valence shell atomic orbitals. (In Chapter 8, only valence electrons are considered and the numbering of the molecular orbitals is different.)

Inactive orbitals:	$1\sigma_g$ and $1\sigma_u$
Active orbitals:	$2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$, $3\sigma_u$, and $1\pi_g$
Virtual orbitals:	$4\sigma_g$, $4\sigma_u$ . . . arising from $n = 3$, . . . atomic orbitals

(b) There are 4 inactive electrons (in inactive orbitals) and 8 active electrons (in active orbitals).

(c) In a restricted active-space (RAS) SCF calculation, the set of active orbitals is further divided into orbital subsets I, II, and III. Subset I could consist of the $2\sigma_g$ and $2\sigma_u$ orbitals, with a minimum of two electrons in the subset. Subset II could consist of the $1\pi_u$, $3\sigma_g$ and $1\pi_g$ orbitals. Subset III could consist of the $3\sigma_u$ orbital with a maximum of two electrons. The total number of electrons in the three subsets is held fixed at 8.

Exercise: With the above distribution of σ and π molecular orbitals into active, inactive, and virtual orbitals, what is the number of Slater determinants that would be used in the CASSCF calculation?

9.13 In the meta-generalized gradient approximation of DFT,

$$\tau(\boldsymbol{r}) = \frac{\hbar^2}{2m_e}\sum_i \nabla\psi_i^*(\boldsymbol{r})\cdot\nabla\psi_i(\boldsymbol{r})$$

where the sum is over occupied orbitals. That such an expression represents a kinetic energy density follows from its integration by parts ($\int u\,dv = uv - \int v\,du$):

$$\begin{aligned}\int \tau(\boldsymbol{r})\mathrm{d}\boldsymbol{r} &= \frac{\hbar^2}{2m_\mathrm{e}}\sum_i \int \nabla\psi_i^*(\boldsymbol{r})\cdot\nabla\psi_i(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\\ &= \frac{\hbar^2}{2m_\mathrm{e}}\sum_i \left\{\psi_i^*(\boldsymbol{r})\nabla\psi_i(\boldsymbol{r}) - \int \psi_i^*(\boldsymbol{r})\nabla^2\psi_i(\boldsymbol{r})\mathrm{d}\boldsymbol{r}\right\}\\ &= -\frac{\hbar^2}{2m_\mathrm{e}}\sum_i \int \psi_i^*(\boldsymbol{r})\nabla^2\psi_i(\boldsymbol{r})\mathrm{d}\boldsymbol{r}\end{aligned}$$

where we have used the fact that ψ vanishes at the boundaries so the first term in the middle line above vanishes when evaluated at the limits of integration.

9.16 For this problem and the next three problems in this chapter, all electronic structure computations were performed using the software package GAMESS. All ground-state energies are reported in hartrees and all internuclear distances in ångströms (1 ångström = 10^{-10} m).

(a) H_2 RHF/6-31G: energy = −1.1268 bond length = 0.7299

F_2 RHF/6-31G: energy = −198.6461 bond length = 1.4125

(b) H_2 RHF/6-31G**: energy = −1.1313 bond length = 0.7326

F_2 RHF/6-31G**: energy = −198.6778 bond length = 1.3449

Exercise: Use electronic structure software to compute the energies of the separated atom limits (H + H and F + F) and, using these values and the above results, calculate the bond dissociation energies of H_2 and F_2. Compare the computed dissociation energies and equilibrium bond distances to the experimental values.

9.19 Electronic structure computations were performed using the software package GAMESS. All enthalpies of formation are reported in kcal mol^{-1} (1 kcal = 4.184 kJ) and all equilibrium bond lengths are in ångströms (1 ångström = 10^{-10} m).

(a)(i) ethanol: AM1

C–C distance = 1.5116

C–O distance = 1.4195

O–H distance = 0.9637

(methyl group) C–H distances = 1.1161, 1.1161, 1.1153

(methylene group) C–H distances = 1.1237, 1.1237

Enthalpy of formation = –62.6632

(a)(ii) ethanol: PM3

C–C distance = 1.5179

C–O distance = 1.4095

O–H distance = 0.9472

(methyl group) C–H distances = 1.0978, 1.0979, 1.0971

(methylene group) C–H distances = 1.1080, 1.1079

Ethalpy of formation = –56.8549

(b)(i) 1,4-dichlorobenzene: AM1

C–C distance = 1.3899

C–Cl distance = 3.0890

C–H distance = 2.5011

Enthalpy of formation = 7.9737

(b)(ii) 1,4-dichlorobenzene: PM3

C–C distance = 1.3799

C–Cl distance = 3.0648

C–H distance = 2.4938

Enthalpy of formation = 10.1113

Exercise: Compare the computed enthalpies of formation and equilibrium bond distances to the experimental values.

Chapter 10

Molecular rotations and vibrations

Exercises

10.1 The rates of stimulated and spontaneous emission are given by eqns 6.87 and 6.90:

$$W^{\text{stim}}_{\text{f}\rightarrow\text{i}} = B_{\text{fi}}\rho \quad W^{\text{spont}}_{\text{f}\rightarrow\text{i}} = A_{\text{fi}}$$

where ρ is the energy density of radiation states and is given by the Planck distribution.

Therefore, the ratio of the rates is (using eqn 6.92b and noting that $B_{\text{fi}} = B_{\text{if}}$):

$$\frac{W^{\text{stim}}_{\text{f}\leftarrow\text{i}}}{W^{\text{spont}}_{\text{f}\leftarrow\text{i}}} = \frac{B_{\text{fi}}\rho}{A_{\text{fi}}} = \frac{1}{\text{e}^{h\nu/kT} - 1}$$

where ν is the transition frequency. In terms of the transition wavelength, the ratio is

$$\frac{W^{\text{stim}}_{\text{f}\leftarrow\text{i}}}{W^{\text{spont}}_{\text{f}\leftarrow\text{i}}} = \frac{1}{\text{e}^{hc/\lambda kT} - 1}$$

and at 298 K,

(a) for $\lambda = 0.10$ nm: ratio $= 1/(\text{e}^{483\,000} - 1)$

(b) for $\lambda = 10$ nm: ratio $= 1/(\text{e}^{4\,830} - 1)$

(c) for $\lambda = 6000$ nm: ratio $= 1/(\text{e}^{480.5} - 1)$

10.2 Begin with eqn 10.7:

$$\mu(t) = 2\alpha(t)\mathcal{E}_0 \cos \omega t$$

If the polarizability of the molecule α changes between α_{min} and α_{max} at a frequency ω_{int} as a result of its rotation or vibration, we can write

$$\alpha(t) = \alpha + \tfrac{1}{2}\Delta\alpha \cos \omega_{\text{int}}t$$

where α is the mean polarizability and $\Delta\alpha = \alpha_{\text{max}} - \alpha_{\text{min}}$. Since

$$\cos (A + B) = \cos A \cos B - \sin A \sin B$$

$$\cos (A - B) = \cos A \cos B + \sin A \sin B$$

we note that

$$\begin{aligned}\cos (\omega + \omega_{\text{int}})t + \cos (\omega - \omega_{\text{int}})t &= \cos \omega t \cos \omega_{\text{int}}t - \sin \omega t \sin \omega_{\text{int}}t + \cos \omega t \cos \omega_{\text{int}}t + \sin \omega t \sin \omega_{\text{int}}t \\ &= 2 \cos \omega t \cos \omega_{\text{int}}t\end{aligned}$$

and therefore

$$\begin{aligned}\mu(t) &= 2\alpha(t)\mathcal{E}_0 \cos \omega t \\ &= 2\alpha\mathcal{E}_0 \cos \omega t + \Delta\alpha\, \mathcal{E}_0 \cos \omega_{\text{int}}t \cos \omega t \\ &= 2\alpha\mathcal{E}_0 \cos \omega t + \tfrac{1}{2}\Delta\alpha\, \mathcal{E}_0[\cos (\omega + \omega_{\text{int}})t + \cos (\omega - \omega_{\text{int}})t]\end{aligned}$$

which is eqn 10.8.

10.3 The centre of mass is where $m_A R_A = m_B R_B$, where R_A is the distance from atom A of mass m_A to the centre of mass, R_B is the distance from atom B of mass m_B to the centre of mass, and $R_A + R_B = R$. Therefore $m_A R_A = m_B(R - R_A)$ and

$$R_A = m_B R/(m_A + m_B) \text{ and } R_B = R - R_A = m_A R/(m_A + m_B)$$

The moment of inertia is then

$$\begin{aligned}I &= m_A R_A^2 + m_B R_B^2 \\ &= m_A\{m_B/(m_A + m_B)\}^2 R^2 + m_B\{m_A/(m_A + m_B)\}^2 R^2 \\ &= \{m_A m_B/(m_A + m_B)\}R^2 = \mu R^2, \quad \mu = m_A m_B/(m_A + m_B)\end{aligned}$$

10.4 (a) $^{1}H_2$:

$$I = \tfrac{1}{2}m(^{1}\mathrm{H})R^2 = \tfrac{1}{2} \times 1.0078\ m_u \times (75.09\ \mathrm{pm})^2$$

$$= \underline{4.718 \times 10^{-48}\ \mathrm{kg\ m^2}}\ [1\ m_u = 1.660\ 56 \times 10^{-27}\ \mathrm{kg, or\ use}\ m = m_e + m_p]$$

(b) $^{2}H_2$:

$$I = \tfrac{1}{2}m(^{2}\mathrm{H})R^2 = \underline{9.429 \times 10^{-48}\ \mathrm{kg\ m^2}}$$

(c) $^{1}H^{35}Cl$:

$$I = \left\{\frac{m(^{1}\mathrm{H})m(^{35}\mathrm{Cl})}{m(^{1}\mathrm{H}) + m(^{35}\mathrm{Cl})}\right\} R^2 = \underline{2.644 \times 10^{-47}\ \mathrm{kg\ m^2}}$$

Exercise: Find the moments of inertia of H_2O about three perpendicular axes.

10.5 Refer to Fig. 10.1.

$I = 4m_BR^2$ [only atoms *a, b, c, d* contribute for the axis shown; all axes are equivalent]

Exercise: Repeat the question for an AB_5 trigonal bipyramid with bond lengths R_{ax}, R_{eq}.

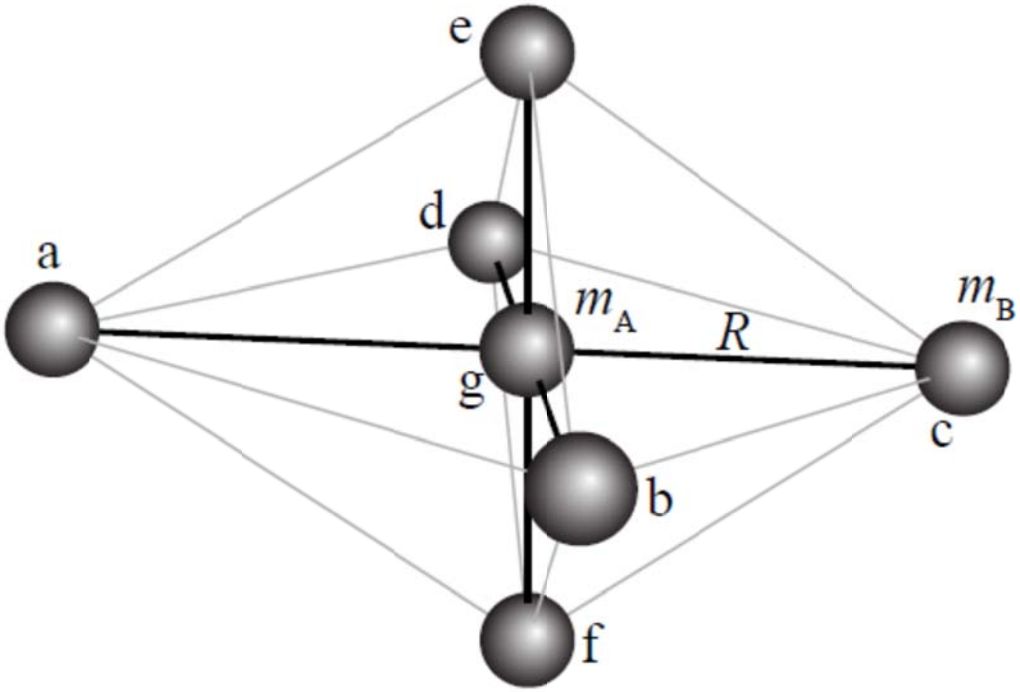


Figure 10.1: An octahedral molecule and the calculation of its moment of inertia.

10.6

$$I' = \sum_i m_i x_i'^2 = \sum_i m_i (x_i + R)^2$$

$$= \sum_i m_i x_i^2 + 2R\sum_i m_i x_i + R^2 \sum_i m_i$$

$$= I + 0 + mR^2 = I + mR^2$$

because $\sum_i m_i x_i = 0$ for centre of mass and $\sum_i m_i = m$.

10.7 The NH_3 molecule is a symmetric rotor; its rotational wavenumbers are given by eqn 10.16.

For each value of J, values of both K and M_J extend in steps of 1 from $-J$ to $+J$.

(J, K, M_J)	$\tilde{F} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$ (cm^{-1})
(0,0,0)	0
(1,±1,±1), (1, ±1,0)	7.321
(1,0,±1), (1,0,0)	1.954
(2,±2,±2), (2,±2,±1), (2,±2,0)	27.330
(2,±1,±2), (2,±1,±1), (2,±1,0)	11.229
(2,0,±2), (2,0,±1), (2,0,0)	5.862
(3,±3,±3), (3,±3,±2), (3,±3,±1), (3,±3,0)	60.027
(3,±2,±3), (3,±2,±2), (3,±2,±1), (3,±2,0)	33.192
(3,±1,±3), (3,±1,±2), (3,±1,±1), (3,±1,0)	17.091
(3,0,±3), (3,0,±2), (3,0,±1), (3,0,0)	11.724

10.8 Polar molecules may show a pure rotational microwave absorption spectrum. Therefore, **(c)**, **(d)**, and **(e)**.

10.9 The line separation is $\Delta E/hc = 2B$. Then, as $\tilde{B} = \hbar/4\pi cI_\perp$, we have (with $I_\perp = \mu R^2$)

$$\tilde{\nu} = \Delta E/hc = \hbar/2\pi cI_\perp = \hbar/2\pi c\mu R^2$$

Therefore,

$$R = \{\hbar/2\pi c\mu\tilde{\nu}\}^{1/2}$$

$$= \underline{162}\text{ pm} \quad [\mu = 0.999\,86\,m_u = 1.6603 \times 10^{-27}\text{ kg}, \Delta E/hc = 12.8\text{ cm}^{-1}]$$

10.10 For $^2H^{127}I$, $\mu = 1.9826\,m_u$. As $\tilde{\nu} \propto 1/\mu$ the line separation will be $0.5043 \times (12.8\text{ cm}^{-1}) = \underline{6.46\text{ cm}^{-1}}$.

Exercise: The bond length of $^1H^2H$ is 74.136 pm. At what wavenumbers would it absorb if its rotational transitions were active?

10.11 Rotational Raman transitions obey the selection rule $\Delta J = \pm 2$ for linear molecules. From the discussion in Section 10.5, with $\tilde{\nu}_0$ the wavenumber of the incident radiation (that is, the Rayleigh line), the wavenumbers of the Stokes and anti-Stokes lines relative to and closest to the Rayleigh line are:

Stokes lines: $\tilde{\nu}_J - \tilde{\nu}_0 = -4\tilde{B}\,(J+3/2) \quad J = 0, 1, 2$

Anti-Stokes lines: $\tilde{\nu}_J - \tilde{\nu}_0 = 4\tilde{B}\,(J-1/2) \quad J = 2, 3, 4$

Since $\tilde{B} = 10.4400\ \text{cm}^{-1}$, the relative wavenumbers are:

Stokes: $J = 0$ $-62.64\ \text{cm}^{-1}$
$J = 1$ $-104.4\ \text{cm}^{-1}$
$J = 2$ $-146.16\ \text{cm}^{-1}$

Anti-Stokes: $J = 0$ $+62.64\ \text{cm}^{-1}$
$J = 1$ $+104.4\ \text{cm}^{-1}$
$J = 2$ $+146.16\ \text{cm}^{-1}$

10.12 The rotational wavenumbers for a linear rotor, including the effects of centrifugal distortion, are given by eqn 10.21:

$$\tilde{F} = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$

The rotational wavenumbers for the states involved in the rotational Raman transitions in Exercise 10.11 are

$J = 0$ $\tilde{F} = 0$ $J = 1$ $\tilde{F} = 2\tilde{B} - 4\tilde{D}$

$J = 2$ $\tilde{F} = 6\tilde{B} - 36\tilde{D}$ $J = 3$ $\tilde{F} = 12\tilde{B} - 144\tilde{D}$

$J = 4$ $\tilde{F} = 20\tilde{B} - 400\tilde{D}$

The three Stokes lines closest to the Rayleigh line and their wavenumbers are:

$J = 0 \rightarrow J = 2$ $\tilde{\nu}_J - \tilde{\nu}_0 = -6\tilde{B} + 36\tilde{D} = -62.6256\ \text{cm}^{-1}$

$J = 1 \rightarrow J = 3$ $\tilde{\nu}_J - \tilde{\nu}_0 = -10\tilde{B} + 140\tilde{D} = -104.344\ \text{cm}^{-1}$

$J = 2 \rightarrow J = 4$ $\tilde{\nu}_J - \tilde{\nu}_0 = -14\tilde{B} + 364\tilde{D} = -146.0144\ \text{cm}^{-1}$

The three anti-Stokes lines closest to the Rayleigh line and their wavenumbers are:

$J = 2 \rightarrow J = 0$ $\qquad \tilde{\nu}_J - \tilde{\nu}_0 = 6\tilde{B} - 36\tilde{D} = +62.6256\ \text{cm}^{-1}$

$J = 3 \rightarrow J = 1$ $\qquad \tilde{\nu}_J - \tilde{\nu}_0 = 10\tilde{B} - 140\tilde{D} = +104.344\ \text{cm}^{-1}$

$J = 4 \rightarrow J = 2$ $\qquad \tilde{\nu}_J - \tilde{\nu}_0 = 14\tilde{B} - 364\tilde{D} = +146.0144\ \text{cm}^{-1}$

10.13 The lowest rotational level for a diatomic molecule is $J = 0$ with zero rotational energy (i.e. no zero-point energy). However, for molecular hydrogen, as discussed in Section 10.6, there are two distinct forms: *para*-hydrogen (even J) and *ortho*-hydrogen (odd J). The conversion of *ortho* to *para* is very slow so as a sample of H_2 at room temperature is cooled, the *ortho*-hydrogen settles into its lowest rotational state $J = 1$; even at $T = 0$, it cannot readily convert to *para*-hydrogen $J = 0$. Thus, with the $J = 1$ state having some population, there is an effective zero-point energy.

Exercise: What can be said about zero-point rotational energy for dioxygen?

10.14 The following table lists value of μ/m_u for the species; to obtain absolute values use $m_u = 1.660\,56 \times 10^{-27}$ kg; additional data will be found in Exercises 10.4 and 10.9. [Tables of nuclide masses are given in the *Handbook of the American Institute of Physics*, D.E. Gray (ed.), McGraw-Hill (1972).] Values of k are obtained from $k_f = \mu\omega^2 = 4\pi^2\mu c^2\tilde{\nu}^2$ [$\omega = 2\pi\nu$, $\nu = c\tilde{\nu}$].

	$^1H_2$	$^1H^{19}F$	$^1H^{35}Cl$	$^1H^{81}Br$	$^1H^{127}I$
μ/m_u	0.5039	0.9570	0.9796	0.9954	0.9999
$k_f/(\text{N m}^{-1})$	574.9	965.7	516.3	411.5	313.8

10.15 For the effect of replacing ^{1}H by ^{2}H, assume that k_f remains constant, and so form $\tilde{\nu} = (1/2\pi c)(k_f/\mu^*)^{1/2}$, with μ^* the reduced mass of the deuterated species. Draw up the following table:

	$^2H^1H$	$^2H^{19}F$	$^2H^{35}Cl$	$^2H^{81}Br$	$^2H^{127}I$
μ^*/m_u	0.6717	1.8210	1.9044	1.9652	1.9826
$\tilde{\nu}/\text{cm}^{-1}$	3811	3000	2145	1885	1639

Exercise: In three dimensions the motion of the centre of mass separates from the internal motion, but rotations and vibrations separate only approximately. Demonstrate these features.

10.16 To show an infrared absorption spectrum, a molecule must have a dipole moment that varies, at least transiently, with atomic displacements (that is, stretching and bending motions). Note that a molecule can be nonpolar but still be infrared active if there is at least one vibrational normal mode that induces, at least temporarily, a dipole moment in the molecule. Homonuclear diatomic molecules are infrared inactive; heteronuclear diatomic molecules are active. Therefore, **(a)**, **(c)**, and **(d)** can show infrared absorption spectra.

10.17 The P-branch line corresponds to a transition from the initial state ($v = 0, J = 2$) to the final state ($v = 1, J = 1$). Since a given vibrational-rotational state (v, J) has an energy (in cm^{-1}) of

$$E/hc = (v + 1/2)\tilde{\nu} + \tilde{B}J(J + 1)$$

the photon wavenumber for the transition is

$E(1,1)/hc - E(0,2)/hc$

$=\{(1 + 1/2) \times 4138.3 + 1(1+1) \times 20.9\}\ \text{cm}^{-1} \ - \{(0 + 1/2) \times 4183.3 + 2(2+1) \times 20.9\}\ \text{cm}^{-1}$

$= 4054.7\ \text{cm}^{-1}$

10.18 The dipole moment of a homonuclear diatomic molecule does not vary with vibrational motion; the molecule remains nonpolar as the bond length changes. However, the molecular polarizability does vary with distance. Therefore, a homonuclear diatomic molecule is infrared inactive but vibrationally Raman active.

10.19 For a linear molecule, there are $3N - 5$ normal modes where N is the number of atoms in the molecule.-For a non-linear molecule, $3N - 6$. Molecules (a) and (b) are non-linear; (c) and (d) are linear.

(a) $N = 4$; $3N - 6 = \underline{6}$

(b) $N = 12$; $3N - 6 = \underline{30}$

(c) $N = 6$; $3N - 5 = \underline{13}$

(d) $N = 3$; $3N - 5 = \underline{4}$

10.20 The molecule has three normal modes so the ground state has zero quanta in each of the vibrational modes; that is, (0, 0, 0) is the ground state. Within the harmonic approximation, each normal mode makes a contribution of $(v_i + ½)\hbar\omega_i$ to the vibrational energy where v_i is the vibrational quanta in mode i of frequency ω_i. Therefore, the ground-state energy in wavenumber units is

$E/hc = (0 + 1/2) \times 1595\ \text{cm}^{-1} + (0 + 1/2) \times 3652\ \text{cm}^{-1} + (0 + 1/2) \times 3756\ \text{cm}^{-1} = \underline{450.1.5\ \text{cm}^{-1}}$

10.21 The point group for NH_3 is C_{3v}. **(a)** Infrared active normal modes must belong to the same symmetry species as x, y, or z, which are A_1 (z) and E (x, y). Therefore all modes are infrared active. **(b)** Raman active modes must belong to the same symmetry species as one of the components of the electric polarizability (x^2, xy, xz, z^2, etc.) Since z^2 is of A_1 symmetry and (x, y)

of E symmetry, both normal modes are Raman active.

10.22 The ground vibrational state is (0, 0, 0). Letting 1595, 3652 and 3756 be the vibrational wavenumber of modes 1, 2 and 3, respectively, we designate an excited state as (v_1, v_2, v_3). The three-lowest frequency overtones correspond to transitions from (0, 0, 0) to the excited states:

$$(2, 0, 0)\text{:}\;\; \text{wavenumber} = 2 \times 1595\ \text{cm}^{-1} = 3190\ \ \text{cm}^{-1}$$

$$(3, 0, 0)\text{:}\;\; \text{wavenumber} = 3 \times 1595\ \text{cm}^{-1} = 4785\ \ \text{cm}^{-1}$$

$$(4, 0, 0)\text{:}\;\; \text{wavenumber} = 4 \times 1595\ \text{cm}^{-1} = 6380\ \ \text{cm}^{-1}$$

The three-lowest frequency combination bands correspond to transitions from (0, 0, 0) to the excited states:

$$(1, 1, 0)\text{:}\;\; \text{wavenumber} = 1595\ \text{cm}^{-1} + 3652\ \text{cm}^{-1} = 5247\ \ \text{cm}^{-1}$$

$$(1, 0, 1)\text{:}\;\; \text{wavenumber} = 1595\ \text{cm}^{-1} + 3756\ \text{cm}^{-1} = 5351\ \ \text{cm}^{-1}$$

$$(2, 1, 0)\text{:}\;\; \text{wavenumber} = 2 \times 1595\ \text{cm}^{-1} + 3652\ \text{cm}^{-1} = 6842\ \ \text{cm}^{-1}$$

Problems

10.1 (a)

$$I = \int_0^R r^2 \mathrm{d}m(r) = \int_0^R (2\pi\rho r \mathrm{d}r) r^2 \qquad [\rho : \text{density}]$$

$$= 2\pi\rho \int_0^R r^3 \mathrm{d}r = \tfrac{1}{2}\pi\rho R^4$$

$$m = \pi R^2 \rho;\ \text{therefore}\ I = \frac{\pi R^4 m}{2\pi R^2} = \underline{\tfrac{1}{2} m R^2}$$

(b) The perpendicular distance of the volume element at (r, θ, ϕ) is $r \sin \theta$; therefore

$$I = \int \rho (r\ \sin\theta)^2 \sin\theta \mathrm{d}\theta\, \mathrm{d}\phi\, r^2 \mathrm{d}r$$

$$= \rho \int_0^R r^4 \mathrm{d}r \int_0^\pi \sin^3\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = \rho \left(\frac{R^5}{5}\right)\left(\frac{4}{3}\right)(2\pi)$$

$$m = \tfrac{4}{3}\pi R^3 \rho$$

Therefore,

$$I = \frac{(8\pi/15)m\,R^5}{(4\pi/3)R^3} = \underline{\tfrac{2}{5}mR^2}$$

10.4 $\tilde{F}(J, K, M_J) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$ [eqn 10.16]

$I_{\parallel} = 4m_{\mathrm{B}}R^2$ [Table 10.1]

$I_{\perp} = 2m_{\mathrm{B}}R^2$ [Table 10.1]

Therefore

$$\tilde{A} = \frac{\hbar}{4\pi c I_{\parallel}} = \frac{\hbar}{16\pi m_{\mathrm{B}} c R^2}, \quad \tilde{B} = \frac{\hbar}{4\pi c I_{\perp}} = \frac{\hbar}{8\pi m_{\mathrm{B}} c R^2}$$

and so $\tilde{A} = \tilde{B}/2$. It follows that

$$\tilde{F}(J, K, M_J) = \tilde{B}J(J+1) - \tfrac{1}{2}\tilde{B}K^2 = \tilde{B}\left\{J(J+1) - \tfrac{1}{2}K^2\right\}$$

Exercise: Establish a similar result for an octahedral AB_6 molecule.

10.7 The wavenumbers of the transitions $J + 1 \leftarrow J$ are given in eqn 10.30. To find a maximum, set the first derivative $\mathrm{d}\tilde{\nu}_J/\mathrm{d}J = 0$:

$$\tilde{\nu}_J = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3$$

$$\frac{\mathrm{d}\tilde{\nu}_J}{\mathrm{d}J} = 2\tilde{B} - 12\tilde{D}(J+1)^2 = 0$$

Therefore,

$$\tilde{B} = 6\tilde{D}(J+1)^2$$

$$(J+1)^2 = \tilde{B}/6\tilde{D}$$

$$J = \left(\tilde{B}/6\tilde{D}\right)^{1/2} - 1$$

Using the date in problem 10.5 for HCl, we find

$$J = (10.4400/\{6 \times 0.0004\})^{1/2} - 1 \approx 65$$

10.10

$$\tilde{B}(^1\mathrm{H}^{35}\mathrm{Cl}) = \hbar/4\pi c I(^1\mathrm{H}^{35}\mathrm{Cl}) \qquad [I = 2.644 \times 10^{-47}\ \mathrm{kg\ m}^2\text{, Exercise 10.4}]$$

$$= \underline{10.59\ \mathrm{cm}^{-1}}$$

The relative populations are given by

$$b(J) = (2J+1)\exp\{-hc\tilde{B}J(J+1)/kT\}$$

$$= (2J+1)\exp\{-0.050\,79\,J(J+1)\} \quad [kT/hc = 208.51\ \mathrm{cm}^{-1}\text{ at 300 K}]$$

Draw up the following table (b' is discussed below):

J	0	1	2	3	4	5	6	7
$b(J)$	1.000	2.710	3.687	3.805	3.259	2.397	1.540	0.873
$b'(J)$	1.000	1.807	2.212	2.175	1.811	1.307	0.829	0.465

J	8	9	10	11	12	13	14	15
$b(J)$	0.439	0.197	0.079	0.028	0.009	0.003	0.001	10^{-4}
$b'(J)$	0.232	0.103	0.041	0.015	0.005	0.001	10^{-4}	10^{-5}

($\Sigma_j\, b(J) = 20.026$, the rotational partition function at 300 K.) **(a)** If the intensities were determined solely by the populations they would be proportional to $b(J)$, and the most intense transition would be 4 ← 3. **(b)** If we take the J-dependence of the transition moment into account we should use

$$b'(J) = \{(J+1)/(2J+1)\}b(J) = (J+1)\exp\{-0.050\,79J(J+1)\},$$

which gives the entries in the table above. The transition of maximum intensity is 3 ← 2. Note that we have considered only absorption intensities, not net intensities.

Exercise: Calculate the relative net absorption intensities.

10.13 Only vibrational transitions of DCl are being considered and the lowest four transitions from the $v = 0$ state correspond to the transitions:

$v = 0 \rightarrow v = 1$ $\quad (E_1 - E_0)/hc = 2091\ \text{cm}^{-1} = E_1^{\text{rel}}/hc$

$v = 0 \rightarrow v = 2$ $\quad (E_2 - E_0)/hc = 4128\ \text{cm}^{-1} = E_2^{\text{rel}}/hc$

$v = 0 \rightarrow v = 3$ $\quad (E_3 - E_0)/hc = 6111\ \text{cm}^{-1} = E_3^{\text{rel}}/hc$

$v = 0 \rightarrow v = 4$ $\quad (E_4 - E_0)/hc = 8043\ \text{cm}^{-1} = E_4^{\text{rel}}/hc$

where $E_v^{\rm rel}/hc$ is the energy in wavenumber units of vibrational level *v* relative to the *v* = 0 level. The vibrational energies are given by eqn 10.53 and, as in Example 10.3, we retain the first two terms. Since we desire energies relative to *v* = 0, we substract the zero-point energy

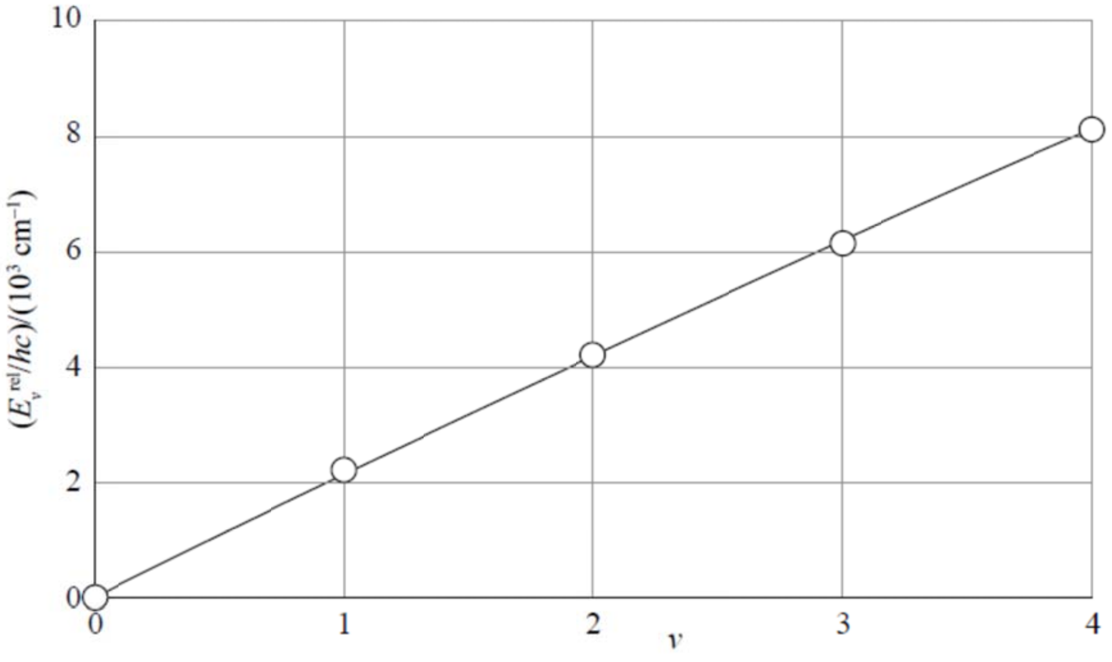
$\frac{1}{2}\hbar\omega - \frac{1}{4}\hbar\omega x_{\rm e}$. The relative energies are therefore given by

$$E_v^{\rm rel} = \left(v + \frac{1}{2}\right)\hbar\omega - \left(v + \frac{1}{2}\right)^2 \hbar\omega x_{\rm e} - \left(\frac{\hbar\omega}{2} - \frac{\hbar\omega x_{\rm e}}{4}\right)$$

$$= (\hbar\omega - \hbar\omega x_{\rm e})v - \hbar\omega x_{\rm e} v^2$$

A plot of $E_v^{\rm rel}/hc$ against *v* is shown in Fig. 10.4; the best quadratic fit is

$$E_v^{\rm rel}/hc = 2117.1v - 26.613v^2$$



$(E_v^{\mathrm{rel}}/hc)/10^3\ \mathrm{cm}^{-1}$

Figure 10.4: The plot of relative energies against vibrational quantum number for Problem 10.13.

It follows that

$$\hbar\omega - \hbar\omega x_{\mathrm{e}} = (2117.1\ \mathrm{cm}^{-1})hc = 4.206 \times 10^{-20}\ \mathrm{J}$$

$$\hbar\omega x_{\mathrm{e}} = (26.613\ \mathrm{cm}^{-1})hc = 5.287 \times 10^{-22}\ \mathrm{J}$$

and, therefore, $\omega = 4.038 \times 10^{14}\ \mathrm{s}^{-1}$ and $\omega x_{\mathrm{e}} = 5.013 \times 10^{12}\ \mathrm{s}^{-1}$.

10.16

$$\tilde{\nu}^{\mathrm{P}} = \tilde{\nu} - 2(v+1)\,\tilde{\nu}x_{\mathrm{e}} + \ldots - (\tilde{B}_{v+1} + \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots \text{ [eqn 10.61]}$$

$$\tilde{\nu}^{\mathrm{Q}} = \tilde{\nu} - 2(v+1)\,\tilde{\nu}x_{\mathrm{e}} + \ldots + (\tilde{B}_{v+1} - \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots \text{ [eqn 10.62]}$$

$$\tilde{\nu}^{\mathrm{R}} = \tilde{\nu} - 2(v+1)\,\tilde{\nu}x_{\mathrm{e}} + \ldots + 2\tilde{B}_{v+1} + (3\tilde{B}_{v+1} - \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots \text{ [eqn 10.63]}$$

If x_{e} is ignored these equations become

$$\tilde{\nu}^{\mathrm{P}} - \tilde{\nu} = -(\tilde{B}_{v+1} + \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots$$

$$\tilde{\nu}^{\mathrm{Q}} - \tilde{\nu} = (\tilde{B}_{v+1} - \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots$$

$$\tilde{\nu}^{\mathrm{R}} - \tilde{\nu} = 2\tilde{B}_{v+1} + (3\tilde{B}_{v+1} - \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots$$

Then, with $\tilde{B}_0 = 10.4400\ \mathrm{cm}^{-1}$ and $\tilde{B}_1 = 10.1366\ \mathrm{cm}^{-1}$

$$(\tilde{\nu}^{\mathrm{P}} - \tilde{\nu})/\mathrm{cm}^{-1} = -20.5766J - 0.3034J^2$$

$$(\tilde{\nu}^{\mathrm{Q}} - \tilde{\nu})/\mathrm{cm}^{-1} = -0.3034J(J+1)$$

$$(\tilde{\nu}^{\mathrm{R}} - \tilde{\nu})/\mathrm{cm}^{-1} = 20.2732 + 19.9698J - 0.3034J^2$$

The wavenumbers of the branches are plotted in Fig. 10.5.

Figure 10.5: The wavenumbers of the P-, Q-, and R-branches calculated in Problem 10.16.

Exercise: Find the location of the lines of the O- and S-branches of the Raman spectrum.

10.19 The energy in wavenumber units of the initial state ($v = 1$, $J = 2$) is [see eqn 10.60 with $\tilde{F} = E/(hc)$]

$$\tilde{F}(v=1, J=2) = (1+\tfrac{1}{2})4401.2\ \text{cm}^{-1} + (2)(2+1)121.3\ \text{cm}^{-1}$$

$$= 7329.6\ \text{cm}^{-1}$$

(a) For the Q-branch Stokes line, $\Delta v = +1$ and $\Delta J = 0$ so the final state of the diatomic molecule is $(v = 2, J = 2)$ with an energy

$$\tilde{F}(v=2, J=2) = (2+\tfrac{1}{2})4401.2\ \text{cm}^{-1} + (2)(2+1)121.3\ \text{cm}^{-1}$$

$$= 11\ 730.8\ \text{cm}^{-1}$$

Therefore, while the diatomic molecule gains an energy given by $\tilde{F}(v=2, J=2) - \tilde{F}(v=1, J=2)$, the scattered radiation *loses* that energy and therefore has a wavenumber of

$$15\ 873.0 - (11\ 730.8 - 7329.6) = \underline{11\ 471.8\ \text{cm}^{-1}}$$

(b) For the O-branch Stokes line, the final state is $(v = 2, J = 0)$ which has an energy of

$$\tilde{F}(v=2, J=0) = (2+\tfrac{1}{2})4401.2\ \text{cm}^{-1} + (0)(0+1)121.3\ \text{cm}^{-1}$$

$$= 11\ 003.0\ \text{cm}^{-1}$$

Therefore, while the diatomic molecule gains an energy given by $\tilde{F}(v=2, J=0) - \tilde{F}(v=1, J=2)$, the scattered radiation *loses* that energy and therefore has a wavenumber of

$$15\ 873.0 - (11\ 003.0 - 7329.6) = \underline{12\ 199.6\ \text{cm}^{-1}}$$

(c) For the anti-Stokes line, $\Delta v = -1$ so the final state of the diatomic molecule is ($v = 0$, $J = 2$) with an energy

$$\tilde{F}(v = 0, J = 2) = (0 + \tfrac{1}{2})4401.2\ \text{cm}^{-1} + (2)(2 + 1)121.3\ \text{cm}^{-1}$$

$$= 2928.4\ \text{cm}^{-1}$$

In this case the diatomic molecule loses an energy given by

$\tilde{F}(v = 1, J = 2) - \tilde{F}(v = 0, J = 2)$, and the scattered radiation *gains* that energy; therefore the scattered radiation occurs at a wavenumber of

$$15\ 873.0 + (7329.6 - 2928.4) = \underline{20\ 274.2\ \text{cm}^{-1}}$$

If anharmonicity effects are included, the spacing between the $v = 1$ and $v = 2$ vibrational levels will decrease (see eqn 10.60) and as a result the scattered Stokes radiation will lose less energy and will thus occur at a <u>higher wavenumber</u> than that computed in part (a).

Exercise: How will the wavenumbers computed in parts (a), (b) and (c) change if the effects of centrifugal distortion are included?

10.22 Consider the system depicted in Fig. 10.6.

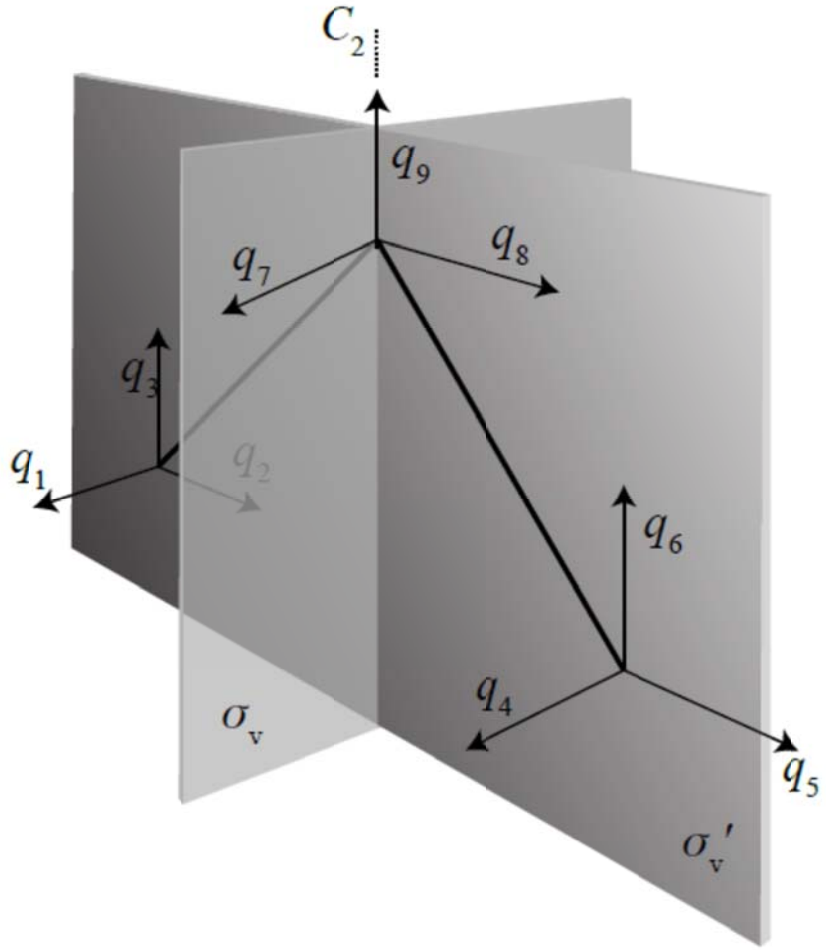


Figure 10.6: The displacement coordinates of a C_{2v} molecule.

Under the operations of the group (C_{2v}) they transform as follows:

	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	χ

E	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	9
C_2	$-q_4$	$-q_5$	q_6	$-q_1$	$-q_2$	q_3	$-q_7$	$-q_8$	q_9	-1
σ_v	q_4	$-q_5$	q_6	q_1	$-q_2$	q_3	q_7	$-q_8$	q_9	1
σ'_v	$-q_1$	q_2	q_3	$-q_4$	q_5	q_6	$-q_7$	q_8	q_9	3

[The characters, final column, are given by the net number of displacements left unchanged by the operation.] The representation decomposes as follows [eqn 5.22]:

$$a(\mathrm{A}_1) = \tfrac{1}{4}\{9 - 1 + 1 + 3\} = 3 \quad a(\mathrm{A}_2) = \tfrac{1}{4}\{9 - 1 - 1 - 3\} = 1$$

$$a(\mathrm{B}_1) = \tfrac{1}{4}\{9 + 1 + 1 - 3\} = 2 \quad a(\mathrm{B}_2) = \tfrac{1}{4}\{9 + 1 - 1 + 3\} = 3$$

That is, the basis spans $3\mathrm{A}_1 + \mathrm{A}_2 + 2\mathrm{B}_1 + 3\mathrm{B}_2$. From the C_{2v} character table, translations span $\mathrm{B}_1 + \mathrm{B}_2 + \mathrm{A}_1$ (for x, y, z respectively) and rotations span $\mathrm{B}_2 + \mathrm{B}_1 + \mathrm{A}_2$ (for R_x, R_y, R_z respectively). Consequently the vibrations span $\underline{2\mathrm{A}_1 + \mathrm{B}_2}$.

(a) Infrared-active transitions are those of the same symmetry species as the electric dipole moment, which spans $\mathrm{B}_1 + \mathrm{B}_2 + \mathrm{A}_1$ (for μ_x, μ_y, μ_z respectively). Therefore, <u>all three modes are infrared active</u> (A_1 is z-polarized, B_2 y-polarized).

(b) Raman-active transitions are those of the same symmetry species as the polarizability, which transforms as the quadratic form x^2, xy, etc. These span $2\mathrm{A}_1 + \mathrm{A}_2 + \mathrm{B}_1 + \mathrm{B}_2$ [character table], and so <u>all three modes are Raman active</u>.

Exercise: Establish the symmetry species and activities of the vibrations of H_2O_2.

10.25 The harmonic oscillator wavefunctions are proportional to $H_0 \propto 1$, $H_1 \propto x$ for oscillations in the x-direction and to $H_0 \propto 1$, $H_1 \propto y$ for oscillations in the y-direction. Therefore, the linear combinations $H_0(y)H_1(x) \pm \mathrm{i}H_1(y)H_0(x)$ of the singly-excited degenerate states are proportional to $x \pm \mathrm{i}y \propto \mathrm{e}^{\pm\mathrm{i}\phi}$, which are eigenfunctions of l_z, the angular momentum about the z-axis, with $m_l = \pm1$.

Exercise: What can be said about the doubly excited bending modes?

Chapter 11

Molecular electronic transitions

Exercises

11.1 See the discussion of the Hund coupling cases in Section 11.1.

(i) We focus on which of the quantum numbers for orbital and spin angular momenta are good quantum numbers. For case (a) Ω, Λ, Σ; for case **(b)** Λ, S; for case **(c)** E, Ω; for case **(d)** L, S.

(ii) In each case, the degeneracy of a rotational energy level is $2J + 1$, where J is the total angular momentum.

Exercise: Describe mechanisms by which the angular momenta are decoupled.

11.2 Refer as needed to the discussion in Section 8.6. (i) A single electron (spin-1/2) gives rise to a doublet term. (ii) Since a d-orbital pertains to $l = 2$, the overlap of two d-orbitals, using the Clebsch-Gordan series (eqn 4.42), gives rise to terms with values of the orbital angular momenta of 0, 1, 2, 3, and 4, pertaining to Σ, Π, Δ, Φ, and Γ terms, respectively. (iii) The Σ term requires a label to describe its behaviour under reflection in a plane containing the internuclear axis. The molecular orbital constructed from face-to-face overlap of d_{xy} orbitals has the character of -1 under this operation so the term is Σ^-. (iv) For the parity classification of the terms, the molecular orbital does not change upon inversion through the center of the diatomic molecule so it has gerade symmetry.

The following terms therefore arise: ${}^2\Sigma_g^-$, ${}^2\Pi_g$, ${}^2\Delta_g$, ${}^2\Phi_g$, ${}^2\Gamma_g$

11.3 Refer to the specification of the selection rules in Section 11.3.

(a) ${}^2\Pi \rightarrow {}^2\Pi$ *allowed* by $\Delta\Lambda = 0$

(b) ${}^1\Sigma \rightarrow {}^1\Sigma$ *allowed* by $\Delta\Lambda = 0$

(c) $\Sigma \rightarrow \Delta$ *forbidden* ($\Delta\Lambda = \pm 2$ not allowed)

(d) $\Sigma^+ \rightarrow \Sigma^-$ *forbidden* by $\Sigma^+ \not\leftrightarrow \Sigma^-$

(e) $\Sigma^+ \rightarrow \Sigma^+$ *allowed* by $\Delta\Lambda = 0$ and $\Sigma^+ \leftrightarrow \Sigma^+$

(f) ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ *allowed* by $\Delta\Lambda = 0$, $\Sigma^+ \leftrightarrow \Sigma^+$, and g $\leftrightarrow$ u

(g) ${}^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^-$ *forbidden* by $\Sigma^- \not\leftrightarrow \Sigma^+$

Exercise: Which of ${}^2\Pi \rightarrow {}^2\Sigma$, ${}^3\Pi_g \rightarrow {}^3\Sigma_u^+$, and ${}^3\Delta_g \rightarrow {}^1\Pi_u$ are allowed?

11.4 When a diatomic molecule with $S = 3/2$ dissociates, the two atoms that form may have spins S_1 and S_2, respectively, such that the Clebsch-Gordan series (eqn 4.42) for the resultant of S_1 and S_2 contains $S = 3/2$. For example, ($S_1 = 2$, $S_2 = 1/2$) results in $S = 5/2$, 3/2 so this combination of spins is allowed. The spin states, (S_1, S_2), of the atoms that may form are

(0, 3/2), (3/2, 0), (1/2, 1), (1, 1/2), (1/2, 2), (2, 1/2), (1, 3/2), (3/2, 1) and so on.

11.5 A Φ state pertains to $\Lambda = 3$. Therefore, the two atoms that form when the diatomic molecule dissociates may have may have orbital angular momenta L_1 and L_2, respectively, such that the Clebsch-Gordan series (eqn 4.42) for the resultant of L_1 and L_2

contains a value of 3. For example, the atomic terms (F, D) pertain to $L_1 = 3$ and $L_2 = 2$ with resultant values of 5, 4, 3, 2, 1, 0; therefore, since a value of 3 is possible, the atomic terms (F, D) are possible. The list of possible terms includes

(F, S), (S, F), (D, P), (P, D), (D, D), (F, D), (D, F) and so on.

11.6 Dissocation of O_2^+ produces O + O$^+$. (i) The $^4\Pi_u$ state has a spin multiplicity of $(2S + 1) = 4$; that is, $S = 3/2$. Therefore, if S_1 is the total spin for the O atom (an integer since the atom has an even number of electrons) and S_2 is the total spin for the O$^+$ ion (a half-integer since the ion has an odd number of electrons), then possible values for S_1 and S_2 are those for which the Clebsch-Gordan series (eqn 4.42) for the coupling of S_1 and S_2 includes a value of 3/2. For example, the combination of $S_1 = 0$ (a singlet term) and $S_2 = 3/2$ (a quartet term) is possible. (ii) The $^4\Pi_u$ pertains to $\Lambda = 1$. Therefore, the states that form when the diatomic molecule dissociates may have orbital angular momenta L_1 and L_2 such that the Clebsch-Gordan series (eqn 4.42) for the resultant of L_1 and L_2 contains a value of 1. For example, the terms (P, D) pertain to $L_1 = 2$ and $L_2 = 3$ with resultant values of 5, 4, 3, 2, 1, 0; therefore, since a value of 1 is possible, the terms (P, D) are possible.

The list of possible terms includes

O(^{1}P) + O$^+$(^{4}S), O(^{3}P) + O$^+$(^{4}S), O(^{3}P) + O$^+$(^{2}S), O(^{1}D) + O$^+$(^{4}S), O(^{3}D) + O$^+$(^{4}S), O(^{1}P) + O$^+$(^{2}D), O(^{1}S) + O$^+$(^{2}P), and so on.

11.7 The transition element $\langle {}^1A_2|\mu_q|{}^1A_1\rangle$ transforms as

$$A_2 \times \Gamma(\mu_q) \times A_1 = A_2 \times \Gamma(\mu_q);$$

but as $\Gamma(\mu_q) = A_1, B_1, B_2$, it must vanish.

The normal coordinates of H_2O are of symmetry species $2A_1 + B_2$. Since $B_2 \times A_2 = B_1$, the vibronic transition matrix element

$$\langle {}^1A_2, {}^1B_2|\mu_q|{}^1A_1, {}^0B_2\rangle$$

is of symmetry species $A_2 \times B_2 \times \Gamma(\mu_q) \times A_1 \times A_1 = B_1 \times \Gamma(\mu_q)$. It is A_1 when $\Gamma(\mu_q) = B_1$, which is so where $q = x$. Therefore, an x-polarized vibronic transition may occur.

Exercise: Show that the transition ${}^2B_2 \leftarrow {}^2B_1$ is forbidden in ClO_2 (a C_{2v} molecule), but may be vibronically allowed.

11.8 Determine which states are mixed by rotations. In D_{6h} rotations transform as A_{2g} and E_{1g}. Therefore, $B_{1u} \times \{A_{2g}, E_{1g}\} = \{B_{2u}, E_{2u}\}$ and $B_{2u} \times \{A_{2g}, E_{1g}\} = \{B_{1u}, E_{2u}\}$. Therefore $\underline{{}^1B_{2u} \text{ and } {}^1E_{2u}}$ may be mixed into ${}^3B_{1u}$ and $\underline{{}^1B_{1u} \text{ and } {}^1E_{2u}}$ may be mixed into ${}^3B_{2u}$.

Exercise: What triplet states may be mixed into the ${}^1E$ state of NH_3? What states would be mixed if the molecule were planar in the ${}^1E$ excited state?

Problems

11.1 $\psi_{2s} = (Z/a_0)^{3/2}(1/2\surd 2)(2 - \rho)e^{-\rho/2}Y$ [Table 3.4] with $\rho = Zr/a_0$

(a)

$$\langle r\rangle = \int_0^\infty rR^2r^2\mathrm{d}r = \int_0^\infty \rho^3R^2(\rho)\mathrm{d}\rho(a_0/Z)^4$$

$$= (a_0/Z)(1/8)\int_0^\infty \rho^3(2-\rho)^2 e^{-\rho}\mathrm{d}\rho \quad [Z = 2]$$

$$= \underline{12a_0/Z\ (318\text{ pm})} \quad \left[\int_0^\infty x^3(2-x)^2e^{-x}\mathrm{d}x = 96\right]$$

(b)

$$P\,(R) = (Z/a_0)^3(1/8)\int_0^R (2-\rho)^2 r^2 \mathrm{e}^{-\rho}\mathrm{d}r$$

$$= \tfrac{1}{8}\int_0^A (2-\rho)^2 \rho^2 \mathrm{e}^{-\rho}\mathrm{d}\rho \;= 0.90 \quad [A = ZR/a_0]$$

That is, we need to solve

$$\text{Integral}(A) = \int_0^A (2-\rho)^2 \rho^2 \mathrm{e}^{-\rho}\mathrm{d}\rho \;= 7.20 \quad \text{for } A$$

The graph of this integral as a function of A is shown in Fig. 11.1. We see that it has the value 7.20 at $A = 9.12539$, so

$$R = \underline{9.12539 a_0 / Z}\ (241\text{ pm})$$

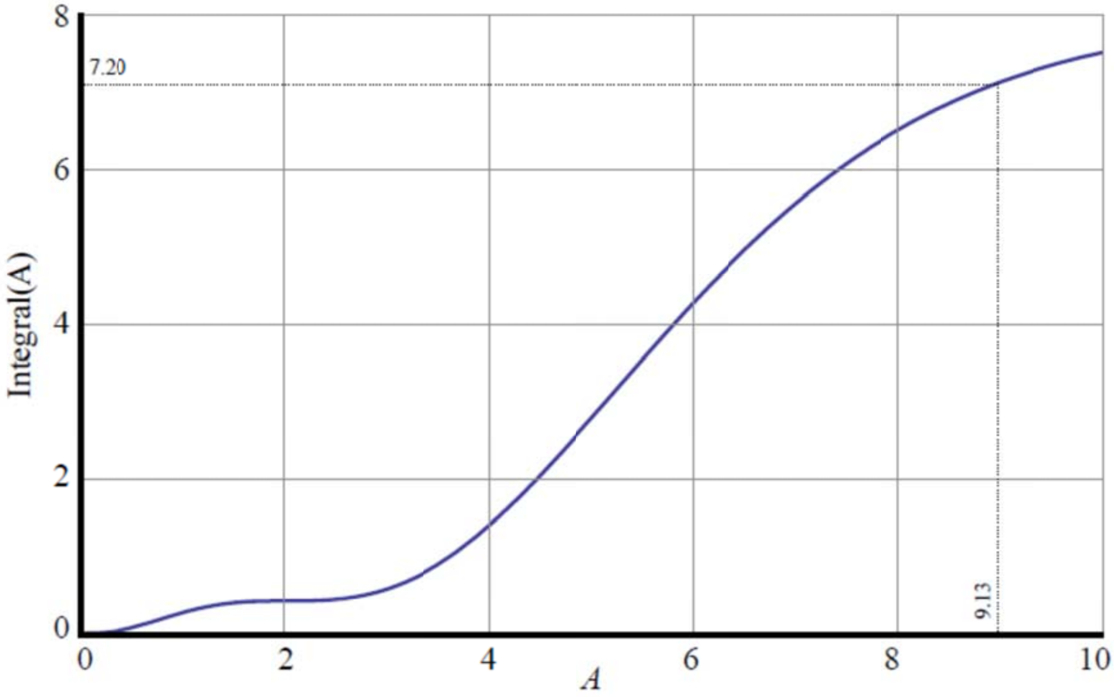


Figure 11.1: The integral in Problem 11.1 as a function of $A = ZR/a_0$.

Exercise: Repeat the calculation for a 3s-orbital.

11.4 The vibrational wavefunctions are:

$$\text{Lower: } \psi_v = N_v H_v(y) e^{-\frac{1}{2}y^2}, \quad y = (m\omega/\hbar)^{1/2}x \quad [x = R - R_e]$$

$$\text{Upper: } \psi_v = N_v H_v(y') e^{-\frac{1}{2}y'^2}, \quad y' = (m\omega/\hbar)^{1/2}(x - \Delta R)$$

Then the overlap integral is

$$S_{v0} = N_v N_0 \int_{-\infty}^{\infty} H_v(y') H_0(y) e^{-\frac{1}{2}(y^2+y'^2)} dx$$

$$= (1/2^v v!\pi)^{1/2}\int_{-\infty}^{\infty} H_v(y')\mathrm{e}^{-\frac{1}{2}(y^2+y'^2)}\mathrm{d}y$$

$$S_{10} = (2/\pi)^{1/2}\int_{-\infty}^{\infty} y'\mathrm{e}^{-\frac{1}{2}(y^2+y'^2)}\mathrm{d}y$$

$$= (2/\pi)^{1/2}\mathrm{e}^{-\frac{1}{4}z^2}\int_{-\infty}^{\infty} y'\mathrm{e}^{-(y'+\frac{1}{2}z)^2}\mathrm{d}y'$$

$$= (2/\pi)^{1/2}\mathrm{e}^{-\frac{1}{4}z^2}\int_{-\infty}^{\infty} (w-\tfrac{1}{2}z)\mathrm{e}^{-w^2}\mathrm{d}w \quad [w = y' + \tfrac{1}{2}z]$$

$$= (2/\pi)^{1/2}\mathrm{e}^{-\frac{1}{4}z^2}(-\tfrac{1}{2}z)\int_{-\infty}^{\infty}\mathrm{e}^{-w^2}\mathrm{d}w = -(z/\sqrt{2})\mathrm{e}^{-\frac{1}{4}z^2}$$

$$S_{10}^2 = \tfrac{1}{2}z^2\mathrm{e}^{-\frac{1}{2}z^2} = \underline{(m\omega/2\hbar)\Delta R^2\exp\{-(m\omega/2\hbar)\Delta R^2\}}$$

11.7 H_2CO belongs to C_{2v}, and μ_q transforms as B_1, B_2, A_1 for x, y, z, respectively. The transition ${}^1A_2 \leftarrow {}^1A_1$ is therefore allowed only if it is vibronic [$\langle A_2|\mu_q|A_1\rangle$ does not span A_1]. Since the six vibrations of H_2CO span $3A_1 + B_1 + 2B_2$, possible singly excited vibronic states of the A_2 electronic state are of symmetry species $A_1 \times A_2 = A_2$, $B_1 \times A_2 = B_2$, and $B_2 \times A_2 = B_1$. These vibronic states may be stimulated from the A_1 state by y-polarized (B_2) or x-polarized (B_1) radiation.

Ethene belongs to D_{2h}, and μ_q transforms as B_{3u}, B_{2u}, B_{1u} for x, y, z, respectively. Therefore $B_{2u} \leftarrow A_g$ is allowed for y-polarized radiation. The vibrations of ethene span

$$3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$$

[Problem 10.23], and so the possible vibronic states of the B_{2u} electronic state are

$$B_{2u} \times (A_g, B_{1g}, B_{2g}, A_u, B_{1u}, B_{2u}, B_{3u}) = B_{2u}, B_{3u}, A_u, B_{2g}, B_{3g}, A_g, B_{1g}$$

[Refer to the character table, form $\chi(R)\chi'(R)$ for $\Gamma \times \Gamma'$, and identify the set of characters so produced]. Of these, B_{2u} and B_{3u} may be reached by an electric dipole transition from the A_g ground state.

Exercise: Assess the polarization of the $^1B_2 \leftarrow {}^1B_1$ transition in H_2CO and the $B_{1g} \leftarrow A_g$ transition in ethene.

11.10

$P_2(t) = (2V/\Omega)^2 \sin^2 (\frac{1}{2}\Omega t)$, $\Omega^2 = \omega_{21}^2 + 4V^2$ [eqn 6.63].

$\hbar\omega_{21} = \hbar J$. For state 2 taken as T_0, $\hbar V = \hbar\xi/\sqrt{2}$ [Problem 11.9];

for state 2 corresponding to $T_\pm$, $\hbar V = \hbar\xi/2$. Therefore,

$$P(T_0) = \underline{\{2\xi^2/(J^2+2\xi^2)\}\sin^2\left\{\tfrac{1}{2}(J^2+2\xi^2)^{1/2}t\right\}}$$

$$P(T_\pm) = \underline{\{\xi^2/(J^2+\xi^2)\}\sin^2\left\{\tfrac{1}{2}(J^2+\xi^2)^{1/2}t\right\}}$$

$$P(T) = \underline{P(T_0)+P(T_+)+P(T_-)}$$

For a range of initial times, $0 \le t_0 \le T$; the time t then corresponds to the duration since initiation, which is $t - t_0$ for a given member of the system. Therefore, since t_0 ranges from 0 to T, the average population is:

$$\mathcal{P}(T_0) = \{2\xi^2/(J^2+2\xi^2)\}(1/T)\int_0^T \sin^2\left\{\tfrac{1}{2}(J^2+2\xi^2)^{1/2}(t-t_0)\right\}\mathrm{d}t_0$$

$$= \{2\xi^2/(J^2+2\xi^2)\}(1/T)\int_{t-T}^{t} \sin^2(a\tau)\mathrm{d}\tau \quad [\tau = t-t_0, a = \tfrac{1}{2}(J^2+2\xi^2)^{1/2}]$$

$$= \{\xi^2/(J^2+2\xi^2)\}\{1 - \gamma/2aT\}$$

$\gamma = [1 - \cos(2aT)]\sin(2at) + \sin(2aT)\cos(2at)$

If T is long in the sense that $2aT >> 1$,

$$\mathcal{P}(T_0) \approx \xi^2/(J^2 + 2\xi^2)$$

Likewise

$$\mathcal{P}(T_\pm) \approx \tfrac{1}{2}\xi^2/(J^2 + \xi^2)$$

Overall, therefore,

$$\mathcal{P}(T) \approx \xi^2/(J^2 + 2\xi^2) + \xi^2/(J^2 + \xi^2) = \underline{\frac{(2J^2 + 3\xi^2)\xi^2}{(J^2 + \xi^2)(J^2 + 2\xi^2)}}$$

When $J^2 >> \xi^2$, $\mathcal{P}(T) \approx 2\xi^2/J^2$.

Exercise: Suppose a magnetic field is present. How does $\mathcal{P}(T)$ depend on it?

11.13 $H\Psi = \mathcal{E}\Psi$, $\Psi = a\psi + \sum_n b_n\phi_n$; $\quad H^{(\text{bath})}\phi_n = E_n\phi_n$.

ψ should be interpreted as $\psi_{\text{system}} f_{\text{bath}}$ and ϕ as $\phi_{\text{bath}}\, g_{\text{system}}$, with $H^{(\text{bath})}f_{\text{bath}} = 0$ and $H^{(\text{sys})}g_{\text{system}} = 0$ (so that in each case no energy resides in the relevant component).

Then

$$H\Psi = aE\psi + \sum_n b_n E_n \phi_n + H'a\psi + \sum_n b_n H'\phi_n$$

$$= \mathcal{E}a\psi + \sum_n b_n \mathcal{E}\phi_n$$

Multiply by (a) ψ^* and integrate, (b) $\phi^*_{n'}$ and integrate (follow that by setting $n' \rightarrow n$):

$$(E - \mathcal{E})a + V\sum_n b_n = 0 \qquad [\langle\psi|\phi_n\rangle = 0, \langle\psi|H'|\psi\rangle = 0]$$

$$V_a + (E_n - \mathcal{E})b_n = 0 \qquad [\langle\phi_n|\psi\rangle = 0, \langle\phi_n|H'|\phi_{n'}\rangle = 0]$$

Then, $b_n = \{V/(\mathcal{E} - E_n)\}a$.

Substitute this expression for b_n back into the first equation of the pair:

$$(E - \mathcal{E}) + V^2\sum_n \{1/\{\mathcal{E} - E_n)\} = 0$$

Then, with $\mathcal{E} - E_n = \gamma\varepsilon - n\varepsilon$ and $\rho = 1/\varepsilon$,

$$E - \mathcal{E} = -(V^2/\varepsilon)\sum_n \{1/\{\gamma - n)\}$$

$$= \underline{(V^2\rho)\pi\cot(\pi\gamma)}$$

As Ψ is normalized to unity, $a^2 + \sum_n b_n^2 = 1$; consequently [from above]

$$a^2 + a^2V^2\sum_n\{1/(E_n - \mathcal{E})^2\} = 1$$

Since

$$\sum_{n=-\infty}^{\infty}(\gamma - n)^{-2} = \pi^2\mathrm{cosec}^2\pi\gamma$$

[*Handbook of mathematical functions*]

$$a^2 = \{1 + \pi^2\rho^2V^2\mathrm{cosec}^2(\pi\gamma)\}^{-1}$$

$$= \{1 + \pi^2\rho^2V^2 + \pi^2\rho^2V^2 \cot^2(\pi\gamma)\}^{-1}$$

$$= \{1 + \pi^2\rho^2V^2 + \pi^2\rho^2V^2[(E - \mathcal{E})/\pi\rho V^2]^2\}^{-1}$$

$$= \underline{\frac{V^2}{(E-\mathcal{E})^2 + V^2 + (\pi V^2\rho)^2}}$$

Exercise: Find an expression for $\sum_n b_n^4$.

Chapter 12

The electric properties of molecules

Exercises

12.1 **(a)** $\langle\mu_z\rangle = \alpha\mathcal{E}$ [eqn 12.9, $\mu_{0z} = 0$; $\alpha_{zz} = \alpha$]

$= 4\pi\varepsilon_0\alpha'\mathcal{E}$ [eqn 12.19, $\alpha = 4\pi\varepsilon_0\alpha'$]

$= (1.112\,65 \times 10^{-10}\ \mathrm{J^{-1}\ C^2\ m^{-1}}) \times (10.5 \times 10^{-30}\ \mathrm{m^3}) \times (1.0 \times 10^4\ \mathrm{V\ m^{-1}})$

$= (1.17 \times 10^{-39}\ \mathrm{J^{-1}\ C^2\ m^2}) \times (1.0 \times 10^4\ \mathrm{V\ m^{-1}})$

$= 1.17 \times 10^{-35}\ \mathrm{C\ m}$ $(\underline{3.5 \times 10^{-6}\ \mathrm{D}})$ $[1\ \mathrm{D} = 3.336 \times 10^{-30}\ \mathrm{C\ m}]$

(b) $E(\mathcal{E}) - E(0) = -\frac{1}{2}\alpha\mathcal{E}^2 = -5.85 \times 10^{-32}\ \mathrm{J}$ $(\underline{-3.52 \times 10^{-11}\ \mathrm{kJ\ mol^{-1}}})$

Exercise: Calculate the dipole moment induced by a singly charged ion at a distance of (a) 0.1 nm, (b) 1.0 nm from a tetrachloromethane molecule.

12.2 Use eqn 12.27 to estimate the polarizibility for the hydrogen atom. The number of valence electrons, N_V, is one; take ΔE to be the ionization energy of hydrogen, 13.6 eV or 2.18×10^{-18} J.

$$\alpha = \frac{\hbar^2 e^2 N_\mathrm{V}}{m_\mathrm{e}\Delta E^2}$$

$$= \frac{(1.055\times10^{-34}\ \mathrm{Js})^2\times(1.602\times10^{-19}\ \mathrm{C})^2\times1}{(9.109\times10^{-31}\ \mathrm{kg})\times(2.18\times10^{-18}\ \mathrm{J})^2}$$

$$= \underline{6.60\times10^{-41}\ \mathrm{J}^{-1}\ \mathrm{C}^2\ \mathrm{m}^2}$$

This answer gives $\underline{\alpha' = 5.93\times10^{-31}\ \mathrm{m}^3}$ which differs by 10.% from the experimental value.

Exercise: Suggest why the agreement between the computed and eperimental values for the polarizibilty volume is reasonably good.

12.3

$$\alpha = (\hbar^2e^2/m_e)\sum_{n\neq0}\left\{f_{n0}/\Delta E_{n0}^2\right\}\ \text{[eqn 12.25]}$$

$$\approx (\hbar^2e^2/m_e)(f/\Delta E^2)\quad\text{[one transition dominating]}$$

$$\approx (e^2/4\pi^2m_ec^2)\lambda^2f\quad[\Delta E = hc/\lambda]$$

$$\alpha' = \alpha/4\pi\varepsilon_0 = (e^2/16\pi^3\varepsilon_0m_ec^2)\lambda^2f$$

$$= (7.138\times10^{-17}\ \mathrm{m})\lambda^2f = (7.138\times10^{-29}\ \mathrm{cm}^3)(\lambda/\mathrm{nm})^2f$$

For $\lambda = 160$ nm and $f = 0.3$, $\alpha' \approx \underline{5\times10^{-31}\ \mathrm{m}^3}$, which is an order of magnitude smaller than the experimental value.

Exercise: Find a expression for α' in terms of the integrated absorption coefficient of a band.

12.4 $E^{(2)} \approx -\frac{3}{2}[I_AI_B/(I_A+I_B)](\alpha'_A\alpha'_B/R^6)$ [eqn 12.40]

$I = I_A = I_B \approx 13.6\ \mathrm{eV} = 1312\ \mathrm{kJ\ mol^{-1}}$; $\alpha'_A = \alpha'_B = 6.6\times10^{-31}\ \mathrm{m}^3$ [Exercise 12.2]

Consequently,

$E^{(2)} \approx -\frac{3}{4} I\alpha'^2/R^6 = \underline{-(4.29 \times 10^{-4}\text{ kJ mol}^{-1}) \times \{1/(R/\text{nm})^6\} = -4.29 \times 10^{-10}\text{ kJ mol}^{-1}}$

Exercise: Evaluate the dispersion energy directly on the basis of eqn 12.17 and the matrix elements listed in the solution to Problem 12.3.

12.5 $E^{(2)} \approx -(23\hbar c/4\pi)(\alpha'_A\alpha'_B/R^7)$ [eqn 12.41]

$= -(23\times1.055\times10^{-34}\text{ J s}\times2.9979\times10^{8}\text{ m s}^{-1}/4\pi)\times(6.6 \times 10^{-31}\text{ m}^3)^2/(10.0\times10^{-9}\text{ m})^7$

$= -2.52\times10^{-30}\text{ J or } -1.52\times10^{-9}\text{ kJ mol}^{-1}$

12.6 The relative permittivity of a non-polar molecule such as tetracholoromethane is given by eqn 12.54:

$\varepsilon_r = (1 + 2\alpha\mathcal{N}/3\varepsilon_0)/(1 - \alpha\mathcal{N}/3\varepsilon_0)$

Since $\alpha = 4\pi\varepsilon_0\alpha'$ (eqn 12.19), $\mathcal{N} = N_A\rho/M$ (Section 12.3), and for tetracholoromethane $\alpha' = 1.05 \times 10^{-29}\text{ m}^3$, $\rho = 1594\text{ kg m}^{-3}$, $M = 0.153822\text{ kg mol}^{-1}$, the relative permittivity is

$\varepsilon_r = (1 + 8\pi\alpha' N_A\rho/3M)/(1 - 4\pi\alpha' N_A\rho/3M)$

$= \underline{2.135}$

12.7 The dipole-moment density is the average of $\mu_0 \cos\theta$ weighted by the Boltzmann factor and divided by the volume V, of the sample:

$$P = \frac{\int_0^{\pi}\mu_0\cos\theta\,\mathrm{d}N(\theta)}{V} = \frac{Nx\mu_0\int_0^{\pi}\cos\theta\,\mathrm{e}^{x\cos\theta}\sin\theta\,\mathrm{d}\theta}{V(\mathrm{e}^{x} - \mathrm{e}^{-x})}$$

where we have used eqn 12.56 for the Boltzmann factor. To evaluate the above integral, let $u = \cos\theta$, $\mathrm{d}u = -\sin\theta\,\mathrm{d}\theta$:

$$\int_0^{\pi}\cos\theta\,\mathrm{e}^{x\cos\theta}\sin\theta\,\mathrm{d}\theta = -\int_1^{-1}u\mathrm{e}^{xu}\mathrm{d}u = \int_{-1}^{1}u\mathrm{e}^{xu}\mathrm{d}u$$

Using the standard integral:

$$\int y\mathrm{e}^{ay}\mathrm{d}y = \frac{\mathrm{e}^{ay}}{a^2}(ay-1) + \text{ constant}$$

we have

$$\int_{-1}^{1} u\mathrm{e}^{xu}\mathrm{d}u = \frac{\mathrm{e}^{xu}}{x^2}(ux-1)\bigg|_{-1}^{1}$$

$$= \frac{\mathrm{e}^{x}}{x^2}(x-1) - \frac{\mathrm{e}^{-x}}{x^2}(-x-1)$$

$$= \frac{\mathrm{e}^{x}+\mathrm{e}^{-x}}{x} - \frac{\mathrm{e}^{x}-\mathrm{e}^{-x}}{x^2}$$

Therefore,

$$P = \frac{Nx\mu_0\int_0^{\pi}\cos\theta\,\mathrm{e}^{x\cos\theta}\sin\theta\,\mathrm{d}\theta}{V(\mathrm{e}^{x}-\mathrm{e}^{-x})}$$

$$= \frac{Nx\mu_0}{V(\mathrm{e}^{x}-\mathrm{e}^{-x})}\left(\frac{\mathrm{e}^{x}+\mathrm{e}^{-x}}{x} - \frac{\mathrm{e}^{x}-\mathrm{e}^{-x}}{x^2}\right)$$

$$= \mu_0\left(\frac{N}{V}\right)\left(\frac{\mathrm{e}^{x}+\mathrm{e}^{-x}}{\mathrm{e}^{x}-\mathrm{e}^{-x}} - \frac{1}{x}\right)$$

which, with $\mathcal{N}=N/V$ and the definition of the Langevin function in eqn 12.58, is eqn 12.57.

12.8 The number density $\mathcal{N} = N_{\mathrm{A}}\rho/M$. Therefore, eqn 12.62b can be written as

$$\varepsilon_{\mathrm{r}} = \frac{1+2C}{1-C}$$

where

$$C = \left(\alpha + \frac{\mu_0^2}{3kT}\right)\rho N_{\mathrm{A}}/3M\varepsilon_0$$

We now confirm that the expression for *C* above matches that given in eqn 12.63.

$$C = \left(4\pi\varepsilon_0\alpha' + \frac{\mu_0^2}{3kT}\right)\rho N_{\mathrm{A}}/3M\varepsilon_0$$

$$= \frac{4\pi\varepsilon_0\alpha'\rho N_{\mathrm{A}}}{3M\varepsilon_0} + \frac{\mu_0^2\rho N_{\mathrm{A}}}{9\varepsilon_0 MkT}$$

$$= \frac{4\pi\rho N_{\mathrm{A}}}{3M}(\alpha' + \mu_0^2/12\pi\varepsilon_0 kT)$$

12.9 Begin with the equation following eqn 12.70:

$$\langle\mu_z\rangle = \mu_{0z} + \sum_{n\neq 0}\left\{\mu_{z,0n}a_n(t)\mathrm{e}^{-\mathrm{i}\omega_{n0}t} + \mu_{z,n0}a_n^*(t)\mathrm{e}^{\mathrm{i}\omega_{n0}t}\right\}$$

We need to substitute into the above equation the expressions for $a_n(t)$ and its complex conjugate obtained from eqn 12.72:

$$a_n(t) = \frac{\mu_{z,n0}\,\mathcal{E}}{\hbar}\left\{\frac{e^{i(\omega+\omega_{n0})t}}{\omega+\omega_{n0}} - \frac{e^{-i(\omega-\omega_{n0})t}}{\omega-\omega_{n0}}\right\}$$

$$a_n^*(t) = \frac{\mu_{z,n0}^*\,\mathcal{E}}{\hbar}\left\{\frac{\mathrm{e}^{-\mathrm{i}(\omega+\omega_{n0})t}}{\omega+\omega_{n0}} - \frac{\mathrm{e}^{\mathrm{i}(\omega-\omega_{n0})t}}{\omega-\omega_{n0}}\right\}$$

Proceed piecewise and use $\mathrm{e}^{\mathrm{i}x} = \cos x + \mathrm{i}\sin x$:

$$\mu_{z,0n}a_n(t)\mathrm{e}^{-\mathrm{i}\omega_{n0}t} = \frac{|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\mathrm{e}^{\mathrm{i}\omega t}}{\omega+\omega_{n0}} - \frac{\mathrm{e}^{-\mathrm{i}\omega t}}{\omega-\omega_{n0}}\right\}$$

$$= \frac{|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\omega(\mathrm{e}^{\mathrm{i}\omega t} - \mathrm{e}^{-\mathrm{i}\omega t}) - \omega_{n0}(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t})}{\omega^2 - \omega_{n0}^2}\right\}$$

$$= \frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\mathrm{i}\omega\sin\omega t - \omega_{n0}\cos\omega t}{\omega^2 - \omega_{n0}^2}\right\}$$

$$\mu_{z,n0}a_n^*(t)e^{i\omega_{n0}t} = \frac{|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{e^{-i\omega t}}{\omega+\omega_{n0}} - \frac{e^{i\omega t}}{\omega-\omega_{n0}}\right\}$$

$$= \frac{|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\omega(e^{-i\omega t}-e^{i\omega t})-\omega_{n0}(e^{i\omega t}+e^{-i\omega t})}{\omega^2-\omega_{n0}^2}\right\}$$

$$= \frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{-i\omega\sin\omega t-\omega_{n0}\cos\omega t}{\omega^2-\omega_{n0}^2}\right\}$$

$$\mu_{z,0n}a_n(t)\mathrm{e}^{-\mathrm{i}\omega_{n0}t}+\mu_{z,n0}a_n^*(t)\mathrm{e}^{\mathrm{i}\omega_{n0}t}$$

$$= \frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\mathrm{i}\omega\sin\omega t-\omega_{n0}\cos\omega t-\mathrm{i}\omega\sin\omega t-\omega_{n0}\cos\omega t}{\omega^2-\omega_{n0}^2}\right\}$$

$$= \frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{2\omega_{n0}\cos\omega t}{\omega_{n0}^2-\omega^2}\right\}$$

Therefore,

$$\langle\mu_z\rangle = \mu_{0z}+\sum_{n\neq 0}\frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{2\omega_{n0}\cos\omega t}{\omega_{n0}^2-\omega^2}\right\}$$

$$= \mu_{0z}+\left\{\frac{2}{\hbar}\sum_{n\neq 0}\left\{\frac{\omega_{n0}\,|\mu_{z,n0}|^2}{\omega_{n0}^2-\omega^2}\right\}\right\}\times 2\,\mathcal{E}\cos\omega t$$

which is eqn 12.73.

12.10 Let $D = \alpha(\omega)\mathcal{N}/\varepsilon_0$. Then, from eqn 12.78,

$$n_\mathrm{r}^2 = \frac{1+2D/3}{1-D/3}$$

which, upon substitution into the left-hand side of eqn 12.79, yields

$$\frac{n_\mathrm{r}^2-1}{n_\mathrm{r}^2+2} = \frac{\dfrac{1+2D/3}{1-D/3}-\dfrac{1-D/3}{1-D/3}}{\dfrac{1+2D/3}{1-D/3}+\dfrac{2-2D/3}{1-D/3}} = \frac{\dfrac{D}{1-D/3}}{\dfrac{3}{1-D/3}} = \frac{D}{3}$$

With $D = \alpha(\omega)\mathcal{N}/\varepsilon_0$, the expression $D/3$ matches the right-hand side of eqn 12.79.

12.11 $\varphi_\pm = \omega t - 2\pi z n_\pm \nu/c = \omega t - z n_\pm \omega/c$ [eqn 12.84, $\omega = 2\pi\nu$]

Letting $n = \frac{1}{2}(n_+ + n_-)$ and $\Delta n = n_+ - n_-$, we obtain $n_+ = n + \Delta n/2, n_- = n - \Delta n/2$ or $n_\pm = n \pm \Delta n/2$. Therefore

$$\varphi_\pm = \omega t - \frac{zn_\pm\omega}{c} = \omega t - \frac{z\left(n \pm \frac{\Delta n}{2}\right)\omega}{c} = \omega t - \frac{zn\omega}{c} \mp \frac{\omega z\Delta n}{2c}$$

which is eqn 12.85.

Problems

12.1 $\alpha_{xx} = 2\sum_{n\neq 0} \{\mu_{x,0n}\mu_{x,\,n0}/\Delta E_{n0}\}$ [eqn 12.16 with $z \to x$]

$$\mu_{x,0n} = \langle 0| - ex + \tfrac{1}{2}eL|n\rangle = -e\langle 0|x|n\rangle \quad [\langle 0|L|n\rangle = \langle 0|n\rangle L = 0,\ n \neq 0]$$

$$\langle 0|x|n\rangle = \begin{cases} -(8/\pi^2)Ln/(n^2-1)^2, & n \text{ even} \\ 0 & n \text{ odd} \end{cases} \quad [\text{Problem 6.8}]$$

$$\Delta E_{n0} = (n^2 - 1)(h^2/8mL^2)$$

$$\alpha_{xx} = 2e^2(8L/\pi^2)^2(8mL^2/h^2)\sum_n^{\text{even}} \{n^2/(n^2-1)^5$$

$$= 2(8/\pi^2)^2 a \sum_n^{\text{even}} \{n^2/(n^2-1)^5 \quad a = (eL)^2/(h^2/8mL^2)$$

$$\sum_n^{\text{even}} \{n^2/(n^2-1)^5 = 0.016\,48 \quad [\text{Problem 6.8}]$$

Therefore, $\alpha_{xx} = 0.021\,66a = \underline{\dfrac{0.021\,66e^2L^2}{h^2/8mL^2}}$.

For $m = m_e$, $\alpha_{xx} = 9.229\ (L/\text{pm})^4 \times 10^{-51}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^2$

$$\alpha'_{xx} = \alpha_{xx}/4\pi\varepsilon_0 = 8.295 \times 10^{-35}\ (L/\text{pm})^4\ \text{cm}^3$$

With $L = 150$ pm, $\alpha'_{xx} = \underline{4.199 \times 10^{-26}\ \mathrm{cm}^3}$.

Exercise: Calculate the polarizability volume of a rectangular, three-dimensional box of sides X, Y, Z, and the mean polarizability volume, and relate α' to $V = XYZ$.

12.4. We continue with Problem 12.3, including the contribution from all p-orbitals:

$$\alpha_{zz} = (2^9 e^2 a_0^2/3hc\mathrm{R_H}) \sum_{n=2}^{\infty} \left\{ \frac{n^9(n-1)^{2n-5}}{(n+1)^{2n+5}(n^2-1)} \right\}$$

$$= (2^9 e^2 a_0^2/3hc\mathrm{R_H}) \sum_{n=2}^{\infty} \left\{ \frac{n^9(n-1)^{2n-6}}{(n+1)^{2n+6}} \right\}$$

$$= (2^9 e^2 a_0^2/3hc\mathrm{R_H})\{0.0087 + 0.0012 + 0.0004 + \ldots\}$$

$$= (2^9 e^2 a_0^2/3hc\mathrm{R_H}) \times 0.0106 = 5.97 \times 10^{-41}\ \mathrm{J^{-1}\ C^2\ m^2}$$

$$\alpha'_{zz} = \alpha_{zz}/4\pi\varepsilon_0 = \underline{5.37 \times 10^{-25}\ \mathrm{cm}^3}$$

Exercise: Calculate the polarizability of one-electron ions with atomic number Z.

12.7 To derive the expression for the third-order correction to the energy, which we denote $E_0^{(3)}$, we follow the procedure set out in Section 6.2. We include the term $\lambda^3 H^{(3)}$ in eqn 6.20a, $\lambda^3 \psi_0^{(3)}$ in eqn 6.20b, and $\lambda^3 E_0^{(3)}$ in eqn 6.20c. We then obtain in addition to the equations shown in eqn 6.21 the following equation by collecting λ^3 coefficients:

$$\{H^{(0)} - E_0^{(0)}\}\,\psi_0^{(3)} = \{E_0^{(3)} - H^{(3)}\}\,\psi_0^{(0)} + \{E_0^{(2)} - H^{(2)}\}\,\psi_0^{(1)} + \{E_0^{(1)} - H^{(1)}\}\,\psi_0^{(2)}$$

The first- and second-order corrections to the energy are given in eqns 6.24 and 6.30, respectively; the first-order correction to the wavefunction is given in eqn 6.27. For later use, the second- and third-order corrections to the wavefunction are written as

$$\Psi_0^{(2)} = \sum_{n\neq 0} b_n \Psi_n^{(0)}$$

$$\Psi_0^{(3)} = \sum_{n\neq 0} c_n \Psi_n^{(0)}$$

The equation above obtained by collection of λ^3 coefficients is written in ket notation as

$$\{H^{(0)} - E_0^{(0)}\}\sum_{n\neq 0} c_n|n\rangle = \{E_0^{(3)} - H^{(3)}\}|0\rangle + \{E_0^{(2)} - H^{(2)}\}\sum_{n\neq 0} a_n|n\rangle$$

$$+ \ \{E_0^{(1)} - H^{(1)}\}\sum_{n\neq 0} b_n|n\rangle$$

where the coefficients a_n for the first-order correction to the wavefunction are given by eqn 6.26. We now multiply this equation through from the left by $\langle 0|$, which gives (recognizing that $H^{(0)}|n\rangle = E_n^{(0)}|n\rangle$)

$$0 = E_0^{(3)} - H_{00}^{(3)} - \sum_{n\neq 0} a_n H_{0n}^{(2)} - \sum_{n\neq 0} b_n H_{0n}^{(1)}$$

If the matrix elements of the second- and third-order perturbations $H^{(2)}$ and $H^{(3)}$ vanish, then the above expression simplies to

$$E_0^{(3)} = \sum_{n\neq 0} b_n H_{0n}^{(1)}$$

To find the third-order correction to the energy, we need the coefficients b_n. To find them, we start with eqn 6.29a and multiply through from the left by $\langle k|$ (setting matrix elements of $H^{(2)}$ to zero):

$$b_k\{E_k^{(0)} - E_0^{(0)}\} = a_k E_0^{(1)} - \sum_{n\neq 0} a_n H_{kn}^{(1)}$$

Therefore, using eqns 6.24 and 6.26, we find

$$b_k = -\frac{H_{00}^{(1)}H_{k0}^{(1)}}{(E_0^{(0)} - E_k^{(0)})^2} - \sum_{n\neq 0}\frac{H_{n0}^{(1)}H_{kn}^{(1)}}{(E_0^{(0)} - E_n^{(0)})(E_k^{(0)} - E_0^{(0)})}$$

When we replace in the above equation the indices n by m, and k by n and substitute the resulting expression for b_n into $E_0^{(3)} = \sum_n b_n H_{0n}^{(1)}$, we obtain

$$E_0^{(3)} = -H_{00}^{(1)}\sum_{n\neq 0}\frac{H_{n0}^{(1)}H_{0n}^{(1)}}{(E_0^{(0)} - E_n^{(0)})^2}$$

$$-\sum_{n\neq 0}\sum_{m\neq 0}\frac{H_{m0}^{(1)}H_{nm}^{(1)}H_{0n}^{(1)}}{(E_0^{(0)} - E_m^{(0)})(E_n^{(0)} - E_0^{(0)})}$$

which matches (upon interchange of the indices m and n in the double summation) the expression given in Problem 12.6.

Exercise: Derive the expression for the third-order correction to the wave-function.

12.10

$$[H, x^2] = -(\hbar^2/2m_e)[(d^2/dx^2), x^2] \qquad [[V, x^2] = 0]$$

$$= -(\hbar^2/2m_e)\{(d^2/dx^2)x^2 - x^2(d^2/dx^2)\}$$

$$= -(\hbar^2/2m_e)\{2 + 4x(d/dx) + x^2(d^2/dx^2) - x^2(d^2/dx^2)\}$$

$$= -(\hbar^2/m_e) - 2(\hbar^2/m_e)x(d/dx)$$

$$= -(\hbar^2/m_e) - 2i(\hbar/m_e)xp$$

$$\langle m|[H, x^2]|n\rangle = (E_m - E_n)\langle m|x^2|n\rangle = \hbar\omega_{mn}(x^2)_{mn}$$

$$= \langle m| - (\hbar^2/m_e) - 2i(\hbar/m_e)xp|n\rangle$$

$$= -(\hbar^2/m_e)\delta_{mn} - 2i(\hbar/m_e)\sum_f x_{mf}\, p_{fn}$$

$$= -(\hbar^2/m_e)\delta_{mn} - 2i(\hbar/m_e)(im_e)\sum_f x_{mf}\,\omega_{fn}x_{fn} \quad \text{[eqn 12.112 in FI 12.2]}$$

$$= -(\hbar^2/m_e)\delta_{mn} + 2\hbar\sum_f x_{mf}x_{fn}\omega_{fn}$$

Therefore

$$\sum_f x_{mf}x_{fn}\omega_{fn} = (\hbar/2m_e)\delta_{mn} + \tfrac{1}{2}\,\omega_{mn}(x^2)_{mn}$$

Exercise: Devise a sum rule based on $[H, x^3]$.

12.13

$$\left.\begin{aligned} n_r(\omega) &\approx 1 + (N_A\rho/3\hbar\varepsilon_0 M)C(\omega) \\ C(\omega) &= \sum_{n\neq 0}\tfrac{\omega_{n0}|\mu_{0n}|^2}{\omega_{n0}^2-\omega^2} \end{aligned}\right\} \quad \text{[eqn 12.77]}$$

Evaluate $C(\omega)$ numerically, drawing on the information in the solution of Problem 12.4.

$$C(\omega) = \sum_{n,l,m_l \neq (1,0,0)} \frac{\omega_{n,1\mathrm{s}} \, |\, \mu_{1\mathrm{s},nlm_l} \,|^2}{\omega_{n,1\mathrm{s}}^2 - \omega^2}$$

$$= 3 \sum_{n,l,m_l \neq (1,0,0)} \frac{\omega_{n,1\mathrm{s}} \, |\, \mu_{z;1\mathrm{s},nlm_l} \,|^2}{\omega_{n,1\mathrm{s}}^2 - \omega^2} \quad [\mu_x^2 = \mu_y^2 = \mu_z^2]$$

$$= 3e^2 \sum_{n \neq 1} \frac{\omega_{n,1\mathrm{s}} \, |\, z_{n\mathrm{p}_z}, 1\mathrm{s} \,|^2}{\omega_{n,1\mathrm{s}}^2 - \omega^2} \quad [\text{only } n\mathrm{p}_z\text{-orbitals contribute}]$$

$$= (3e^2 \mathrm{R_H}/2\pi c) \sum_{n \neq 1} \frac{[1-(1/n^2)] \,|\, z_{n\mathrm{p}_z}, 1\mathrm{s} \,|^2}{[1-(1/n^2)]^2 \mathrm{R_H^2} - (1/\lambda^2)}$$

$$\left[\hbar \omega_{n,1\mathrm{s}} = hc\mathrm{R_H} \left(1 - \frac{1}{n^2} \right) \right]$$

$$= (2^7/\pi)(e^2 a_0^2 \mathrm{R_H}/c) \sum_{n \neq 1} \frac{[1-(1/n^2)] n^7 (n-1)^{2n-5} / (n+1)^{2n+5}}{[1-(1/n^2)]^2 \mathrm{R_H^2} - (1/\lambda^2)}$$

$$= (2^7/\pi)(e^2 a_0^2 / \mathrm{R_H} c) D(\lambda),$$

$$D(\lambda) = \sum_{n \neq 1} \frac{[1-(1/n^2)] n^7 (n-1)^{2n-5} / (n+1)^{2n+5}}{[1-(1/n^2)]^2 - (1/\lambda \mathrm{R_H})^2}$$

$$= \sum_{n \neq 1} \frac{n^9 (n-1)^{2n-4} / (n+1)^{2n+4}}{(n^2-1)^2 - \gamma^2 n^4}, \quad \gamma = 1/\lambda \mathrm{R_H}$$

Since $\gamma = 1/(590 \text{ nm}) \times (1.097 \times 10^5 \text{ cm}^{-1}) = 0.155$, numerical evaluation of the sum (up to $n \approx 20$) leads to D(590 nm) = 0.0112. Therefore,

$$C = (8.91 \times 10^{-73} \text{ C}^2 \text{ m}^2 \text{ s}) D = 9.98 \times 10^{-75} \text{ C}^2 \text{ m}^2 \text{ s}$$

Consequently,

$$n_r \approx 1 + (\mathcal{N}/3\hbar\varepsilon_0)C \quad [\rho = Nm_{\mathrm{H}}/V,\ m_{\mathrm{H}} = M(H)/N_{\mathrm{A}}]$$

$$\approx 1 + (\mathcal{N}/\text{atoms m}^{-3}) \times (3.56 \times 10^{-30})$$

When $\mathcal{N} \approx 10^5$ atoms m^{-3}

$$n_r - 1 \approx \underline{3.6 \times 10^{-25}}$$

For a gas of atoms at 1.00 atm and 25°C,

$$\mathcal{N} = p/kT = 2.46 \times 10^{25}\ \mathrm{m}^{-3}$$

and then $n_r \approx 1.000\ 088$.

Exercise: Find an expression for the refractive index of a gas of one-electron ions of atomic number Z.

12.16 Take as a trial function $\psi = \psi_{1\mathrm{s}} + a\psi_{2\mathrm{p}_z}$ for each atom, so that the overall trial function is

$$\psi = (\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z})(\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{B,2p}_z})$$

The denominator of the Rayleigh ratio is therefore

$$\int \psi^2 \mathrm{d}\tau = \int (\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z})^2(\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{B,2p}_z})^2 \mathrm{d}\tau_{\mathrm{A}}\mathrm{d}\tau_{\mathrm{B}}$$

$$= (1 + a_{\mathrm{A}}^2)(1 + a_{\mathrm{B}}^2) \quad \text{[basis functions are orthonormal]}$$

The hamiltonian is

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + H^{(1)}, \quad H_{\mathrm{A}}\psi_{\mathrm{A},nl} = E_n\psi_{\mathrm{A},nl}$$

The numerator of the Rayleigh ratio is therefore

$$\begin{aligned}
\int \psi H \psi \mathrm{d}\tau &= \int (\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z})(\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{B,2p}_z}) \\
&\quad \times \{(E_1\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}E_2\psi_{\mathrm{A,2p}_z})(\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{B,2p}_z}) \\
&\quad + (\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z})(E_1\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}E_2\psi_{\mathrm{B,2p}_z}) \\
&\quad + H^{(1)}(\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z})(\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{B,2p}_z})\} \\
&= (E_1 + a_{\mathrm{A}}^2E_2)(1 + a_{\mathrm{B}}^2) + (E_1 + a_{\mathrm{B}}^2E_2)(1 + a_{\mathrm{A}}^2) \\
&\quad + \int (\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,1s}} \\
&\qquad + a_{\mathrm{B}}\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,2p}_z} + a_{\mathrm{A}}a_{\mathrm{B}}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,2p}_z}) \\
&\quad \times H^{(1)}(\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,2p}_z} \\
&\qquad + a_{\mathrm{A}}a_{\mathrm{B}}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,2p}_z})\mathrm{d}\tau_{\mathrm{A}}\mathrm{d}\tau_{\mathrm{B}}
\end{aligned}$$

Only the $z_{\mathrm{A}}z_{\mathrm{B}}$ components of $H^{(1)}$ contribute to the integral (because only it has nonvanishing matrix elements between 1s and 2p$_z$), so we take

$$H^{(1)} = -2(1/4\pi\varepsilon_0R^3)\mu_{\mathrm{A}z}\mu_{\mathrm{B}z}$$

Then the only surviving terms are

$$\begin{aligned}
&2a_{\mathrm{A}}a_{\mathrm{B}}\Big\{\int \psi_{\mathrm{A,1s}}\psi_{\mathrm{B,1s}}H^{(1)}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,2p}_z}\mathrm{d}\tau_{\mathrm{A}}\mathrm{d}\tau_{\mathrm{B}} \\
&\quad + \int \psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,2p}_z}H^{(1)}\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,1s}}\mathrm{d}\tau_{\mathrm{A}}\mathrm{d}\tau_{\mathrm{B}}\Big\} \\
&= -(e^2/\pi\varepsilon_0R^3)a_{\mathrm{A}}a_{\mathrm{B}}z_{\mathrm{A;1s,2p}_z}z_{\mathrm{B;1s,2p}_z} \\
&= -a_{\mathrm{A}}a_{\mathrm{B}}KZ, \quad K = e^2/\pi\varepsilon_0R^3, \quad Z = z_{\mathrm{A;1s,2p}_z}z_{\mathrm{B;1s,2p}_z}
\end{aligned}$$

The Rayleigh ratio is then

$$\epsilon = \frac{E_1 + a_A^2 E_2}{(1+a_A^2)+(E_1+a_B^2 E_2)/(1+a_B^2)}$$

$$-\frac{a_A a_B KZ}{(1+a_A^2)+(1+a_B^2)}$$

The optimum values of $a_A a_B$ are those for which $\partial\epsilon/\partial a_A = \partial\epsilon/\partial a_B = 0$.

$$\partial\epsilon/\partial a_A = 2a_A E_2/(1+a_A^2) - 2a_A(E_1 + a_A^2 E_2)/(1+a_A^2)^2$$

$$- a_B KZ/(1+a_A^2)(1+a_B^2) + 2a_A^2 a_B KZ/(1+a_A^2)^2(1+a_B^2) = 0$$

Likewise for $\partial\epsilon/\partial a_B$. Therefore we must solve

$$2(E_2 - E_1)a_A + 2(E_2 - E_1)\, a_B^2 a_A - a_B KZ + a_B a_A^2 KZ = 0$$

$$2(E_2 - E_1)a_B + 2(E_2 - E_1)\, a_A^2 a_B - a_A KZ + a_A a_B^2 KZ = 0$$

Let $\Delta E = E_2 - E_1 = \frac{3}{4}hc\mathcal{R}_H$. Then, since $a_A^2 = a_B^2$ by symmetry, we have

$$a_A = \pm\left(\frac{KZ - 2\Delta E}{KZ + 2\Delta E}\right)^{1/2} \qquad a_B = \pm\left(\frac{KZ - 2\Delta E}{KZ + 2\Delta E}\right)^{1/2}$$

It follows that, setting $\gamma = (KZ - 2\Delta E)/(KZ + 2\Delta E)$,

$$\epsilon = \left\{\frac{2E_1 + 2\gamma E_2}{1+\gamma}\right\} - \left\{\frac{\gamma KZ}{(1+\gamma)^2}\right\}$$

Exercise: Calculate the dispersion energy on the basis that the trial function (a) also includes a 3p-orbital component, (b) includes a ‘1p-orbital’ component.

Chapter 13

The magnetic properties of molecules

Exercises

13.1 $\mathcal{B} = \mu_0 \mathcal{H}$ [eqn 13.1a]

In terms of magnitudes: (Note: 1 T = 1 V s m^{-2} and 1 J = 1 V A s = 1 N m)

$$\mathcal{B} = \mu_0 \mathcal{H}$$

$$\mathcal{H} = \mathcal{B}/\mu_0 = 1.0\ \text{T}/(4\pi \times 10^{-7}\ \text{N A}^{-2}) = \underline{8.0 \times 10^{5}\ \text{A m}^{-1}}$$

13.2 **(a)** $\mathcal{M} = \chi\mathcal{H}$ [eqn 13.3b]

$$\mathcal{M} = \chi\mathcal{H} = (-9.02 \times 10^{-6}) \times (80 \times 10^{3}\text{A m}^{-1}) = \underline{-0.72\ \text{A m}^{-1}}$$

(b) $\mathcal{M} = \frac{1}{\mu_0}\left(\frac{\chi}{1+\chi}\right)\mathcal{B}$ [eqn 13.3c]

$$\mathcal{B} = (1 + \chi)\mu_0 \mathcal{M}/\chi$$

$$= (1 - 9.02 \times 10^{-6}) \times (4\pi \times 10^{-7}\ \text{N A}^{-2}) \times (-0.72\ \text{A m}^{-1}) / (-9.02 \times 10^{-6})$$

$$= \underline{0.10\ \text{T}}$$

13.3 Follow the first *brief illustration* of Section 13.2. For a mass density of 5.0 g cm^{-3} and a molar mass of 210 g mol^{-1}, the number density is

$$\mathcal{N} = \frac{\rho N_A}{M} = \frac{5.0\times 10^{6}\ \text{g m}^{-3}}{210\ \text{g mol}^{-1}} \times \left(6.022 \times 10^{23}\ \text{mol}^{-1}\right) = 1.43 \times 10^{28}\ \text{m}^{-3}$$

The magnetic susceptibility at 293 K due to complexes with $S = 1$

(so $m_0 = 2\mu_B\{S(S+1)\}^{1/2} = 8^{1/2}\mu_B$) is

$$\chi = \frac{(4\pi \times 10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3}) \times 8\ \times (9.274 \times 10^{-24}\ \mathrm{J\ T^{-1}})^2 \times (1.43 \times 10^{28}\ \mathrm{m^{-3}})}{3 \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (293\ \mathrm{K})}$$

$$\underline{= 1.0 \times 10^{-3}}$$

Note that the final answer is consistent with the assumption that $\chi << 1$ (as required in the derivation of eqn 13.7); all the units cancel.

13.4 The molar magnetic susceptibility is given by eqn 13.10.

$$\chi_\mathrm{m} = \frac{\mu_0 m_0^2 N_\mathrm{A}}{3kT}$$

$$= \frac{(4\pi \times 10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3}) \times 8\ \times (9.274 \times 10^{-24}\ \mathrm{J\ T^{-1}})^2 \times (6.022 \times 10^{23}\ \mathrm{mol^{-1}})}{3 \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (293\ \mathrm{K})}$$

$$= \underline{4.3 \times 10^{-8}\ \mathrm{m^3\ mol^{-1}}}$$

13.5 The Curie constant C is given by eqn 13.11:

$$C = \frac{\mu_0 m_0^2 N_\mathrm{A}}{3k}$$

$$= \frac{(4\pi \times 10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3}) \times 8\ \times (9.274 \times 10^{-24}\ \mathrm{J\ T^{-1}})^2 \times (6.022 \times 10^{23}\ \mathrm{mol^{-1}})}{3 \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}})}$$

$$= \underline{1.3 \times 10^{-5}\ \mathrm{m^3\ K\ mol^{-1}}}$$

13.6 $\chi_\mathrm{m} = C/T$ [eqn 13.11]. For hydrogen atoms at 298 K, $C = 4.7 \times 10^{-6}\ \mathrm{m^3\ K\ mol^{-1}}$, and $T/K = 298$; then $\chi_\mathrm{m} = \underline{1.6 \times 10^{-8}\ \mathrm{m^3\ mol^{-1}}}$.

Exercise: Calculate the spin contribution to χ_m for the ground state of a nitrogen atom at 298 K.

13.7 Because $\langle S_x^2 \rangle = \langle S_y^2 \rangle = \langle S_z^2 \rangle$, it follows that

$$\langle S_z^2 \rangle = \tfrac{1}{3}\langle S_x^2 + S_y^2 + S_z^2 \rangle = \tfrac{1}{3}\langle S^2 \rangle$$

But $\langle S^2 \rangle = \hbar^2 S(S+1)$ for each state. Therefore, $\langle S_z^2 \rangle = \underline{\tfrac{1}{3}S(S+1)\hbar^2}$.

Exercise: Evaluate $\langle S_z^4 \rangle$ in this way.

13.8 See Fig. 13.1.

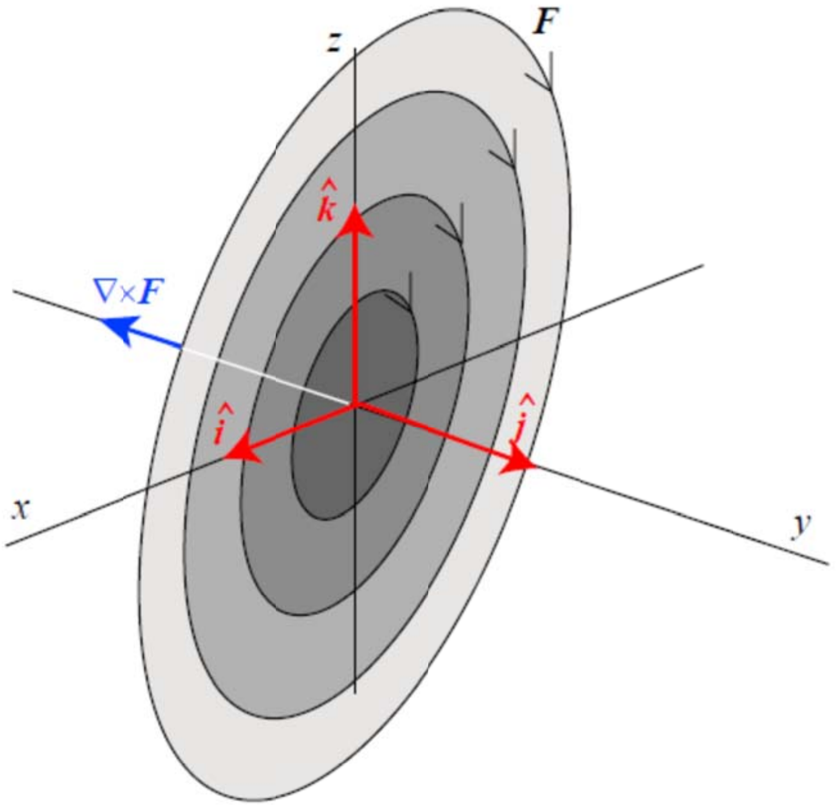


Figure 13.1: The vector function used in Exercise 13.8.

Because $F_x = -z$, $F_y = 0$, and $F_z = x$, we have

$$\nabla\cdot\boldsymbol{F} = (\partial/\partial x)(-z) + (\partial/\partial y)0 + (\partial/\partial z)x = \underline{0}$$

$$\nabla\times\boldsymbol{F} = \begin{vmatrix} \hat{\boldsymbol{i}} & \hat{\boldsymbol{j}} & \hat{\boldsymbol{k}} \\ (\partial/\partial x) & (\partial/\partial y) & (\partial/\partial z) \\ -z & 0 & x \end{vmatrix} = \hat{\boldsymbol{\imath}}\,[(\partial x/\partial y) - (\partial 0/\partial z)]$$

$$-\hat{\boldsymbol{j}}\,[(\partial x/\partial x) + (\partial z/\partial z)] + \widehat{\boldsymbol{k}}\,[(\partial 0/\partial x) + (\partial z/\partial y)]$$

$$= -2\,\hat{\boldsymbol{j}}$$

Exercise: Sketch the form of $\boldsymbol{F} = x^2\hat{\boldsymbol{k}} - z^2\hat{\boldsymbol{\imath}}$, and calculate its divergence and curl.

13.9 **(a)**

$$\boldsymbol{\mathcal{B}} = \mathcal{B}\hat{\boldsymbol{\imath}};$$

$$\boldsymbol{A} = \tfrac{1}{2}\mathcal{B}\hat{\boldsymbol{\imath}} \times \boldsymbol{r} = \tfrac{1}{2}\begin{vmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\boldsymbol{k}} \\ \mathcal{B} & 0 & 0 \\ x & y & z \end{vmatrix} = \underline{\tfrac{1}{2}\mathcal{B}(-z\hat{\boldsymbol{\jmath}} + y\hat{\boldsymbol{k}})}$$

(b)

$$\boldsymbol{\mathcal{B}} = \mathcal{B}(\hat{\boldsymbol{\imath}} + \hat{\boldsymbol{\jmath}})/\sqrt{2}$$

$$\boldsymbol{A} = (\mathcal{B}/2\sqrt{2})(\hat{\boldsymbol{\imath}} + \hat{\boldsymbol{\jmath}}) \times \boldsymbol{r}$$

$$= (\mathcal{B}/2\sqrt{2})\begin{vmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\boldsymbol{k}} \\ 1 & 1 & 0 \\ x & y & z \end{vmatrix} = (\mathcal{B}/2\sqrt{2})\{(z\hat{\boldsymbol{\imath}} - z\hat{\boldsymbol{\jmath}} + (y-x)\hat{\boldsymbol{k}}\}$$

For a uniform field,

$$A^2 = \{\tfrac{1}{2}(\boldsymbol{\mathcal{B}} \times \boldsymbol{r})\} \cdot \{\tfrac{1}{2}(\boldsymbol{\mathcal{B}} \times \boldsymbol{r})\}$$

$$= \tfrac{1}{4}\{(\boldsymbol{\mathcal{B}} \cdot \boldsymbol{\mathcal{B}})(\boldsymbol{r} \cdot \boldsymbol{r}) - (\boldsymbol{\mathcal{B}} \cdot \boldsymbol{r})(\boldsymbol{r} \cdot \boldsymbol{\mathcal{B}})\} = \underline{\tfrac{1}{4}\{\mathcal{B}^2 r^2 - (\boldsymbol{\mathcal{B}} \cdot \boldsymbol{r})^2\}}$$

(a) $\boldsymbol{\mathcal{B}} \cdot \boldsymbol{r} = \mathcal{B}x;\quad A^2 = \tfrac{1}{4}\mathcal{B}^2(r^2 - x^2) = \underline{\tfrac{1}{4}\mathcal{B}^2(z^2 + y^2)}$

(b) $\boldsymbol{\mathcal{B}} \cdot \boldsymbol{r} = (\mathcal{B}/\sqrt{2})(x + y);\ A^2 = \tfrac{1}{4}\mathcal{B}^2\{r^2 - \tfrac{1}{2}(x^2 + y^2)^2\}$

Exercise: Find the expressions for the vector potentials representing uniform fields directed towards the corners of a regular tetrahedron. Evaluate $\boldsymbol{\mathcal{B}}$ for $\boldsymbol{A} = \mathcal{B}(x^2\hat{\boldsymbol{k}} - z^2\hat{\boldsymbol{\imath}})$.

13.10 Streamlines representing the vector function $\boldsymbol{C} + \lambda\boldsymbol{D}$ are shown in Fig. 13.2 for various values of λ.

$$\boldsymbol{C} = -y\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}} \qquad \boldsymbol{D} = x\hat{\boldsymbol{\imath}} + y\,\hat{\boldsymbol{\jmath}} \qquad \boldsymbol{C} + \lambda\boldsymbol{D} = (-y + \lambda x)\hat{\boldsymbol{\imath}} + (x + \lambda y)\,\hat{\boldsymbol{\jmath}}$$

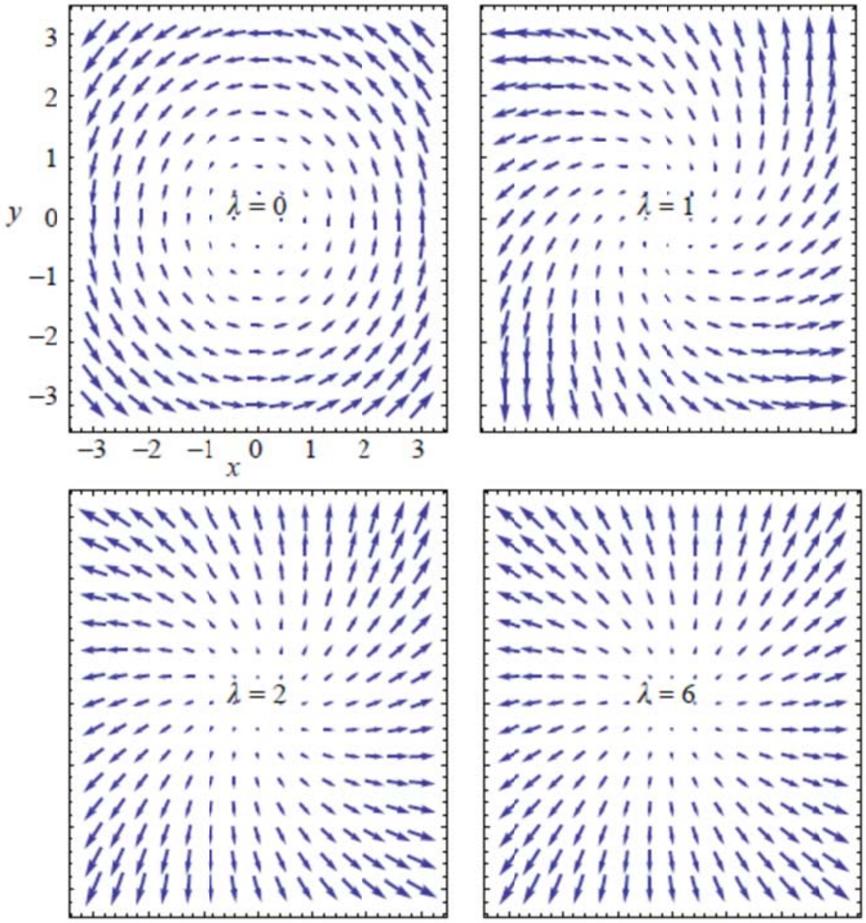


Fig. 13.2 Streamlines of $\boldsymbol{C} + \lambda\boldsymbol{D}$ for indicated values of λ.

13.11 $\boldsymbol{C} = -y\,\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}}$

$$\boldsymbol{A} = \boldsymbol{C}\,\mathrm{e}^{-\boldsymbol{k}\cdot\boldsymbol{r}} = (-y\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}})\,\mathrm{e}^{-kz}$$

$\mathcal{B} = \nabla \times \boldsymbol{A}$ [eqn 13.14]

$$= \begin{vmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\boldsymbol{k}} \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \\ -y\mathrm{e}^{-kz} & x\mathrm{e}^{-kz} & 0 \end{vmatrix} \quad \text{[Section MB6.2]}$$

$$= -\hat{\boldsymbol{\imath}}\frac{\partial}{\partial z}(x\mathrm{e}^{-kz}) - \hat{\boldsymbol{\jmath}}\frac{\partial}{\partial z}(y\mathrm{e}^{-kz}) + \hat{\boldsymbol{k}}\left\{\frac{\partial}{\partial x}(x\mathrm{e}^{-kz}) + \frac{\partial}{\partial y}(y\mathrm{e}^{-kz})\right\}$$

$$= \mathrm{e}^{-kz}\{kx\hat{\boldsymbol{\imath}} + ky\hat{\boldsymbol{\jmath}} + 2\hat{\boldsymbol{k}}\}$$

$$\boldsymbol{\nabla}\cdot\mathcal{B} = \frac{\partial}{\partial x}(kx\mathrm{e}^{-kz}) + \frac{\partial}{\partial y}(ky\mathrm{e}^{-kz}) + \frac{\partial}{\partial z}(2\mathrm{e}^{-kz}) = 2k\mathrm{e}^{-kz} - 2k\mathrm{e}^{-kz}$$

$$= 0$$

Therefore, the magnetic field does not have non-zero divergence.

13.12

$$\chi_\mathrm{m} = -(e^2\mu_0 N_\mathrm{A}/6m_\mathrm{e})\langle r^2\rangle \quad \text{[eqn 13.40]}$$

$$\psi_{1\mathrm{s}} = (Z^{*3}/\pi a_0^3)^{1/2}\,\mathrm{e}^{-Z^*r/a_0}$$

$$\psi_{2\mathrm{s}} = (Z^{*5}/96\pi a_0^5)^{1/2}\,r\mathrm{e}^{-Z^*r/2a_0}$$

$$\langle r^2\rangle_{1\mathrm{s}} = (Z^{*3}/\pi a_0^3)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{\infty} r^2\{r^2\mathrm{e}^{-2Z^*r/a_0}\}\mathrm{d}r$$

$$= (Z^{*3}/\pi a_0^3)(2\pi)(2)\{4!/(2Z^*/a_0)^5\} = 3a_0^2/Z^{*2}$$

$$\langle r^2\rangle_{2\mathrm{s}} = (Z^{*5}/96\pi a_0^5)(2\pi)(2)\int_0^{\infty} r^6\mathrm{e}^{-Z^*r/a_0}\mathrm{d}r$$

$$= (Z^{*5}/96\pi a_0^5)(4\pi)\{6!/(Z^*/a_0)^7\} = 30a_0^2/Z^{*2}$$

Therefore, in each case we write

$$\chi_m = -(e^2\mu_0 N_A/6m_e)\,Ka_0^2/Z^{*2}, \quad \textbf{(a)}\ K = 3 \text{ for 1s, } \textbf{(b)}\ K = 30 \text{ for 2s}$$

$$= \underline{-(9.95 \times 10^{-12})K/Z^{*2}}$$

(i) For the hydrogen atom, take $Z^* = 1$, $K = 3$;

$$\underline{\chi_m(\mathrm{H}) = -2.99 \times 10^{-11}\,\mathrm{m^3\ mol^{-1}}}$$

(ii) For the carbon atom, take $Z^*(1s) = 5.67$, $Z^*(2s) = 3.22$ [Table 7.3];

$$\chi_m(\mathrm{C, 1s}) = \underline{-9.28 \times 10^{-13}\ \mathrm{m^3\ mol^{-1}}};\ \chi(\mathrm{C, 2s}) = \underline{-2.88 \times 10^{-11}\ \mathrm{m^3\ mol^{-1}}}$$

Exercise: Use the true hydrogenic 2s-orbitals to calculate $\chi(\mathrm{H, 2s})$ and compare it with the Slater orbital result. Does the orthogonalization of the Slater H1s and H2s improve the agreement?

13.13 $\chi = \mu_0 \mathcal{N}\xi$ [eqn 13.33]. Using eqns 13.8 and 13.9, we obtain

$$\chi_m = \chi V_m = \mu_0 \mathcal{N}\xi\, V_m = \mu_0 \xi N_A$$

and therefore

$$\xi = \chi_m/(\mu_0 N_A).$$

(a)(i) $\xi(\mathrm{H, 1s}) = -2.99 \times 10^{-11}\,\mathrm{m^3\,mol^{-1}}/\{(4\pi \times 10^{-7}\,\mathrm{T^2\,J^{-1}\,m^3}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})\}$

$$= \underline{-3.95 \times 10^{-29}\,\mathrm{N^{-1}\,A^2\,m^3}}$$

(a)(ii) $\xi(\mathrm{C, 1s}) = -9.28 \times 10^{-13}\,\mathrm{m^3\,mol^{-1}}/\{(4\pi \times 10^{-7}\,\mathrm{T^2\,J^{-1}\,m^3}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})\}$

$$= \underline{-1.23 \times 10^{-30}\,\mathrm{N^{-1}\,A^2\,m^3}}$$

(b)(ii) $\xi(\mathrm{C, 2s}) = -2.88 \times 10^{-11}\,\mathrm{m^3\,mol^{-1}}/\{(4\pi \times 10^{-7}\,\mathrm{T^2\,J^{-1}\,m^3}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})\}$

$$= \underline{-3.81 \times 10^{-29}\,\mathrm{N^{-1}\,A^2\,m^3}}$$

13.14 We desire contour diagrams of the type shown in Fig. 13.9 in the text.

$$\boldsymbol{j}^{\mathrm{d}} = -(e^2\mathcal{B}/2\pi m_{\mathrm{e}} a_0^3)(-y\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}})\mathrm{e}^{-2r/a_0} \text{ [eqn 13.54b]}$$

$$= -(e^2\mathcal{B}/2\pi m_{\mathrm{e}} a_0^3)(-\hat{\boldsymbol{\imath}}\sin\phi + \hat{\boldsymbol{\jmath}}\cos\phi)\sin\theta\, r\mathrm{e}^{-2r/a_0}$$

$$= -(e^2\mathcal{B}/2\pi m_{\mathrm{e}} a_0^2)(-\hat{\boldsymbol{\imath}}\sin\phi + \hat{\boldsymbol{\jmath}}\cos\phi)\sin\theta\, s\mathrm{e}^{-2s},\ s = r/a_0$$

The heights 0, a_0, $2a_0$ correspond to the following values of r, θ for horizontal distances σa_0 from the nucleus (Fig. 13.3):

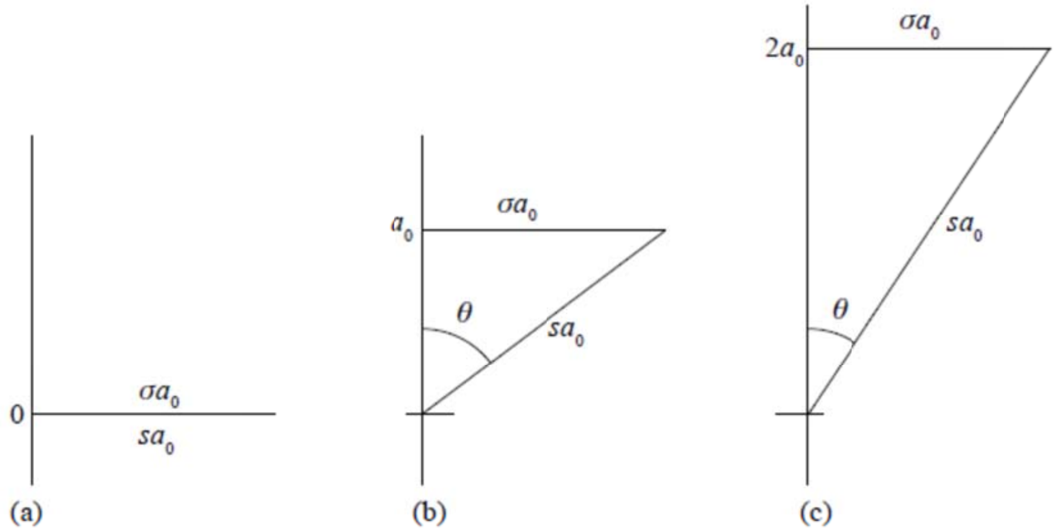


Figure 13.3: The geometry of the arrangement treated in Exercise 13.14.

(a) $0 : s = \sigma,\ \theta = 90°$,

(b) $a_0 : s\sin\theta = \sigma, \quad s = (1 + \sigma^2)^{1/2}$,

(c) $2a_0 : s\sin\theta = \sigma, \quad s = (4 + \sigma^2)^{1/2}$.

Write $j^{\ominus} = -(e^2\mathcal{B}/2\pi m_e a_0^2)$

then

$$\boldsymbol{j}^{\mathrm{d}}/\, j^{\ominus} = (-\hat{\boldsymbol{i}}\sin\phi + \hat{\boldsymbol{j}}\cos\phi)\sin\theta\, s\mathrm{e}^{-2s}$$

which correspond to circles denoting magnitudes

(a) $j^{\mathrm{d}}/j^{\ominus} = \underline{\sigma \mathrm{e}^{-2\sigma}}$

(b) $j^{\mathrm{d}}/j^{\ominus} = \underline{\sigma \exp\{-2(1+\sigma^2)^{1/2}\}}$

(c) $j^{\mathrm{d}}/j^{\ominus} = \underline{\sigma \exp\{-2(4+\sigma^2)^{1/2}\}}$

These functions are plotted in Fig. 13.4.

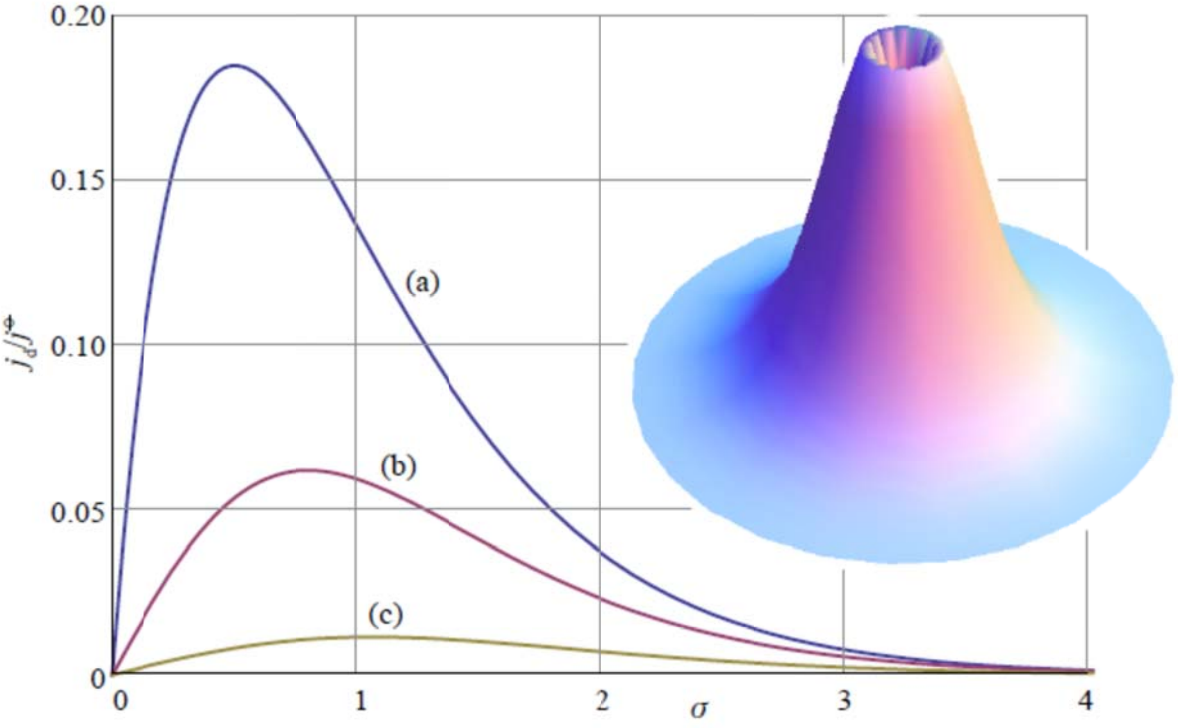


Figure 13.4: The diamagnetic current density at heights of 0, a_0, and $2a_0$ above the

xy-plane for a ground-state hydrogen atom in a magnetic field.

Exercise: Calculate and plot the current densities in the same three planes for an electron in a hydrogenic 2s-orbital.

13.15 Take the following hydrogenic orbitals [$s = r/a_0$]:

$$\psi_{2\mathrm{s}} = R_{20}Y_{00} = (Z^3/8\pi a_0^3)^{1/2}(1 - \tfrac{1}{2}Zs)\mathrm{e}^{-Zs/2}$$

$$\psi_{3\mathrm{p}} = R_{31}Y_{10} = (1/27)(2Z^5/\pi a_0^3)^{1/2}s(2 - \tfrac{1}{3}Zs)\mathrm{e}^{-Zs/3}\cos\theta$$

When the field is along *z* there is no paramagnetic contribution. The diamagnetic current densities are given by

$$\boldsymbol{j}^{\mathrm{d}} = -(e^2\mathcal{B}/2m_\mathrm{e})\psi_0^2\boldsymbol{C} \quad \text{[eqn 13.54a]}$$

(a) $\boldsymbol{j}^{\mathrm{d}}(2\mathrm{s}) = -(Z^3e^2\mathcal{B}/16\pi m_\mathrm{e}a_0^3)(1 - \tfrac{1}{2}Zs)^2\boldsymbol{C}\mathrm{e}^{-Zs}$

$$= -(Z^3e^2\mathcal{B}/16\pi m_\mathrm{e}a_0^2)s(1 - \tfrac{1}{2}Zs)^2(-\hat{\boldsymbol{\imath}}\sin\phi + \hat{\boldsymbol{\jmath}}\cos\phi)\mathrm{e}^{-Zs}\sin\theta$$

which correspond to circular contours denoting magnitudes

$$j^{d}(2\mathrm{s})/j^* = s(1 - \tfrac{1}{2}Zs)^2\mathrm{e}^{-Zs}\sin\theta, \quad j^* = Z^3e^2\mathcal{B}/16\pi m_\mathrm{e}a_0^2$$

When $\theta = 90°$ and $Z = 1$,

$$j^{\mathrm{d}}(2\mathrm{s})/j^* = \underline{s(1-\tfrac{1}{2}s)^2\mathrm{e}^{-s}}$$

which is sketched in Fig. 13.5.

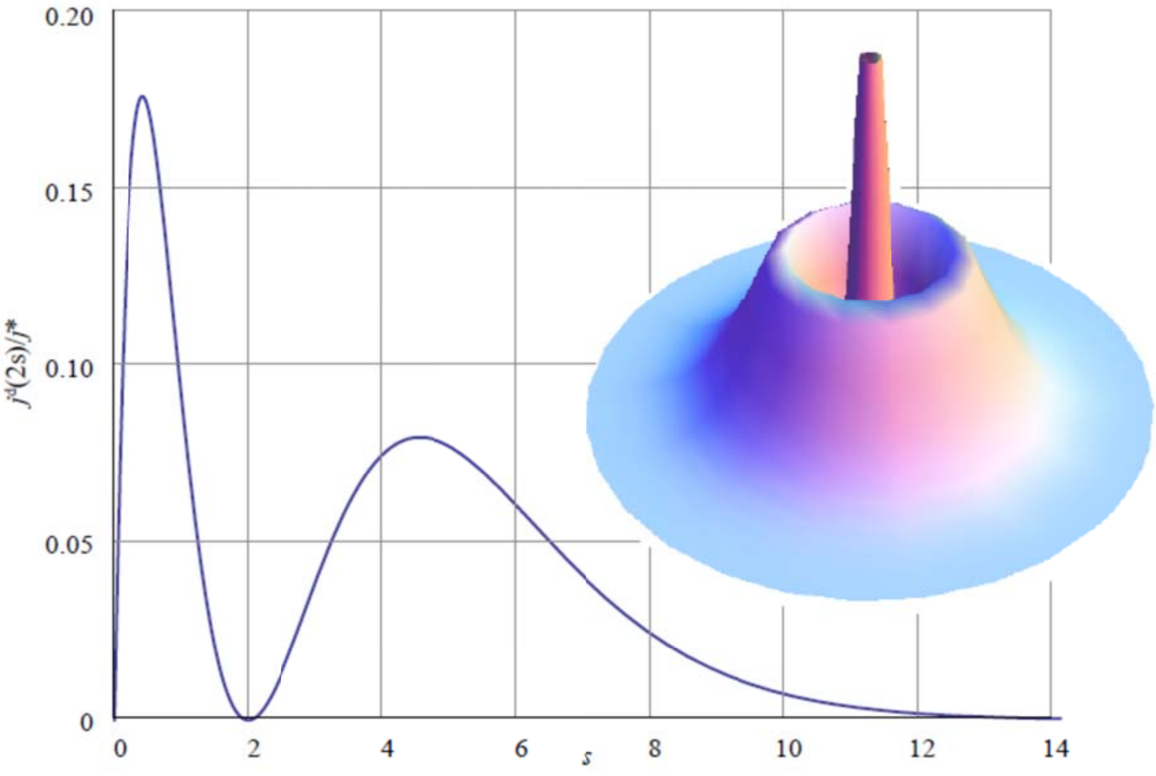


Figure 13.5: The diamagnetic current density in a 2s-orbital in a plane through the nucleus.

(b)

$$\boldsymbol{j}^{\mathrm{d}}(3\mathrm{p}_z) = -(Z^5e^2\mathcal{B}/729m_{\mathrm{e}}\pi a_0^2)s^3(2-\tfrac{1}{3}Zs)^2\mathrm{e}^{-2Zs/3}\cos^2\theta\sin\theta$$

$$\times(-\hat{\boldsymbol{\imath}}\sin\phi+\hat{\boldsymbol{\jmath}}\cos\phi)$$

This expression also corresponds to circular contours denoting magnitudes

$$j^{\mathrm{d}}(3p_z)/j^{**} = s^3(2-\tfrac{1}{3}Zs)^2\cos^2\theta\sin\theta\,\mathrm{e}^{-2Zs/3}, j^{**} = Z^5e^2\mathcal{B}/729m_{\mathrm{e}}\pi a_0^2$$

The magnitudes are zero in the equatorial plane ($\sin\theta = 0$). For a plane parallel to the equatorial plane but at a height ha_0 above it, we have $s\sin\theta = \sigma$, as in Fig. 13.3 (Exercise 13.14), $\cos\theta = h/s$, and $s^2 = \sigma^2 + h^2$. Then, with $Z = 1$,

$$j^{\mathrm{d}}(3\mathrm{p}_z)/j^{**} = \underline{h^2\sigma(2-\tfrac{1}{3}[\sigma^2+h^2]^{1/2})^2\exp\{-\tfrac{2}{3}[\sigma^2+h^2]^{1/2}\}}$$

This expression is sketched in Fig. 13.6 for $h = 1$, when

$$j^{\mathrm{d}}(3\mathrm{p}_z)/j^{**} = \sigma\{2-\tfrac{1}{3}\sqrt{(1+\sigma^2)}\}^2\exp\{-\tfrac{2}{3}\sqrt{(1+\sigma^2)}\}$$

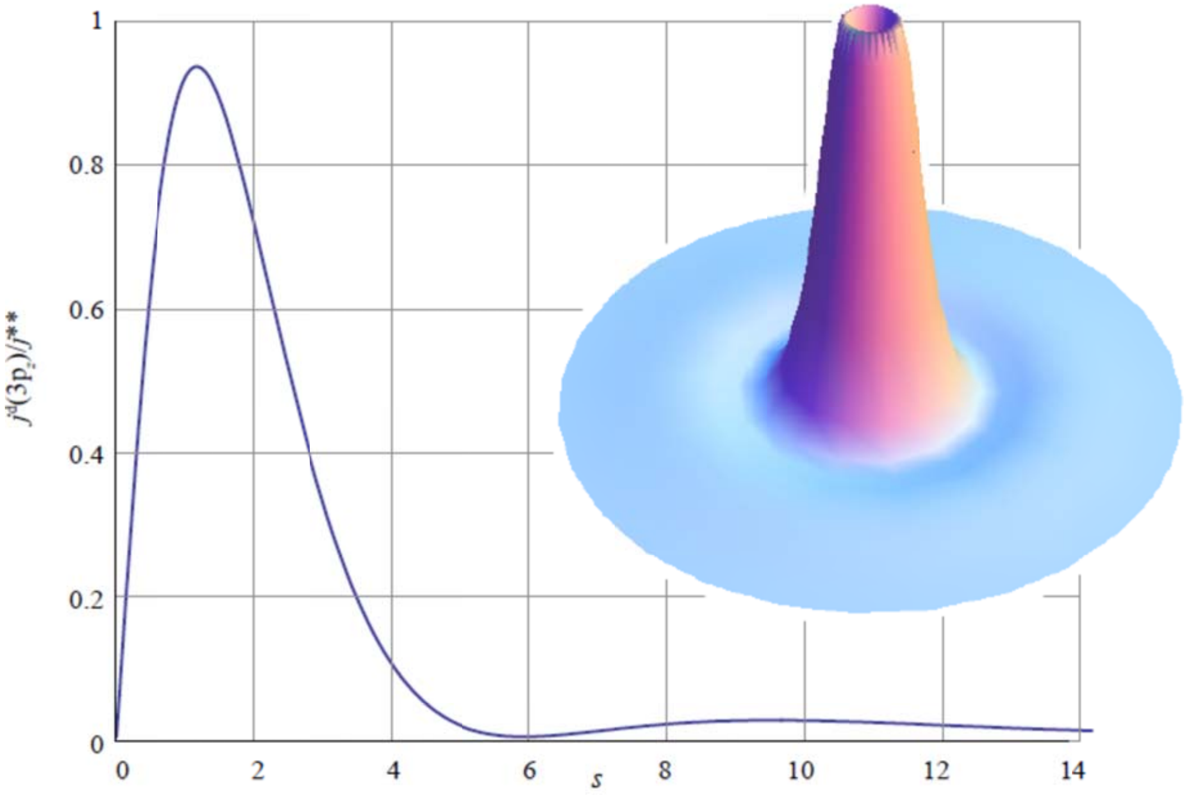


Figure 13.6: The diamagnetic current density in a $3\mathrm{p}_z$-orbital in a plane at a height a_0 above the xy-plane.

Exercise: Evaluate $\boldsymbol{j}(4\mathrm{p}_z)$ and $\boldsymbol{j}(3\mathrm{s})$ for hydrogenic orbitals, the magnetic field being applied in the z-direction.

13.16 We need to show that the vector potential given in eqn 13.62b has zero divergence. If the spin angular momentum $\boldsymbol{I}$ and the position vector $\boldsymbol{r}$ are written in terms of their components

$$\boldsymbol{I} = I_x\,\hat{\boldsymbol{\imath}} + I_y\hat{\boldsymbol{\jmath}} + I_z\hat{\boldsymbol{k}} \qquad \boldsymbol{r} = x\hat{\boldsymbol{\imath}} + y\hat{\boldsymbol{\jmath}} + z\hat{\boldsymbol{k}}$$

then, using the definition of the vector product (eqn MB3.4e), we find

$$\boldsymbol{A}_{\text{nuc}} = \left(\frac{\gamma_{\text{N}}\mu_0}{4\pi r^3}\right)\{\hat{\boldsymbol{\imath}}(I_yz - yI_z) + \hat{\boldsymbol{\jmath}}\,(I_zx - zI_x) + \hat{\boldsymbol{k}}\,(I_xy - xI_y)\}$$

Using the definition of the divergence (eqn MB6.3), we obtain

$$\nabla\cdot\boldsymbol{A}_{\text{nuc}} = \left(\frac{\gamma_{\text{N}}\mu_0}{4\pi r^3}\right)\left[\frac{\partial}{\partial x}(I_yz - yI_z) + \frac{\partial}{\partial y}(I_zx - zI_x) + \frac{\partial}{\partial z}(I_xy - xI_y)\right]$$

$$= 0$$

because I_y and z are independent of x and so forth.

Exercise: Evaluate the curl of the vector potential given in eqn 13.62b.

13.17 A magnetic dipole that has only a z-component can be written $\boldsymbol{m} = m_z\,\boldsymbol{k}$. The vector potential $\boldsymbol{A}$ then takes the form (see eqn 13.62a):

$$\boldsymbol{A} = \left(\frac{\mu_0}{4\pi r^3}\right)\boldsymbol{m}\times\boldsymbol{r}$$

$$= \left(\frac{\mu_0}{4\pi r^3}\right)\begin{vmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \widehat{\boldsymbol{k}} \\ 0 & 0 & m_z \\ x & y & z \end{vmatrix}$$

$$= \left(\frac{\mu_0 m_z}{4\pi r^3}\right)(-y\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}})$$

13.18

$$\sigma^{\mathrm{d}} = (e^2\mu_0/12\pi m_{\mathrm{e}})\langle(1/r)\rangle \quad \text{[eqn 13.74]}$$

$$\psi(2\mathrm{s}) = (Z^{*5}/96\pi a_0^5)^{1/2}\, r\mathrm{e}^{-Z^*r/2a_0} \quad \text{[Exercise 13.12]}$$

$$\psi(2\mathrm{p}_z) = (Z^{*5}/32\pi a_0^5)^{1/2}\, r\cos\theta\,\mathrm{e}^{-Z^*r/2a_0} \quad \text{[Problem 13.4]}$$

$$\langle(1/r)\rangle_{2\mathrm{s}} = (Z^{*5}/96\pi a_0^5)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\mathrm{d}\theta\int_0^{\infty} r^2\,\{r^2(1/r)\mathrm{e}^{-Z^*r/a_0}\}\mathrm{d}r$$

$$= (Z^{*5}/96\pi a_0^5)\,(2\pi)(2)\{3!/(Z^*/a_0)^4\} = \tfrac{1}{4}(Z^*/a_0)$$

$$\langle(1/r)\rangle_{2\mathrm{p}_z} = (Z^{*5}/32\pi a_0^5)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\mathrm{d}\theta\int_0^{\infty} r^2\,\{r^2(1/r)\cos^2\theta\,\mathrm{e}^{-Z^*r/a_0}\}\mathrm{d}r$$

$$= (Z^{*5}/32\pi a_0^5)\,(2\pi)(2/3)\{3!/(Z^*/a_0)^4\} = \tfrac{1}{4}(Z^*/a_0)$$

Therefore, for each type of orbital,

$$\sigma^{\mathrm{d}} = (e^2\mu_0/12\pi m_{\mathrm{e}})(Z^*/4a_0) = e^2\mu_0 Z^*/48\pi m_{\mathrm{e}} a_0$$

$$= 4.44\times10^{-6}\,Z^*$$

For an electron in a carbon atom, for which $Z^*(2\mathrm{s}) = 3.22$ and $Z^*(2\mathrm{p}) = 3.14$ [Table 7.3],

(a) $\underline{2\mathrm{s} : \sigma^{\mathrm{d}} = 1.43\times10^{-5}}$ **(b)** $\underline{2\mathrm{p} : \sigma^{\mathrm{d}} = 1.39\times10^{-5}}$

Exercise: Calculate the contribution to σ^{d} of an electron in (a) a hydrogenic 2s-orbital, (b) Slater 3s- and 3p-orbitals.

13.19 The 2s-orbital gives zero paramagnetic contribution. The 2p-electron contributes

$$\sigma^{\mathrm{p}} = -(e^2\mu_0/12\pi\, m_{\mathrm{e}}^2)\sum_{n\neq 0}\frac{\boldsymbol{l}_{0n}\cdot(r^{-3}\boldsymbol{l})_{n0}}{\Delta E_{n0}}\} \quad [\text{eqn } 13.75]$$

$$= -(e^2\mu_0/12\pi\, m_{\mathrm{e}}^2)\,\langle \mathrm{p}_z|l_x|\mathrm{p}_y\rangle\langle \mathrm{p}_y|r^{-3}l_x|\mathrm{p}_z\rangle/\Delta E$$

[We are assuming that the orbital mixed in is p_y, so only l_x contributes; another p_x-orbital nearby would give an additional contribution through l_y.] Because $l_x\mathrm{p}_z = -\mathrm{i}\hbar\mathrm{p}_y$ this expression becomes

$$\sigma^{\mathrm{p}} = -(e^2\mu_0\hbar^2/12\pi\, m_{\mathrm{e}}^2)\,\langle \mathrm{p}_y|(1/r^3)|\mathrm{p}_y\rangle/\Delta E$$

$$\langle(1/r^3)\rangle_{2\mathrm{p}_y} = \langle(1/r^3)\rangle_{2\mathrm{p}_z}$$

$$= (Z^{*5}/32\pi\, a_0^5)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\mathrm{d}\theta\int_0^{\infty}r^2\,\{r^2(1/r^3)\cos^2\theta\,\mathrm{e}^{-Z^*r/a_0}\}\mathrm{d}r$$

$$= (Z^{*5}/32\pi\, a_0^5)\,(2\pi)(2/3)\{1/(Z^*/a_0)^2\} = Z^{*3}/\,24a_0^3$$

Consequently,

$$\sigma^{\mathrm{p}} = -(e^2\mu_0\hbar^2/12\pi\, m_{\mathrm{e}}^2)\;(Z^{*3}/24a_0^3)\,(1/\Delta E)$$

$$= -(e^2\mu_0\hbar^2/288\pi\, m_{\mathrm{e}}^2 a_0^3)\,(Z^{*3}/\Delta E)$$

$$= \underline{-2.013\times 10^{-5}\,Z^{*3}/(\Delta E/\mathrm{eV})}$$

For carbon, $Z^* = 3.14$ [Table 7.3], so

$$\sigma^{\mathrm{p}} = -6.23 \times 10^{-4}/(\Delta E/\mathrm{eV}) = -1.2 \times 10^{-4} \text{ when } \Delta E/\mathrm{eV} = 5.0$$

Exercise: Calculate the paramagnetic contribution to the shielding of an electron in a $3\mathrm{p}_z$-orbital.

13.20 The magnetic perturbation transforms as a rotation. In $C_{2\mathrm{v}}$, R_x, R_y, R_z transform as $\underline{\mathrm{B}_2, \mathrm{B}_1, \mathrm{A}_2}$ respectively. Therefore, because

$$\mathrm{A}_1 \times \{\mathrm{B}_2, \mathrm{B}_1, \mathrm{A}_2\} = \{\mathrm{B}_2, \mathrm{B}_1, \mathrm{A}_2\}$$

it follows that for NO_2 the components g_{xx}, g_{yy}, g_{zz} depend on the admixture of $\underline{{}^2\mathrm{B}_2, {}^2\mathrm{B}_1, {}^2\mathrm{A}_2}$ terms respectively. Because

$$\mathrm{B}_1 \times \{\mathrm{B}_2, \mathrm{B}_1, \mathrm{A}_2\} = \{\mathrm{A}_2, \mathrm{A}_1, \mathrm{B}_2\}$$

it follows that for ClO_2, g_{xx}, g_{yy}, g_{zz} depend on the admixture of ${}^2\mathrm{A}_2$, ${}^2\mathrm{A}_1$, ${}^2\mathrm{B}_2$ respectively.

Exercise: What states contribute to g_{xx}, g_{yy}, g_{zz} in the ${}^2\mathrm{E}_1'$ state of a $D_{5\mathrm{h}}$ molecule?

13.21 $\psi(\mathrm{d}_{z_2}) = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} R_{n2}(r)(3\cos^2\theta - 1)$ [eqn 3.74a]

$$\langle 1 - 3\cos^2\theta \rangle = \int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty} \psi(\mathrm{d}_{z_2})(1 - 3\cos^2\theta)\psi(\mathrm{d}_{z_2}) r^2 \sin\theta \mathrm{d}\theta \mathrm{d}\varphi \mathrm{d}r$$

$$= \frac{5}{16\pi}\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty} R_{n2}^2(r)(3\cos^2\theta - 1)^2(1 - 3\cos^2\theta) r^2 \sin\theta \mathrm{d}\theta \mathrm{d}\varphi \mathrm{d}r$$

Since the radial function R_{n2} is normalized, integration over r contributes unity; integration over φ contributes 2π. Therefore,

$$\langle 1-3\cos^2\theta\rangle = \frac{5}{8}\int_{\theta=0}^{\pi}(3\cos^2\theta-1)^2(1-3\cos^2\theta)\sin\theta\mathrm{d}\theta$$

$$= \frac{5}{8}\int_{\theta=0}^{\pi}(-27\cos^6\theta+27\cos^4\theta-9\cos^2\theta+1)\sin\theta\mathrm{d}\,\theta$$

$$= \frac{5}{8}\left\{\frac{-2\times 27}{7}+\frac{2\times 27}{5}-2\times 3+2\right\}$$

$$= -4/7$$

13.22 The spherical average of $(1-3\cos^2\theta)^2$ is given by the integral

$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}(1-3\cos^2\theta)^2\sin\theta\mathrm{d}\theta\mathrm{d}\varphi = 2\pi\int_{\theta=0}^{\pi}(1-3\cos^2\theta)^2\sin\theta\mathrm{d}\theta$$

$$= 2\pi\int_{\theta=0}^{\pi}(9\cos^4\theta-6\cos^2\theta+1)\sin\theta\mathrm{d}\theta$$

$$= 2\pi\left\{\frac{9}{5}\times 2+2\times(-2)+2\right\}$$

$$= 16\pi/5$$

Problems

13.1 Under the influence of the perturbation $H^{(1)} = -\gamma_e l_z \mathcal{B}$ the non-degenerate, real, ground state ψ_0 changes to $\psi = \psi_0 + c\psi_1$, with $c = -\langle\psi_1|H^{(1)}|\psi_0\rangle/\Delta E$ [eqn 6.26]. In this case $c = \gamma_e \mathcal{B} l_{z,10}/\Delta E$; which is imaginary. Therefore ψ is complex. It follows that

$$\langle\psi|l_q|\psi\rangle = \langle\psi|l_q|\psi\rangle^* \quad \text{[hermiticity]}$$

$$\langle\psi|l_q|\psi\rangle = \langle\psi_0|l_q|\psi_0\rangle + \langle\psi_0|l_q|\psi_1\rangle c + c^*\langle\psi_1|l_q|\psi_0\rangle + \mathrm{O}(c)^2$$

$$\langle\psi|l_q|\psi\rangle^* = \langle\psi_0|l_q|\psi_0\rangle^* + \langle\psi_0|l_q|\psi_1\rangle^* c^* + c\langle\psi_1|l_q|\psi_0\rangle^* + \mathrm{O}(c^2)$$

$$= -\langle\psi_0|l_q|\psi_0\rangle - \langle\psi_0|l_q|\psi_1\rangle c^* - c\langle\psi_1|l_q|\psi_0\rangle + \mathrm{O}(c^2)$$

On comparing the two expressions, noting that $\langle\psi_0|l_q|\psi_0\rangle = 0$, we are left with

$$\langle\psi_0|l_q|\psi_1\rangle c + c^*\langle\psi_1|l_q|\psi_0\rangle = \langle\psi_0|l_q|\psi_1\rangle c + c^*\langle\psi_1|l_q|\psi_0\rangle$$

which does not require a value of zero. Hence $\langle\psi|l_q|\psi\rangle$ need not disappear.

Exercise: Show that the expectation value of linear momentum is zero when the state is real but may be nonzero in the presence of an appropriate perturbation.

13.4. $\psi = (\psi_\mathrm{N} - \psi_\mathrm{O})/\sqrt{2}$

$$\psi_{2\mathrm{p}} = (Z^{*5}/32\pi a_0^5)^{1/2} r \cos\theta\, \mathrm{e}^{-Z^*r/2a_0}, \quad Z_\mathrm{N}^* = 3.83,\ Z_\mathrm{O}^* = 4.45 \text{ [Table 7.3]}$$

Let the vector potential be centred on a point a fraction λ of the bond (of length R) from N, Fig. 13.7.

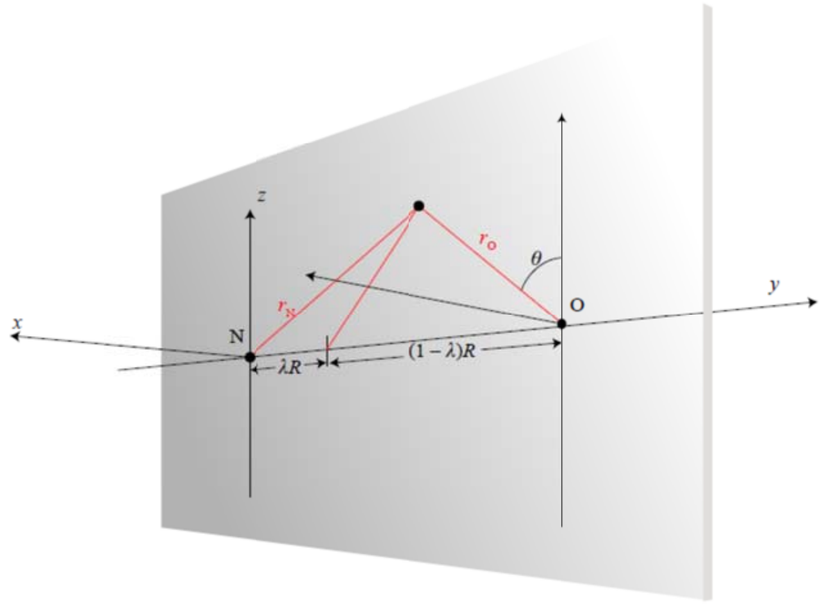


Figure 13.7: The coordinates used in Problem 13.4.

Then for a uniform field along *x*,

$$\boldsymbol{A} = \tfrac{1}{2}\boldsymbol{\mathcal{B}} \times \boldsymbol{r} = \tfrac{1}{2}\mathcal{B}(-z\hat{\boldsymbol{j}} + y\hat{\boldsymbol{k}})$$

We need to express cos θ and r (on both N and O) in terms of the same y and z coordinates. (Note in passing that there is no 'natural' origin for $\boldsymbol{A}$: different values of λ correspond to different choices of gauge. In due course we shall see that the diamagnetic current density depends on the choice of gauge. The total current density, however, is independent of gauge.)

On N:

$$r_N^2 = y_N^2 + z_N^2 = (y + \lambda R)^2 + z^2$$

$$\cos\theta_N = z_N/r_N = z/\{(y + \lambda R)^2 + z^2\}^{1/2}$$

On O:

$$r_O^2 = y_O^2 + z_O^2 = [y - (1 - \lambda)R]^2 + z^2$$

$$\cos\,\theta_O = z_O/r_O = z/\{[y - (1 - \lambda)R]^2 + z^2\}^{1/2}$$

Consequently,

$$\psi_{N2p_z} = (Z_N^{*5}/32\pi a_0^5)^{1/2}\, z\, \exp\{-Z_N^*\,[(y + \lambda R)^2 + z^2]^{1/2}/2a_0\}$$

$$\psi_{O2p_z} = (Z_O^{*5}/32\pi a_0^5)^{1/2}\, z\, \exp\{-Z_O^*\,\{[y - (1 - \lambda)R]^2 + z^2\}^{1/2}/2a_0\}$$

The diamagnetic current density in the *yz*-plane is therefore

$$\boldsymbol{j}^{\mathrm{d}} = -(e^2\mathcal{B}/2m_e)\,\psi_0^2\boldsymbol{C} \quad [\text{eqn 13.54a, } \boldsymbol{C} = -z\hat{\boldsymbol{j}} + y\hat{\boldsymbol{k}}]$$

$$= -(e^2\mathcal{B}/4m_e)\,(\psi_N^2 + \psi_O^2 - 2\psi_N\psi_O)\,(-z\hat{\boldsymbol{j}} + y\hat{\boldsymbol{k}})$$

$$= -j^{\#}\left\{Z_N^{*5}\mathrm{e}^{-2f_N} + Z_O^{*5}\mathrm{e}^{-2f_O} - 2(Z_N^*Z_O^*)^{5/2}\,\mathrm{e}^{-(f_N+f_O)}\right\}z^2(-z\hat{\boldsymbol{j}} + y\hat{\boldsymbol{k}})$$

with

$$j^{\#} = e^2\mathcal{B}/128\pi m_e\, a_0^5$$

$$f_N = (Z_N^*/2a_0)\,\{[y + \lambda R]^2 + z^2\}^{1/2}$$

$$f_O = (Z_O^*/2a_0)\,\{[y - (1 - \lambda)R]^2 + z^2\}^{1/2}$$

Now write

$$\zeta = z/a_0,\ \eta = y/a_0,\ s = R/a_0,\ \gamma = (Z_N^*/Z_O^*)^{5/2},\ j^{\dagger} = (Z_N^*/Z_O^*)^{5/2}\,j^{\#}$$

Then

$$-\boldsymbol{j}^{\mathrm{d}}/j^{\dagger} = \{\gamma\,\mathrm{e}^{-2f_{\mathrm{N}}} + (1/\gamma)\,\mathrm{e}^{-2f_{\mathrm{O}}} - 2\mathrm{e}^{-(f_{\mathrm{O}}+f_{\mathrm{N}})}\}\ \zeta^{2}(-\zeta\hat{\boldsymbol{j}} + \eta\hat{\boldsymbol{k}})\,a_0^3$$

$$f_{\mathrm{N}} = \tfrac{1}{2}Z_{\mathrm{N}}^{*}\,\{(\eta + \lambda s)^2 + \zeta^2\}^{1/2}$$

$$f_{\mathrm{O}} = \tfrac{1}{2}Z_{\mathrm{O}}^{*}\,\{[\eta - (1-\lambda)s]^2 + \zeta^2\}^{1/2}$$

Take $R = 115$ pm (so $s = 2.17$). The current densities should be plotted for (a) $\lambda = 0$, (b) $\lambda = \tfrac{1}{2}$, (c) $\lambda = 1.0$.

Exercise: Use mathematical software to plot the current densities. Calculate and plot the current density for a plane parallel to the one considered above, but offset from it by a distance a_0.

13.7

$$\chi_{\mathrm{m},\parallel} = -(e^2\mu_0 N_{\mathrm{A}}/4m_{\mathrm{e}})\langle x^2 + y^2\rangle \quad \text{[eqns 13.40 and 13.35]}$$

$$\chi_{\mathrm{m},\perp} = -(e^2\mu_0 N_{\mathrm{A}}/4m_{\mathrm{e}})\langle x^2 + z^2\rangle$$

$$x^2 + y^2 = r^2\sin^2\theta\,(\cos^2\phi + \sin^2\phi) = r^2\sin^2\theta$$

$$\psi_{2\mathrm{p}_z} = (Z^{*5}/32\pi a_0^5)^{1/2}\,r\cos\theta\,\mathrm{e}^{-Z^{*}r/2a_0}$$

(a)

$$\langle x^2 + y^2\rangle = (Z^{*5}/32\pi a_0^5)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{\infty} r^2\,\{r^4\sin^2\theta\cos^2\theta\,\mathrm{e}^{-Z^{*}r/a_0}\}\mathrm{d}r$$

$$= (Z^{*5}/32\pi a_0^5)\,(2\pi)(4/15)\{6!/(Z^{*}/a_0)^7\} = 12a_0^2/Z^{*2}$$

(b)

$$\langle x^2 + z^2\rangle = r^2(\sin^2\theta\cos^2\phi + \cos^2\theta)\rangle$$

$$= (Z^{*5}/32\pi a_0^5)\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \sin\theta \,\mathrm{d}\theta \int_0^{\infty} r^2 \,\{r^4(\sin^2\theta\cos^2\theta + \cos^2\theta)$$

$$\times \cos^2\theta \,\mathrm{e}^{-Z^*r/a_0}\}\mathrm{d}r$$

$$= (Z^{*5}/32\pi a_0^5)\,\{(\pi)(4/15) + (2\pi)(2/5)\}\,\{6!/(Z^*/a_0)^7\}$$

$$= 24a_0^2/Z^{*2}$$

(a)

$$\chi_{\parallel,\mathrm{m}} = -(3e^2 a_0^2\, \mu_0 N_\mathrm{A}/m_\mathrm{e})(1/Z^{*2})$$

$$= \underline{-1.791 \times 10^{-10}/Z^{*2}\ \mathrm{m^3\ mol^{-1}}}$$

(b)

$$\chi_{\perp,\mathrm{m}} = -(6e^2 a_0^2\, \mu_0 N_\mathrm{A}/m_\mathrm{e})(1/Z^{*2})$$

$$= \underline{-3.583 \times 10^{-10}/Z^{*2}\ \mathrm{m^3\ mol^{-1}}}$$

$$\chi_\mathrm{m} = \tfrac{1}{3}(\chi_\parallel + 2\chi_\perp) = \tfrac{5}{3}\chi_\parallel \quad [\chi_\perp = 2\chi_\parallel]$$

$$= \underline{-2.985 \times 10^{-10}/Z^{*2}\ \mathrm{m^3\ mol^{-1}}}$$

For the carbon atom, $Z^* = 3.14$ [Table 7.3]; consequently

$$\underline{\chi_{\parallel,\mathrm{m}} = -1.82\times10^{-11}};\quad \underline{\chi_{\perp,\mathrm{m}} = -3.63\times10^{-11}};$$

$$\underline{\chi_\mathrm{m} = -3.03\times10^{-11}\ \mathrm{m^3\ mol^{-1}}}$$

Exercise: Evaluate $\chi_\parallel$ and $\chi_\perp$ for Slater 3d$_{z^2}$ -orbitals.

13.10 The normalized forms of the d-orbitals are

$$\mathrm{d}_{z^2} = (5/16\pi)^{1/2}(3\cos^2\theta - 1)r^2 f(r) = (5/16\pi)^{1/2}(3z^2 - r^2)f(r)$$

$$\mathrm{d}_{xz} = -(15/4\pi)^{1/2}\cos\theta\sin\theta\cos\phi\, r^2 f(r) = -(15/4\pi)^{1/2}\, xzf(r)$$

$$\mathrm{d}_{yz} = -(15/4\pi)^{1/2}\cos\theta\sin\theta\sin\phi\, r^2 f(r) = -(15/4\pi)^{1/2}\, yzf(r)$$

Consequently,

$$l_z\mathrm{d}_{z^2} = 0$$

$$l_y\mathrm{d}_{z^2} = (5/16\pi)^{1/2}(\hbar/\mathrm{i})\{z(\partial/\partial x) - x(\partial/\partial z)\}(3z^2 - r^2)f(r)$$

$$= 6\mathrm{i}\hbar(5/16\pi)^{1/2}\, xzf(r) = -\mathrm{i}\hbar\sqrt{3}\,\mathrm{d}_{xz}$$

$$l_x\mathrm{d}_{z^2} = (5/16\pi)^{1/2}(\hbar/\mathrm{i})\{y(\partial/\partial z) - z(\partial/\partial y)\}(3z^2 - r^2)f(r)$$

$$= -6\mathrm{i}\hbar(5/16\pi)^{1/2} yzf(r) = +\mathrm{i}\hbar\sqrt{3}\,\mathrm{d}_{yz}$$

Therefore,

$$g_{zz} = \underline{g_e}$$

$$g_{yy} = g_\mathrm{e} - 2\lambda\langle \mathrm{d}_{xz}|l_y|\mathrm{d}_{z^2}\rangle^2/\Delta E \text{ [eqn 13.87a]}$$

$$= g_\mathrm{e} - 6\lambda\hbar^2/\Delta E = \underline{g_\mathrm{e} - 6hc\zeta/\Delta E}$$

$$g_{xx} = g_\mathrm{e} - 2\lambda\langle \mathrm{d}_{yz}|l_x|\mathrm{d}_{z^2}\rangle^2/\Delta E = \underline{g_\mathrm{e} - 6hc\zeta/\Delta E}$$

Taking $\zeta = 154\ \mathrm{cm}^{-1}$ and $\Delta E/hc = 10^4\ \mathrm{cm}^{-1}$ gives

$$g_{zz} = g_\mathrm{e} = \underline{2.002}, \quad g_{yy} = g_{xx} = g_\mathrm{e} - 0.092 = \underline{1.910}$$

Exercise: In a similar complex the d_{xy} orbital was the lowest; calculate the g-values.

13.13 $J \approx (2\mu_0 g_e \mu_B/3)^2 \gamma_A \gamma_B |\chi_A(0)|^2 |\chi_B(0)|^2 c_A^2 c_B^2 /\Delta E^{(T)}$ [eqn 13.110]

$$c_A^2 = c_B^2 \approx \tfrac{1}{2}; \quad \chi_A^2(0) = \chi_B^2(0) = 1/\pi a_0^3$$

$$\gamma_A = \gamma(^1\text{H}) = g(^1\text{H})\mu_N/\hbar, \quad g(^1\text{H}) = 5.5857$$

$$\gamma_B = \gamma(^2\text{H}) = g(^2\text{H})\mu_N/\hbar, \quad g(^2\text{H}) = 0.85745$$

$$J \approx (2\mu_0 g_e \mu_B/3)^2\, g(^1\text{H})g(^2\text{H})\,\mu_N^2 (1/\pi a_0^3)^2 (1/2)^2/\Delta E^{(T)}\hbar^2$$

$$\approx (g_e\mu_0\mu_B\mu_N/3\pi a_0^3)^2 g(^1\text{H})g(^2\text{H})/\Delta E^{(T)}\hbar^2$$

$$\approx 7.122 \times 10^{-51}\, g(^1\text{H})g(^2\text{H})/\hbar^2(\Delta E^{(T)}/\text{J})$$

$$\approx 4.445 \times 10^{-32}\, g(^1\text{H})g(^2\text{H})/\hbar^2(\Delta E^{(T)}/\text{eV})$$

$$\hbar^2 J/h = (67.1\ \text{Hz}) \times \frac{g(^1\text{H})g(^2\text{H})}{(\Delta E^{(T)}/\text{eV})} = \frac{321\,\text{Hz}}{\Delta E^{(T)}/\text{eV}}$$

$$\approx \underline{32\ \text{Hz}} \text{ when } \Delta E^{(T)} \approx 10\ \text{eV}$$

Exercise: Find an expression for the spin–spin coupling involving two nuclei, one of atomic number Z_1 and the other of atomic number Z_2. Express c_A and c_B in terms of α_1, α_2, and β in a Hückel type of approximation.

13.16 Write $\psi = a\psi_{2s} + b\psi_{1s}$, and choose a and b so that

$$\int \psi_{1s}\psi\,d\tau = a\int \psi_{1s}\psi_{2s}\,d\tau + b = 0$$

$$\int \psi^2 d\tau = \int (a\psi_{2s} + b\psi_{1s})^2 d\tau = a^2 + b^2 + 2ab\int \psi_{2s}\psi_{1s}\,d\tau = 1$$

Write $S = \int \psi_{1s}\psi_{2s}\,d\tau$, then

$$b = -aS \text{ and } a = \frac{1}{(1-S^2)^{1/2}}$$

Consequently, the orthogonalized 2s-orbital is

$$\psi = \frac{\psi_{2s} - S\psi_{1s}}{(1-S^2)^{1/2}}, \quad S = \int \psi_{1s}\psi_{2s}\,d\tau$$

Then, since $\psi_{2s}(0) = 0$,

$$\psi^2(0) = S^2\psi_{1s}^2(0)/(1-S^2)$$

$$\psi_{1s} = (Z_{1s}^{*3}/\pi a_0^3)^{1/2}\,e^{-Z_{1s}^{*}r/a_0} \qquad \text{[Exercise 13.12]}$$

$$\psi_{1s}^2(0) = Z_{1s}^{*3}/\pi a_0^3$$

$$\psi_{2s} = (Z_{2s}^{*5}/96\pi a_0^5)^{1/2}\,r e^{-Z_{2s}^{*}r/2a_0}$$

$$S = 4\pi(Z_{1s}^{*3}Z_{2s}^{*5}/96\pi^2 a_0^8)^{1/2}\int_0^\infty r^2\{re^{-Z_{2s}^{*}r/2a_0}\}\{e^{-Z_{1s}^{*}r/a_0}\}dr$$

$$= 4\pi\left(\frac{Z_{1s}^{*3}Z_{2s}^{*5}}{96\pi^2 a_0^8}\right)^{1/2}\left\{\frac{3!a_0^4}{(Z_{1s}^{*}+\frac{1}{2}Z_{2s}^{*})^4}\right\}$$

$$= \frac{(6Z_{1s}^{*3}Z_{2s}^{*5})^{1/2}}{(Z_{1s}^{*}+\frac{1}{2}Z_{2s}^{*})^4}$$

Consequently,

$$\psi^2(0) = \frac{(6/\pi a_0^3)Z_{1s}^{*6}Z_{2s}^{*5}\,/\,(Z_{1s}^{*}+\frac{1}{2}Z_{2s}^{*})^8}{1-6Z_{1s}^{*3}Z_{2s}^{*5}\,/\,(Z_{1s}^{*}+\frac{1}{2}Z_{2s}^{*})^8}$$

$$= \frac{(6/\pi a_0^3) Z_{1s}^{*6} Z_{2s}^{*5}}{\underline{(Z_{1s}^* + \frac{1}{2} Z_{2s}^*)^8 - 6 Z_{1s}^{*3} Z_{2s}^{*5}}}$$

In the case of ^{14}N, $Z_{1s}^* = 6.67$, $Z_{2s}^* = 3.85$ [Table 7.3], and $\psi^2(0) = 15.8/\pi a_0^3$. Therefore, with

$$H^{(\text{spin})} = CI_z s_z \quad C = (2g_e g_N \mu_B \mu_N \mu_0 / 3\hbar^2)\psi^2(0) \quad [\text{eqn } 13.97\text{b}]$$

$$\hbar^2 C = 10.5(g_e g_N \mu_B \mu_N \mu_0 / \pi a_0^3)$$

Since $g_N(^{14}\text{N}) = 0.40356$

$$\hbar^2 C = 1.1 \times 10^{-24} \text{ J}; \quad \underline{\hbar^2 C/h = 1.7 \text{ GHz}}$$

(The experimental value is 1.5 GHz.)

Exercise: Find an expression for the contact interaction involving an electron in an orthogonalized Slater 3s-orbital (i.e. one orthogonalized to both ψ_{1s} and the orthogonalized ψ_{2s}).

Chapter 14

Scattering Theory

Exercises

14.1 **(a)** The process is *inelastic* because the electronic state of atomic oxygen changes.

(b) The process is *elastic* because the initial and final states are the same.

(c) The process is *inelastic* because the vibrational state of HF changes.

(d) The process is *reactive* because a chemical reaction has occurred; the reactant HF is not retained in the product.

(e) The process is *elastic* because the initial and final states are the same.

Exercise: Characterize each of the following as elastic, inelastic or reactive:

$$\mathrm{O}(^3\mathrm{P}_2) + \mathrm{H}_2(v=0, j=0) \rightarrow \mathrm{O}(^3\mathrm{P}_1) + \mathrm{H}_2(v=0, j=0)$$

$$\mathrm{O}(^3\mathrm{P}_2) + \mathrm{H}_2(v=0, j=0) \rightarrow \mathrm{O}(^3\mathrm{P}_2) + 2\mathrm{H}(^2\mathrm{S})$$

14.2 For scattering by a one-dimensional potential energy barrier of finite width (Section 14.1), the continuity conditions for the wavefunction and its slope at $x = L$ are given by the last two equations in eqn 14.1.

$$A'\mathrm{e}^{\mathrm{i}k'L} + B'\mathrm{e}^{-\mathrm{i}k'L} = A''\mathrm{e}^{\mathrm{i}kL} + B''\mathrm{e}^{-\mathrm{i}kL} \text{ (i)}$$

$$\mathrm{i}k'A'\mathrm{e}^{\mathrm{i}k'L} - \mathrm{i}k'B'\mathrm{e}^{-\mathrm{i}k'L} = \mathrm{i}kA''\mathrm{e}^{\mathrm{i}kL} - \mathrm{i}kB''\mathrm{e}^{-\mathrm{i}kL} \text{ (ii)}$$

Multiplying (i) by ik and adding (ii) yields:

$$2\mathrm{i}kA''\,\mathrm{e}^{\mathrm{i}kL} = \mathrm{i}kA'\mathrm{e}^{\mathrm{i}k'L} + \mathrm{i}k'A'\mathrm{e}^{\mathrm{i}k'L} + \mathrm{i}kB'\mathrm{e}^{-\mathrm{i}k'L} - \mathrm{i}k'B'\mathrm{e}^{-\mathrm{i}k'L}$$

or

$$A'' = \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}(k+k')A' + \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}(k-k')B'\mathrm{e}^{-2\mathrm{i}k'L} \text{(iii)}$$

Similarly, multiplying (i) by i*k* and subtracting (ii) yields:

$$2\mathrm{i}kB''\,\mathrm{e}^{-\mathrm{i}kL} = \mathrm{i}kA'\mathrm{e}^{\mathrm{i}k'L} - \mathrm{i}k'A'\mathrm{e}^{\mathrm{i}k'L} + \mathrm{i}kB'\mathrm{e}^{-\mathrm{i}k'L} + \mathrm{i}k'B'\mathrm{e}^{-\mathrm{i}k'L}$$

or

$$B'' = \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}(k-k')A'\mathrm{e}^{2\mathrm{i}kL} + \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}(k+k')B'\mathrm{e}^{2\mathrm{i}kL}\mathrm{e}^{-2\mathrm{i}k'L} \text{(iv)}$$

Equations (iii) and (iv) can be written in matrix form as

$$\begin{pmatrix} A'' \\ B'' \end{pmatrix} = \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}\begin{pmatrix} k+k' & (k-k')\mathrm{e}^{-2\mathrm{i}k'L} \\ (k-k')\mathrm{e}^{2\mathrm{i}kL} & (k+k')\mathrm{e}^{2\mathrm{i}kL}\mathrm{e}^{-2\mathrm{i}k'L} \end{pmatrix}\begin{pmatrix} A' \\ B' \end{pmatrix}$$

from which we confirm the form of the matrix ***Q*** given in *Justification* 14.1.

14.3 From eqns 14.2 and 14.3a:

$$\begin{pmatrix} B \\ A'' \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} A \\ B'' \end{pmatrix}$$

If the particle is incident from the right of the one-dimensional barrier, then $A = 0$ (see Fig. 14.1 of the text). As a result:

$B = S_{12}\,B''$ $\qquad T = |S_{12}|^2$

$A'' = S_{22} B''$ $R = |S_{22}|^2$

14.4 Use eqn 14.15

$$\sigma = |f_k(\theta, \phi)|^2 = \sin^2\theta \cos^2\phi$$

Exercise: Proceed to evaluate the integral scattering cross-section σ_{tot}.

14.5 Use eqn 14.7:

$$\sigma_{\text{tot}} = \int_0^{\pi}\int_0^{2\pi} C \sin\theta \mathrm{d}\theta \mathrm{d}\phi$$

$$= C\left[\int_0^{\pi} \sin\theta \mathrm{d}\theta\right] \times \left[\int_0^{2\pi} d\phi\right]$$

$$= 4\pi C$$

Exercise: What scattering amplitude f_k corresponds to the above σ_{tot}? Within the Born approximation, find the potential that gives rise to this scattering amplitude.

14.6 We show in *Justification* 14.2 that in the limit $r \to \infty$, $\mathrm{e}^{\mathrm{i}kz}$ and $f_k\mathrm{e}^{\mathrm{i}kr}/r$ are each eigenfunctions of the hamiltonian with the same eigenvalue $k^2\hbar^2/2\mu$. Therefore, the total wavefunction has an asymptotic form given by the sum of $\mathrm{e}^{\mathrm{i}kz}$ and $f_k\mathrm{e}^{\mathrm{i}kr}/r$ with eigenvalue $k^2\hbar^2/2\mu$:

$$H(\mathrm{e}^{\mathrm{i}kz} + f_k\mathrm{e}^{\mathrm{i}kr}/r) = H\,\mathrm{e}^{\mathrm{i}kz} + H f_k\mathrm{e}^{\mathrm{i}kr}/r$$

$$= (k^2\hbar^2/2\mu)\,\mathrm{e}^{\mathrm{i}kz} + (k^2\hbar^2/2\mu) f_k\mathrm{e}^{\mathrm{i}kr}/r$$

$$= (k^2\hbar^2/2\mu)(\mathrm{e}^{\mathrm{i}kz} + f_k\mathrm{e}^{\mathrm{i}kr}/r)$$

14.7 The free-particle radial wave equation, eqn 14.23, is

$$\frac{\mathrm{d}^2 u_l^0}{\mathrm{d}r^2} + \left\{k^2 - \frac{l(l+1)}{r^2}\right\} u_l^0 = 0$$

(i) $u_l^0 = \hat{j}_0(kr) \;= = \sin(kr)$; $l = 0$ implies $l(l+1)/r^2 = 0$

$$\frac{\mathrm{d}^2 u_l^0}{\mathrm{d}r^2} = \frac{\mathrm{d}^2 \sin(kr)}{\mathrm{d}r^2} = -k^2 \sin(kr)$$

Therefore

$$-k^2 \sin(kr) + \{k^2 - 0\} \sin(kr) = 0$$

(ii)

$$u_l^0 = \hat{j}_1(kr) = \frac{\sin(kr)}{kr} - \cos(kr)$$

$$\frac{\mathrm{d}\hat{j}_1(kr)}{\mathrm{d}r} = \frac{\cos(kr)}{r} - \frac{\sin(kr)}{kr^2} + k \sin(kr)$$

$$\frac{\mathrm{d}^2 \hat{j}_1(kr)}{\mathrm{d}r^2} = \frac{-k \sin(kr)}{r} - \frac{2 \cos(kr)}{r^2} + \frac{2 \sin(kr)}{kr^3} + k^2 \cos(kr)$$

Therefore

$$-\frac{k \sin(kr)}{r} - \frac{2 \cos(kr)}{r^2} + \frac{2 \sin(kr)}{kr^3} + k^2 \cos(kr)$$

$$+ \left\{k^2 - \frac{2}{r^2}\right\}\left\{\frac{\sin(kr)}{kr} - \cos(kr)\right\} = 0$$

Exercise: Repeat the confirmation for the first three ($l = 0, 1, 2$) Riccati–Neumann functions.

14.8 The general relation between E and K is given in the equation proceeding eqn 14.51:

$\hbar^2 K^2 = 2\mu(E + V_0)$

Therefore

$$E = \frac{\hbar^2 K^2}{2\mu} - V_0$$

$$E_{\text{res}} = \frac{\hbar^2 K_{\text{res}}^2}{2\mu} - V_0$$

and, using eqn 14.62,

$$E_{\text{res}} = \frac{(2n+1)^2 \pi^2 \hbar^2}{8\mu a^2} - V_0$$

14.9 The relation between the mean lifetime τ of the resonance state and the full width at half-maximum Γ is given by eqn 14.75. If the full width at half-maximum expressed in cm^{-1} units is denoted Δ, then $\Gamma = hc\Delta$; therefore

$$\tau = \frac{\hbar}{hc\Delta} = (2\pi c\Delta)^{-1}$$

(a)

$$\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 0.05\ \text{cm}^{-1})^{-1}$$

$$= 1.1 \times 10^{-10}\ \text{s} = \underline{0.11\ \text{ns}}$$

(b)

$$\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 3.5\ \text{cm}^{-1})^{-1}$$

$$= 1.5 \times 10^{-12}\ \text{s} = \underline{1.5\ \text{ps}}$$

(c)

$$\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 45\ \text{cm}^{-1})^{-1}$$

$$= 1.2 \times 10^{-13}\ \text{s} = \underline{0.12\ \text{ps}}$$

Exercise: If the mean lifetime of the resonance state is 10 fs, what would be the expected full width at half-maximum for the Breit–Wigner peak?

14.10 At scattering energy E_1, the total number of open channels is 11 + 6 + 16 = 33. Therefore, the scattering matrix is a 33 × 33 square matrix. The dimension is 33.

Exercise: Explore how the dimension of the scattering matrix varies with the scattering energy. Take $J = 0$. Assume that only rotational levels in the ground vibrational states of BC, AB, and AC are open. Treat the rotational constants of the three diatomic molecules as equivalent.

14.11 We need to evaluate the integral on the right-hand side of eqn 14.102 assuming that the cumulative reaction probability $P(E)$ is independent of energy:

$$\begin{aligned}\int_0^\infty P(E)\mathrm{e}^{-E/kT}\mathrm{d}E &= P\int_0^\infty \mathrm{e}^{-E/kT}\mathrm{d}E\\ &= -PkT\mathrm{e}^{-E/kT}\Big|_0^\infty\\ &= -PkT(0-1)\\ &= PkT\end{aligned}$$

Therefore the rate constant is directly proportional to the temperature.

14.12 The classical model of chemical reactivity yields a cumultive reaction probability of

$P(E) = 0 \quad 0 \le E < V_0$

$P(E) = 1 \quad V_0 \le E < \infty$

Therefore

$$k_\mathrm{r}(T) \propto \int_0^\infty P(E)\mathrm{e}^{-E/kT}\mathrm{d}E = \int_{V_0}^\infty \mathrm{e}^{-E/kT}\mathrm{d}E$$

$$= -kT\mathrm{e}^{-E/kT}\Big|_{V_0}^{\infty}$$

$$= kT\mathrm{e}^{-V_0/kT}$$

This has a form similar to the Arrhenius equation if we allow the pre-exponential factor A to be directly proportional to temperature and identify the activation energy E_a with $E_a/RT = V_0/kT$ or, since $R = kN_A$, $E_a = N_A V_0$.

14.13 According to eqn 14.103 and the discussion in Section 14.10, a pole in the scattering matrix (i.e. a resonance) will appear in each scattering matrix element. Therefore scattering cross-sections connecting all possible incoming and outgoing channels should have peaks at the same energy E_{res} with the same width Γ. In this case, the resonance which appears in the neutron–Te scattering process effects both the elastic scattering and non-elastic scattering processes and therefore the cross-sections show Breit–Wigner peaks at the same energy and of the same width.

Exercise: It is found experimentally that the scattering cross-sections have peaks at an energy of 2.3 eV with a width of 0.11 eV. Determine the resonance energy of the resonance state in the neutron–Te scattering process.

14.14 The scattering matrix $\boldsymbol{S}$ is often symmetric, $S_{ij} = S_{ji}$. (It is always symmetric when the scattering process has a property known as time-reversal invariance). The probability in general for a transition from incident channel i to final channel j is given by

$$P_{ji} = |S_{ji}|^2$$

Thus, for a two-channel scattering process with a symmetric scattering matrix,

$$\begin{aligned} P_{12} &= |S_{12}|^2 \\ &= |S_{21}|^2 \\ &= P_{21} \end{aligned}$$

consistent with the principle of microscopic reversibility.

Exercise: Give examples of scattering systems for which the principle of microscopic reversibility is not satisfied.

Problems

14.1 For Zone II (see Section 14.1), the potential energy is $V(x) = -V$ (rather than $+V$) and all solutions are oscillatory for positive energies:

$$\text{Zone II: } \psi = A'\mathrm{e}^{iKx} + B'\mathrm{e}^{-iKx} \quad K\hbar = \{2m(E+V)\}^{1/2}$$

Hence S can be constructed from eqn 14.3 by replacing k' in eqn 14.3c with K. The transmission probability for a particle incident from the left is given by $|S_{21}|^2$.

14.4. From Example 14.3

$$\begin{aligned} \sigma &= \frac{4\mu^2 V_0^2/\hbar^4}{(\alpha^2 + 4k^2\sin^2\tfrac{1}{2}\theta)^2} \\ &= \frac{4\mu^2 V_0^2}{\hbar^4\alpha^4(1+(4k^2/\alpha^2)\sin^2\tfrac{1}{2}\theta)^2} \end{aligned}$$

$$\frac{\sigma}{(2\mu V_0/\hbar^2\alpha^2)^2} = \frac{1}{(1+(4k^2/\alpha^2)\sin^2\tfrac{1}{2}\theta)^2}$$

(a) For zero energy, $k = 0$

$$\frac{\sigma}{(2\mu V_0/\hbar^2\alpha^2)^2} = 1$$

independent of θ.

(b) For moderate energy ($k = \alpha/2$)

$$k^2/\alpha^2 = \tfrac{1}{4}$$

$$\frac{\sigma}{(2\mu V_0/\hbar^2\alpha^2)^2} = \frac{1}{(1+\sin^2\tfrac{1}{2}\theta)^2}$$

(c) For high energy ($k = 10\alpha$)

$$k^2/\alpha^2 = 100$$

$$\frac{\sigma}{(2\mu V_0/\hbar^2\alpha^2)^2} = \frac{1}{(1+400\sin^2\tfrac{1}{2}\theta)^2}$$

Plots of the differential cross-section as a function of θ are shown in Fig. 14.1 for **(a)**, **(b)** and **(c)**. For $k \gg \alpha$, σ falls off very rapidly as θ increases from 0 to $\pi/2$.

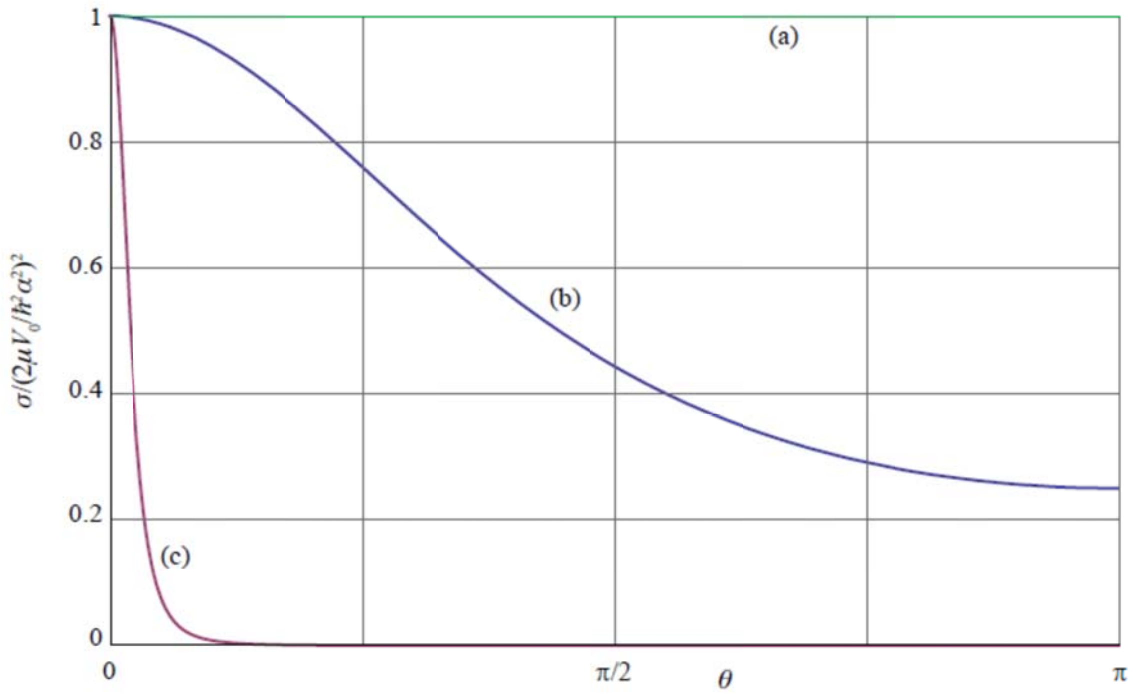


Figure 14.1 The differential cross-section for the Yukawa potential within the Born approximation for (a) zero energy ($k = 0$), (b) moderate energy ($k = \alpha/2$), and (c) high energy ($k = 10\alpha$).

Exercise: Compare the plots to those for $k = \alpha$ and $k = 20\alpha$.

14.7 To derive eqns 14.41 and 14.42, we begin with the equation following eqn 14.40

$$\frac{C_l}{r}\sin(kr - \tfrac{1}{2}l\pi + \delta_l) = i^l(2l+1)\frac{\sin(kr - \tfrac{1}{2}l\pi)}{kr} + f_l\frac{\mathrm{e}^{ikr}}{r}$$

Since

$$\sin x = \frac{\mathrm{e}^{\mathrm{i}x} - \mathrm{e}^{-\mathrm{i}x}}{2\mathrm{i}}$$

$$\frac{C_l}{r}\frac{\mathrm{e}^{\mathrm{i}(kr-\frac{1}{2}l\pi+\delta_l)}-\mathrm{e}^{-\mathrm{i}(kr-\frac{1}{2}l\pi+\delta_l)}}{2\mathrm{i}} = \frac{\mathrm{i}^l(2l+1)[\mathrm{e}^{\mathrm{i}(kr-\frac{1}{2}l\pi)}-\mathrm{e}^{\mathrm{i}(kr-\frac{1}{2}l\pi)}]}{2\mathrm{i}kr}+\frac{f_l\mathrm{e}^{\mathrm{i}kr}}{r}$$

Collect terms with a common factor of $\mathrm{e}^{-\mathrm{i}kr}$

$$\mathrm{e}^{-\mathrm{i}kr}\left\{-\frac{C_l}{r}\frac{\mathrm{e}^{\frac{1}{2}\mathrm{i}l\pi}\mathrm{e}^{-\mathrm{i}\delta_l}}{2\mathrm{i}}\right\} = \mathrm{e}^{-\mathrm{i}kr}\left\{-\frac{i^l(2l+1)}{2\mathrm{i}kr}\mathrm{e}^{\frac{1}{2}\mathrm{i}l\pi}\right\}$$

Cancel common terms:

$$C_l\mathrm{e}^{-\mathrm{i}\delta_l} = \frac{\mathrm{i}^l(2l+1)}{k}$$

or

$$C_l = \frac{\mathrm{i}^l(2l+1)}{k}\mathrm{e}^{\mathrm{i}\delta_l} \qquad \text{[eqn 14.41]}$$

Now collect terms with a common factor of $\mathrm{e}^{-\mathrm{i}kr}$

$$\mathrm{e}^{\mathrm{i}kr}\left\{\frac{C_l}{r}\frac{\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}\mathrm{e}^{\mathrm{i}\delta_l}}{2\mathrm{i}}\right\} = \mathrm{e}^{\mathrm{i}kr}\left\{\frac{\mathrm{i}^l(2l+1)\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}}{2\mathrm{i}kr}+\frac{f_l}{r}\right\}$$

Cancel common terms:

$$C_l\frac{\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}\mathrm{e}^{\mathrm{i}\delta_l}}{2\mathrm{i}} = \frac{\mathrm{i}^l(2l+1)\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}}{2\mathrm{i}k}+f_l$$

Use eqn 14.41:

$$\frac{\mathrm{i}^l(2l+1)\mathrm{e}^{\mathrm{i}\delta_l}}{k}\frac{\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}\mathrm{e}^{\mathrm{i}\delta_l}}{2\mathrm{i}}=\frac{\mathrm{i}^l(2l+1)\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}}{2\mathrm{i}k}+f_l$$

Because $\mathrm{e}^{\mathrm{i}\pi/2} = \mathrm{i}$, $\mathrm{e}^{\mathrm{i}\pi l/2} = \mathrm{i}^l$.

Therefore

$$\frac{(2l+1)\mathrm{e}^{2\mathrm{i}\delta_l}}{2\mathrm{i}k}=\frac{(2l+1)}{2\mathrm{i}k}+f_l$$

$$f_l=\frac{(2l+1)}{2\mathrm{i}k}(\mathrm{e}^{2\mathrm{i}\delta_l}-1)$$

$$=\frac{(2l+1)}{k}\mathrm{e}^{\mathrm{i}\delta_l}\frac{(\mathrm{e}^{\mathrm{i}\delta_l}-\mathrm{e}^{-\mathrm{i}\delta_l})}{2\mathrm{i}}$$

$$=\frac{(2l+1)}{k}\mathrm{e}^{\mathrm{i}\delta_l}\sin\delta_l \quad \text{[eqn 14.42]}$$

Exercise: Derive eqn 14.49.

14.10

If $V(r) > 0$ for all r, then $\delta_l(E) < 0$.

If $V(r) < 0$ for all r, then $\delta_l(E) > 0$.

Note that if $V(r) = 0$, $\delta_l(E) = 0$ by definition.

If the potential is purely repulsive for all r, then, since the energy E of the particle is conserved in elastic scattering, the particle's kinetic energy is decreased as a result of scattering. The wavelength of the particle is therefore increased (recall $\lambda = h/p$), corresponding to a negative phase shift δ_l. (Recall that $\sin(kr + \delta)$ has a longer wavelength than $\sin kr$ if $\delta < 0$.)

Conversely, if the potential is purely attractive for all r, the particle is accelerated as it scatters. The increase in kinetic energy corresponds to a shortened wavelength and a positive phase shift δ_l.

Exercise: Sketch the form of the scattering wavefunctions for $V(r) > 0$, $V(r) = 0$, and $V(r) < 0$; qualitatively verify the above conclusions.

14.13

$$V(r) = \begin{cases} \infty & \text{if } r = 0 \\ V_0 & \text{if } 0 < r < a \\ 0 & \text{if } r \geq a \end{cases}$$

Consider energies $E > V_0$ and find δ_0.

At $r = 0$, $V(r) = \infty$ which implies $u_0(0) = 0$ for the radial wavefunction.

For $0 < r < a$, $V(r) = V_0$ $\quad (V_0 > 0)$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u_0}{\mathrm{d}r^2} + V_0u_0 = Eu_0 \quad \text{(centrifugal potential = 0)}$$

$$\frac{\mathrm{d}^2u_0}{\mathrm{d}r^2} + \frac{2m}{\hbar^2}(E - V_0)u_0 = 0$$

$$u_0(r) = A \sin k_1r + B \cos k_1r$$

$$k_1^2 = \frac{2m}{\hbar^2}(E - V_0)$$

For $r \geq a$, $V(r) = 0$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u_0}{\mathrm{d}r^2} = Eu_0$$

$$u_0(r) = C\sin kr + D\cos kr$$

$$k^2 = \frac{2mE}{\hbar^2}$$

As $r \to \infty$

$$u_0(r) = C\sin kr + D\cos kr$$

$$= E\sin(kr + \delta_0)$$

where

$$\tan\delta_0 = D/C$$

To find δ_0, we need to obtain an expression for D/C. We require that $u_0(r)$ and $(\mathrm{d}u_0/\mathrm{d}r)$ are continuous at $r = a$.

First, require $u_0(r)$ be continuous at $r = 0$. (We do not impose continuity of $(\mathrm{d}u_0/\mathrm{d}r)$ at $r = 0$ because $V(0) = \infty$.)

$$r = 0: \quad u_0(r = 0) = 0 = A\sin k_1 0 + B\cos k_1 0 = B$$

Therefore for $0 < r < a$, $u_0(r) = A\sin k_1 r$

$$r = a: \quad u_0(r = a) = A\sin k_1 a = C\sin ka + D\cos ka$$

$$\frac{\mathrm{d}u_0}{\mathrm{d}r}(r = a) = k_1 A\cos k_1 a = kC\cos ka - kD\sin ka$$

Divide the above two equations:

$$\frac{1}{k_1}\tan k_1a = \frac{C\sin ka + D\cos ka}{kC\cos ka - kD\sin ka}$$

$$= \frac{\sin ka + (D/C)\cos ka}{k\cos ka - k(D/C)\sin ka}$$

$$= \frac{\sin ka + \tan\delta_0\cos ka}{k\cos ka - k\tan\delta_0\sin ka}$$

$$\frac{k}{k_1}\tan k_1a\cos ka - \frac{k}{k_1}\tan k_1a\tan\delta_0\sin ka = \sin ka + \tan\delta_0\cos ka$$

$$\frac{k}{k_1}\tan k_1a\cos ka - \sin ka = \tan\delta_0\left\{\cos ka + \frac{k}{k_1}\tan k_1a\sin ka\right\}$$

$$\tan\delta_0 = \frac{(k/k_1)\tan k_1a\cos ka - \sin ka}{(k/k_1)\tan k_1a\sin ka + \cos ka}$$

with

$$\frac{k}{k_1} = \left(\frac{E}{E - V_0}\right)^{1/2}$$

Exercise: First, plot δ_0 as a function of E ($E > V_0$) for fixed V_0 and a. Second, for $E > V_0$, find an expression for the P-wave phase shift δ_1 for scattering off the same central potential and plot δ_1 as a function of energy.

14.16 The spherical square well potential is given in Section 14.5: $V = -V_0$ for $r \le a$ and $V = 0$ for $r > a$. We solve this problem by requiring that the radial solution $u_l(r)$ and its first derivative be continuous at $r = a$.

In the region $r \le a$, we have to solve the equation

$$\frac{\mathrm{d}^2 u_l}{\mathrm{d}r^2} + \left[K^2 - \frac{l(l+1)}{r^2}\right] u_l = 0$$

where

$$\hbar^2 K^2 = 2\mu(E + V_0)$$

The general solution is a linear combination of the Riccati–Bessel and Riccati–Neumann functions:

$$u_l(r) = A_l \hat{j}_l(Kr) + A_l' \hat{n}_l(Kr)$$

To ensure that $R(r) = u_l/r$ is finite at the origin, we require $u_l(0) = 0$. Since the Riccati–Neumann function $\hat{n}_l(z)$ behaves like z^{-l} as $z \to 0$, we must have $A_l' = 0$. Therefore, inside the well the solution is of the form

$$u_l(r) = A_l \hat{j}_l(Kr)$$

For $r > a$, the potential vanishes and u_l is the solution of the free-particle equation (which includes the $l(l+1)/r^2$ centrifugal potential term). We can immediately write down the solution as

$$u_l(r) = C_l \hat{j}_l(kr) + D_l \hat{n}_l(kr)$$

where, as usual, $E = k^2\hbar^2/2\mu$. The scattering phase shift δ_l is introduced via

$$C_l = B_l \cos \delta_l \quad D_l = B_l \sin \delta_l$$

so we can write

$$u_l(r) = B_l \cos \delta_l \hat{j}_l(kr) + B_l \sin \delta_l \hat{n}_l(kr)$$

We require that $u_l(r)$ and its first derivative be continuous at $r = a$. The continuity of the wavefunction requires that

$$A_l \hat{j}_l(Ka) = B_l \cos \delta_l \hat{j}_l(ka) + B_l \sin \delta_l \hat{n}_l(ka)$$

and the continuity of the first derivative requires that

$$KA_l \hat{j}_l'(Ka) = kB_l \cos \delta_l \hat{j}_l'(ka) + kB_l \sin \delta_l \hat{n}_l'(ka)$$

where the prime denotes the derivative with respect to r. Division of the above two equations results in the following complicated expression for the phase shift:

$$K\frac{\hat{j}_l'(Ka)}{\hat{j}_l(Ka)} = k\frac{\hat{j}_l'(ka) + \tan \delta_l \, \hat{n}_l'(ka)}{\hat{j}_l(ka) + \tan \delta_l \, \hat{n}_l(ka)}$$

or

$$\tan \delta_l = \frac{K\hat{j}_l'(Ka)\hat{j}_l(ka) - k\hat{j}_l(Ka)\hat{j}_l(ka)}{k\hat{j}_l(Ka)\hat{n}_l'(ka) - K\hat{j}_l'(Ka)\hat{n}_l(ka)}$$

From the above equation, for a given energy (and corresponding K and k), we can determine the phase shift δ_l.

Exercise: Write down the expression for δ_l for P-wave scattering by a spherical square-well potential.

14.19 Begin with the asymptotic expression (eqn 14.92) for the multichannel stationary scattering state

$$\Psi_{\alpha 0} \simeq \mathrm{e}^{\mathrm{i}k_{\alpha_0}z}\chi_{\alpha_0} + \sum_{\alpha} f_{\alpha\alpha_0}\frac{\mathrm{e}^{\mathrm{i}k_\alpha r_\mathrm{A}}}{r_\mathrm{A}}\chi_\alpha$$

The incident flux J_i is determined by the plane wave $\mathrm{e}^{ik\alpha_0 z}$ which is the term containing all the (relative) initial kinetic energy. By analogy with the results in *Justification* 14.3, the magnitude of the incident flux is $k_{\alpha_0}\hbar/\mu$.

Likewise, by analogy with the result for J_r in *Justification* 14.3,

$$J_r = \frac{k\hbar\,|f_k|^2}{\mu r^2}$$

for the radial component of the flux density corresponding to $(f_k\mathrm{e}^{ikr}/r)$, we have here

$$J_r = \frac{k_\alpha\hbar\,|f_{\alpha\alpha_0}|^2}{\mu r^2}$$

where we have equated r_A with r, the relative position.

Only J_r needs to be retained as $r \to \infty$ and we have focused on a single term α in the summation for ψ_{α_0}.

Following the argument in Section 14.3, we then have

$$dN_s = J_r r^2 \mathrm{d}\Omega$$

$$= \frac{k_\alpha \hbar |f_{\alpha\alpha_0}|^2}{\mu} \mathrm{d}\Omega$$

$$= \sigma_{\alpha\alpha_0} J_i \mathrm{d}\Omega$$

$$= \sigma_{\alpha\alpha_0} \frac{k_{\alpha_0}\hbar}{\mu} \mathrm{d}\Omega$$

and therefore

$$\sigma_{\alpha\alpha_0} = \frac{k_\alpha}{k_{\alpha_0}} |f_{\alpha\alpha_0}|^2$$

Exercise: Show in detail why χ_α and χ_{α_0} do not need to be considered in the above argument and also why we can treat each term α in the summation of eqn 14.92 individually.

14.22 (i) Model the cumulative reaction probability as $P(E) = \alpha \arctan(\beta E)$.

(a) In the limit $E \to 0$, $P = \alpha \arctan(0) = 0$, consistent with the model.

(b) At $E = V_0$, $P = \alpha \arctan(\beta V_0) = ½$.

(c) In the limit $E \to \infty$, $P = \alpha \arctan(\infty) = \alpha\pi/2 = 1$.

From condition (c), $\underline{\alpha = 2/\pi}$. Therefore, from condition (b),

$(2/\pi) \arctan(\beta V_0) = ½$

$\arctan(\beta V_0) = \pi/4$

$\beta V_0 = 1$ [since $\tan \pi/4 = 1$]

$\underline{\beta = 1/V_0}$

(ii) Model the cumulative reaction probability as $P(E) = 1 - \mathrm{e}^{-\alpha E}$.

(a) In the limit $E \rightarrow 0$, $P = 1 - 1 = 0$, consistent with the model.

(b) At $E = V_0$, $P = 1 - \mathrm{e}^{-\alpha V_0} = ½$

(c) In the limit $E \rightarrow \infty$, $P = 1 - 0 = 1$, consistent with the model.

From condition (b), $\mathrm{e}^{-\alpha V_0} = ½$ or $\underline{\alpha = (\ln 2)/V_0}$.

For part (ii), the temperature dependence of the rate constant predicted by eqn 14.102 is

$$k_\mathrm{r}(T) \propto \int_0^\infty P(E)\mathrm{e}^{-E/kT}\mathrm{d}E = \int_0^\infty (1 - \mathrm{e}^{-\alpha E})\mathrm{e}^{-E/kT}\mathrm{d}E$$

$$= \int_0^\infty \mathrm{e}^{-E/kT}\mathrm{d}E - \int_0^\infty \mathrm{e}^{-E(\alpha+1/kT)}\,\mathrm{d}E$$

$$= -kT\mathrm{e}^{-E/kT}\Big|_0^\infty + \frac{1}{\alpha + 1/kT}\mathrm{e}^{-E(\alpha+1/kT)}\Big|_0^\infty$$

$$= kT - \frac{1}{\alpha + 1/kT}$$

$$= kT - \frac{1}{(\ln 2/V_0) + (1/kT)}$$

$$= kT\left\{1 - \frac{1}{kT(\ln 2/V_0) + 1}\right\}$$

$$= kT\left\{1 - \frac{V_0}{kT\ln 2 + V_0}\right\}$$