9 Quantum theory: techniques and applications

Answers to discussion questions

D9.2 The correspondence principle states that in the limit of very large quantum numbers quantum mechanics merges with classical mechanics. An example is a molecule of a gas in a box. At room temperature, the particle-in-a-box quantum numbers corresponding to the average energy of the gas molecules ($\frac{1}{2}kT$ per degree of freedom) are extremely large; consequently the separation between the levels is relatively so small (n is always small compared to n^2, compare eqn 9.7 to eqn 9.4a) that the energy of the particle is effectively continuous, just as in classical mechanics. We may also look at these equations from the point of view of the mass of the particle. As the mass of the particle increases to macroscopic values, the separation between the energy levels approaches zero. The quantization disappears as we know it must. Tennis balls do not show quantum mechanical effects. (Except those served by Pete Sampras.) We can also see the correspondence principle operating when we examine the wavefunctions for large values of the quantum numbers. The probability density becomes uniform over the path of motion, which is again the classical result. This aspect is discussed in more detail in Section 9.1(c).

The harmonic oscillator provides another example of the correspondence principle. The same effects mentioned above are observed. We see from Figure 9.26 of the text that probability distributions for large values on n approach the classical picture of the motion. (Look at the graph for $v = 20$.)

D9.4 The physical origin of tunnelling is related to the probability density of the particle, which according to the Born interpretation is the square of the wavefunction that represents the particle. This interpretation requires that the wavefunction of the system be everywhere continuous, even at barriers. Therefore, if the wavefunction is non-zero on one side of a barrier it must be non-zero on the other side of the barrier and this implies that the particle has tunnelled through the barrier. The transmission probability depends upon the mass of the particle (specifically $m^{1/2}$, through eqns 9.16 and 9.20): the greater the mass the smaller the probability of tunnelling. Electrons and protons have small masses, molecular groups large masses; therefore, tunnelling effects are more observable in process involving electrons and protons.

D9.6 Macroscopic synthesis and material development always contains elements of molecular randomness. Crystal structures are never perfect. A product of organic synthesis is never absolutely free of impurities, although impurities may be at a level that is lower than measurement techniques make possible. Alloys are grainy and slightly non-homogeneous within any particular grain. Furthermore, the random distribution of atomic/molecular positions and orientations within, and between, macroscopic objects causes the conversion of energy to non-useful heat during manufacturing processes. Production efficiencies are difficult to improve. Nanometer technology on the 1 nm to 100 nm scale may resolve many of these problems. Self-organization and production processes by nanoparticles and nanomachines may be able

to exclude impurities and greatly improve homogeneity by effective examination and selection of each atom/molecule during nanosynthesis and nanoproduction processes. Higher efficiencies of energy usage may be achievable as nanomachines produce idealized materials at the smaller sizes and pass their products to larger nanomachines for production of larger scale materials.

The directed, non-random, use of atoms and molecules by nanotechniques holds the promise for the production of smaller transistors and wires for the electronics and computer industries. Unusual material strengths, optical properties, magnetic properties, and catalytic properties may be achievable. Higher efficiencies of photo-electronic conversion would be a boon to mankind. There is hope that science will devise nanoparticles that destroy pathogens and repair tissues. See Impact 9.1 for discussion of SPM examination of atom positions on a macroscopic surface and for the current nanotechnological method for positioning atoms on a surface. See Impact 9.2 for discussion of nano-quantum dots that have unusual optical and magnetic properties.

Solutions to exercises

E9.1(b) $$E = \frac{n^2h^2}{8m_eL^2} \text{ [9.4a]}$$

$$\frac{h^2}{8m_eL^2} = \frac{(6.626 \times 10^{-34}\,\text{J s})^2}{8(9.109 \times 10^{-31}\,\text{kg}) \times (1.50 \times 10^{-9}\,\text{m})^2} = 2.67\overline{8} \times 10^{-20}\,\text{J}$$

The conversion factors required are

$$1\,\text{eV} = 1.602 \times 10^{-19}\,\text{J}; \quad 1\,\text{cm}^{-1} = 1.986 \times 10^{-23}\,\text{J}; \quad 1\,\text{eV} = 96.485\,\text{kJ mol}^{-1}$$

(a) $$E_3 - E_1 = (9-1)\frac{h^2}{8m_eL^2} = 8(2.678 \times 10^{-20}\,\text{J})$$

$$= \boxed{2.14 \times 10^{-19}\,\text{J}} = \boxed{1.34\,\text{eV}} = \boxed{1.08 \times 10^4\,\text{cm}^{-1}} = \boxed{129\,\text{kJ mol}^{-1}}$$

(b) $$E_7 - E_6 = (49-36)\frac{h^2}{8m_eL^2} = 13(2.678 \times 10^{-20}\,\text{J})$$

$$= \boxed{3.48 \times 10^{-19}\,\text{J}} = \boxed{2.17\,\text{eV}} = \boxed{1.75 \times 10^4\,\text{cm}^{-1}} = \boxed{210\,\text{kJ mol}^{-1}}$$

E9.2(b) The probability is

$$P = \int \psi^*\psi\,dx = \frac{2}{L}\int \sin^2\left(\frac{n\pi x}{L}\right)dx \approx \frac{2\Delta x}{L}\sin^2\left(\frac{n\pi x}{L}\right)$$

where $\Delta x = 0.02L$ and the function is evaluated at $x = 0.66\,L$.

(a) For $n = 1$ $\quad P = \frac{2(0.02L)}{L}\sin^2(0.66\pi) = \boxed{0.03\overline{1}}$

(b) For $n = 2$ $\quad P = \frac{2(0.02L)}{L}\sin^2[2(0.66\pi)] = \boxed{0.02\overline{9}}$

E9.3(b) The expectation value is

$$\langle\hat{p}\rangle = \int \psi^* \hat{p} \psi \, \mathrm{d}x$$

but first we need $\hat{p}\psi$

$$\hat{p}\psi = -\mathrm{i}\hbar \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) = -\mathrm{i}\hbar\left(\frac{2}{L}\right)^{1/2} \frac{n\pi}{L} \cos\left(\frac{n\pi x}{L}\right)$$

$$\text{so } \langle\hat{p}\rangle = \frac{-2\mathrm{i}\hbar n\pi}{L^2} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) \mathrm{d}x = \boxed{0}$$

$$\text{and } \langle\hat{p}^2\rangle = 2m\langle\hat{H}\rangle = 2mE_n = \frac{h^2 n^2}{4L^2}$$

for all n. So for $n = 2$

$$\langle\hat{p}^2\rangle = \boxed{\frac{h^2}{L^2}}$$

E9.4(b) The zero-point energy is the ground-state energy, that is, with $n_x = n_y = n_z = 1$:

$$E = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8mL^2} \text{ [9.12b with equal lengths]} = \frac{3h^2}{8mL^2}$$

Set this equal to the rest energy mc^2 and solve for L:

$$mc^2 = \frac{3h^2}{8mL^2} \quad \text{so } L = \boxed{\left(\frac{3}{8}\right)^{1/2} \frac{h}{mc} = \left(\frac{3}{8}\right)^{1/2} \lambda_C}$$

where λ_C is the Compton wavelength of a particle of mass m.

E9.5(b)

$$\psi_5 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{5\pi x}{L}\right)$$

$$P(x) \propto \psi_5^2 \propto \sin^2\left(\frac{5\pi x}{L}\right)$$

Maxima and minima in $P(x)$ correspond to $\dfrac{\mathrm{d}P(x)}{\mathrm{d}x} = 0$

$$\frac{\mathrm{d}}{\mathrm{d}x}P(x) \propto \frac{\mathrm{d}\psi^2}{\mathrm{d}x} \propto \sin\left(\frac{5\pi x}{L}\right) \cos\left(\frac{5\pi x}{L}\right) \propto \sin\left(\frac{10\pi x}{L}\right) \quad [2\sin\alpha\cos\alpha = \sin 2\alpha]$$

$\sin\theta = 0$ when $\theta = 0, \pi, 2\pi, \ldots, n'\pi$ $(n' = 0, 1, 2, \ldots)$

$$\frac{10\pi x}{L} = n'\pi \quad \text{for } n' \leq 10 \quad \text{so} \quad x = \frac{n'L}{10}$$

$x = 0, x = L$ are minima. Maxima and minima alternate, so maxima correspond to

$$n' = 1, 3, 5, 7, 9 \quad x = \boxed{\frac{L}{10}}, \boxed{\frac{3L}{10}}, \boxed{\frac{L}{2}}, \boxed{\frac{7L}{10}}, \boxed{\frac{9L}{10}}$$

E9.6(b) The energy levels are

$$E_{n_1,n_2,n_3} = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = E_1(n_1^2 + n_2^2 + n_3^2)$$

where E_1 combines all constants besides quantum numbers. The minimum value for all the quantum numbers is 1, so the lowest energy is

$$E_{1,1,1} = 3E_1$$

The question asks about an energy 14/3 times this amount, namely $14E_1$. This energy level can be obtained by any combination of allowed quantum numbers such that

$$n_1^2 + n_2^2 + n_3^2 = 14 = 3^2 + 2^2 + 1^2$$

The degeneracy, then, is $\boxed{6}$, corresponding to (n_1, n_2, n_3) = (1, 2, 3), (1, 3, 2), (2, 1, 3), (2, 3, 1), (3, 1, 2), or (3, 2, 1).

E9.7(b) $E = \frac{3}{2}kT$ is the average translational energy of a gaseous molecule (see Chapter 17).

$$E = \frac{3}{2}kT = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = \frac{n^2h^2}{8mL^2}$$

$$E = \left(\frac{3}{2}\right) \times (1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (300\,\text{K}) = 6.21\overline{4} \times 10^{-21}\,\text{J}$$

$$n^2 = \frac{8mL^2}{h^2}E$$

If $L^3 = 1.00\,\text{m}^3$, then $L^2 = 1.00\,\text{m}^2$.

$$\frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34}\,\text{J s})^2}{(8) \times \left(\dfrac{0.02802\,\text{kg mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}}\right) \times 100\,\text{m}^2} = 1.18\overline{0} \times 10^{-42}\,\text{J}$$

$$n^2 = \frac{6.21\overline{4} \times 10^{-21}\,\text{J}}{1.180 \times 10^{-42}\,\text{J}} = 5.26\overline{5} \times 10^{21}; \quad n = \boxed{7.26 \times 10^{10}}$$

$$\Delta E = E_{n+1} - E_n = E_{7.26\times10^{10}+1} - E_{7.26\times10^{10}}$$

$$\Delta E = (2n + 1) \times \left(\frac{h^2}{8mL^2}\right) = [(2) \times (7.26 \times 10^{10}) + 1] \times \left(\frac{h^2}{8mL^2}\right) = \frac{14.5\overline{2} \times 10^{10}h^2}{8mL^2}$$

$$= (14.5\overline{2} \times 10^{10}) \times (1.18\overline{0} \times 10^{-42}\,\text{J}) = \boxed{1.71 \times 10^{-31}\,\text{J}}$$

The de Broglie wavelength is obtained from

$$\lambda = \frac{h}{p} = \frac{h}{mv} \text{ [8.12]}$$

The velocity is obtained from

$$E_K = \tfrac{1}{2}mv^2 = \tfrac{3}{2}kT = 6.21\bar{4} \times 10^{-21}\,\text{J}$$

$$v^2 = \frac{6.21\bar{4} \times 10^{-21}\text{J}}{\left(\frac{1}{2}\right) \times \left(\frac{0.02802\,\text{kg mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}}\right)} = 2.67\bar{1} \times 10^5\,\text{m}^2\,\text{s}^{-2}; \quad v = 517\,\text{m s}^{-1}$$

$$\lambda = \frac{6.626 \times 10^{-34}\,\text{J s}}{(4.65 \times 10^{-26}\,\text{kg}) \times (517\,\text{m s}^{-1})} = 2.75 \times 10^{-11}\,\text{m} = \boxed{27.5\,\text{pm}}$$

The conclusion to be drawn from all of these calculations is that the translational motion of the nitrogen molecule can be described classically. The energy of the molecule is essentially continuous,

$$\frac{\Delta E}{E} \lll 1.$$

E9.8(b) The zero-point energy is

$$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \frac{1}{2}(1.0546 \times 10^{-34}\,\text{J s}) \times \left(\frac{285\,\text{N m}^{-1}}{5.16 \times 10^{-26}\,\text{kg}}\right)^{1/2}$$

$$= \boxed{3.92 \times 10^{-21}\,\text{J}}$$

E9.9(b) The difference in adjacent energy levels is

$$\Delta E = E_{v+1} - E_v = \hbar\omega\ [9.26] = \hbar\left(\frac{k}{m}\right)^{1/2} [9.25]$$

$$\text{so } k = \frac{m(\Delta E)^2}{\hbar^2} = \frac{(2.88 \times 10^{-25}\,\text{kg}) \times (3.17 \times 10^{-21}\,\text{J})^2}{(1.0546 \times 10^{-34}\,\text{J s})^2} = \boxed{260\,\text{N m}^{-1}}$$

E9.10(b) The difference in adjacent energy levels, which is equal to the energy of the photon, is

$$\Delta E = \hbar\omega = h\nu \text{ so } \hbar\left(\frac{k}{m}\right)^{1/2} = \frac{hc}{\lambda}$$

and

$$\lambda = \frac{hc}{\hbar}\left(\frac{k}{m}\right)^{1/2} = 2\pi c\left(\frac{m}{k}\right)^{1/2}$$

$$= 2\pi(2.998 \times 10^8\,\text{m s}^{-1}) \times \left(\frac{(15.9949\,\text{u}) \times (1.66 \times 10^{-27}\,\text{kg u}^{-1})}{544\,\text{N m}^{-1}}\right)^{1/2}$$

$$\lambda = 1.32 \times 10^{-5}\,\text{m} = \boxed{13.2\,\mu\text{m}}$$

E9.11(b) The difference in adjacent energy levels, which is equal to the energy of the photon, is

$$\Delta E = \hbar\omega = h\nu \text{ so } \hbar\left(\frac{k}{m}\right)^{1/2} = \frac{hc}{\lambda}$$

$$\text{and } \lambda = \frac{hc}{\hbar}\left(\frac{k}{m}\right)^{1/2} = 2\pi c\left(\frac{m}{k}\right)^{1/2}$$

Doubling the mass, then, increases the wavelength by a factor of $2^{1/2}$. So taking the result from Exercise 9.10(b), the new wavelength is

$$\lambda = 2^{1/2}(13.2\,\mu\text{m}) = \boxed{18.7\,\mu\text{m}}$$

E9.12(b) $\Delta E = \hbar\omega = h\nu$

(a) $\Delta E = h\nu = (6.626 \times 10^{-34}\,\text{J Hz}^{-1}) \times (33 \times 10^{3}\,\text{Hz}) = \boxed{2.2 \times 10^{-29}\,\text{J}}$

(b) $\Delta E = \hbar\omega = \hbar\left(\frac{k}{m_{\text{eff}}}\right)^{1/2} \quad \left[\frac{1}{m_{\text{eff}}} = \frac{1}{m_1} + \frac{1}{m_2} \text{ with } m_1 = m_2\right]$

For a two-particle oscillator m_{eff}, replaces m in the expression for ω. (See Chapter 13 for a more complete discussion of the vibration of a diatomic molecule.)

$$\Delta E = \hbar\left(\frac{2k}{m}\right)^{1/2} = (1.055 \times 10^{-34}\,\text{J s}) \times \left(\frac{(2) \times (1177\,\text{N m}^{-1})}{(16.00) \times (1.6605 \times 10^{-27}\,\text{kg})}\right)^{1/2}$$

$$= \boxed{3.14 \times 10^{-20}\,\text{J}}$$

E9.13(b) The first excited-state wavefunction has the form

$$\psi = 2N_1 y \exp\left(-\tfrac{1}{2}y^2\right)$$

where N_1 is a collection of constants and $y \equiv x(m\omega/\hbar)^{1/2}$. To see if it satisfies Schrödinger's equation, we see what happens when we apply the energy operator to this function

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2\psi$$

We need derivatives of ψ

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{\mathrm{d}\psi}{\mathrm{d}y}\frac{\mathrm{d}y}{\mathrm{d}x} = \left(\frac{m\omega}{\hbar}\right)^{1/2}(2N_1) \times (1 - y^2) \times \exp\left(-\frac{1}{2}y^2\right)$$

$$\text{and } \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{\mathrm{d}^2\psi}{\mathrm{d}y^2}\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 = \left(\frac{m\omega}{\hbar}\right) \times (2N_1) \times (-3y + y^3) \times \exp\left(-\frac{1}{2}y^2\right) = \left(\frac{m\omega}{\hbar}\right) \times (y^2 - 3)\psi$$

$$\text{So } \hat{H}\psi = -\frac{\hbar^2}{2m} \times \left(\frac{m\omega}{\hbar}\right) \times (y^2 - 3)\psi + \frac{1}{2}m\omega^2x^2\psi$$

$$= -\frac{1}{2}\hbar\omega \times (y^2 - 3) \times \psi + \frac{1}{2}\hbar\omega y^2\psi = \frac{3}{2}\hbar\omega\psi$$

Thus, ψ is a solution of the Schrödinger equation with energy eigenvalue

$$E = \boxed{\tfrac{3}{2}\hbar\omega}$$

E9.14(b) The harmonic oscillator wavefunctions have the form

$$\psi_v(x) = N_v H_v(y) \exp\left(-\frac{1}{2}y^2\right) \quad \text{with } y = \frac{x}{\alpha} \text{ and } \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4} \quad [9.28]$$

The exponential function approaches zero only as x approaches $\pm\infty$, so the nodes of the wavefunction are the nodes of the Hermite polynomials.

$$H_5(y) = 32y^5 - 160y^3 + 120y = 0 \text{ [Table 9.1]} = 8y(4y^4 - 20y^2 + 15)$$

So one solution is $y = 0$, which leads to $x = 0$. The other factor can be made into a quadratic equation by letting $z = y^2$

$$4z^2 - 20z + 15 = 0$$

$$\text{so} \quad z = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{20 \pm \sqrt{20^2 - 4 \times 4 \times 15}}{2 \times 4} = \frac{5 \pm \sqrt{10}}{2}$$

Evaluating the result numerically yields $z = 0.92$ or 4.08, so $y = \pm 0.96$ or ± 2.02. Therefore $x = \boxed{0, \pm 0.96\alpha, \text{ or } \pm 2.02\alpha}$.

COMMENT. Numerical values could also be obtained graphically by plotting $H_5(y)$.

E9.15(b) The zero-point energy is

$$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\left(\frac{k}{m_{\text{eff}}}\right)^{1/2}$$

For a homonuclear diatomic molecule, the effective mass is half the mass of an atom, so

$$E_0 = \frac{1}{2}(1.0546 \times 10^{-34}\,\text{J s}) \times \left(\frac{2293.8\,\text{N m}^{-1}}{\frac{1}{2}(14.0031\,\text{u}) \times (1.66054 \times 10^{-27}\,\text{kg u}^{-1})}\right)^{1/2}$$

$$E_0 = \boxed{2.3421 \times 10^{-20}\,\text{J}}$$

E9.16(b) Orthogonality requires that

$$\int \psi_m^* \psi_n \, d\tau = 0$$

if $m \neq n$.

Performing the integration

$$\int \psi_m^* \psi_n \, d\tau = \int_0^{2\pi} N e^{-im\phi} N e^{in\phi} \, d\phi = N^2 \int_0^{2\pi} e^{i(n-m)\phi} \, d\phi$$

If $m \neq n$, then

$$\int \psi_m^* \psi_n \, d\tau = \frac{N^2}{i(n-m)} e^{i(n-m)\phi} \Big|_0^{2\pi} = \frac{N^2}{i(n-m)}(1-1) = 0$$

Therefore, they are orthogonal.

E9.17(b) The magnitude of angular momentum is

$$\left\langle \hat{L}^2 \right\rangle^{1/2} = \{l(l+1)\}^{1/2}\hbar \text{ [9.54a]} = \{2(3)\}^{1/2}(1.0546 \times 10^{-34} \text{ J s}) = \boxed{2.58 \times 10^{-34} \text{ J s}}$$

Possible projections onto an arbitrary axis are

$$\left\langle \hat{L}_z \right\rangle = m_l \hbar \text{ [9.54b]}$$

where $m_l = 0$ or ± 1 or ± 2. So possible projections include

$$\boxed{0, \pm 1.0546 \times 10^{-34} \text{ J s and } \pm 2.1109 \times 10^{-34} \text{ J s}}$$

E9.18(b) The cones are constructed as described in Section 9.7(d) and Figure 9.40(b) of the text; their edges are of length $\{6(6+1)\}^{1/2} = 6.48$ and their projections are $m_j = +6, +5, \ldots, -6$. See Figure 9.1(a).

The vectors follow, in units of $\hbar$. From the highest-pointing to the lowest-pointing vectors (Figure 9.1(b)), the values of m_l are 6, 5, 4, 3, 2, 1, 0, −1, −2, −3, −4, −5, and −6.

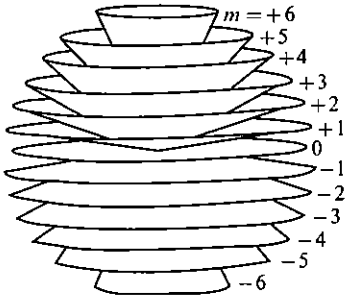


Figure 9.1(a)

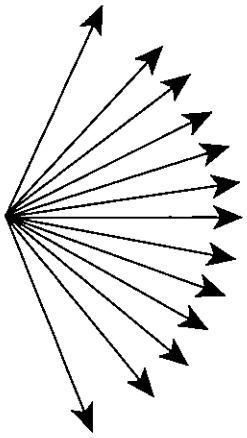


Figure 9.1(b)

Solutions to problems

Solutions to numerical problems

P9.2 $\omega = \left(\frac{k}{\mu}\right)^{1/2}$ [9.25 with μ in place of m]

Also, $\omega = 2\pi\nu = \frac{2\pi c}{\lambda} = 2\pi c\tilde{\nu}$

Therefore $k = \omega^2\mu = 4\pi^2c^2\tilde{\nu}^2\mu = \frac{4\pi^2c^2\tilde{\nu}^2m_1m_2}{m_1 + m_2}$.

We draw up the following table using information from the Data Section, p. 991.

	$^1H^{35}Cl$	$^1H^{81}Br$	$^1H^{127}I$	$^{12}C^{16}O$	$^{14}N^{16}O$
$\tilde{\nu}/m^{-1}$	299 000	265 000	231 000	217 000	190 400
$10^{27}m_1/kg$	1.6735	1.6735	1.6735	19.926	23.253
$10^{27}m_2/kg$	58.066	134.36	210.72	26.560	26.560
$k/(N\ m^{-1})$	516	412	314	1902	1595

Therefore, the order of stiffness, is $\boxed{HI < HBr < HCl < NO < CO}$.

P9.4 $E = \frac{l(l+1)\hbar^2}{2I}$ [9.53] $= \frac{l(l+1)\hbar^2}{2m_{\text{eff}}R^2}$ [$I = m_{\text{eff}}R^2$, m_{eff} in place of m]

$$E = \left(\frac{l(l+1) \times (1.055 \times 10^{-34}\,\text{J s})^2}{(2) \times (1.6605 \times 10^{-27}\,\text{kg}) \times (160 \times 10^{-12}\,\text{m})^2}\right) \times \left(\frac{1}{1.008} + \frac{1}{126.90}\right)$$

$$\left[\frac{1}{m_{\text{eff}}} = \frac{1}{m_1} + \frac{1}{m_2}\right]$$

Therefore,

$$E = l(l+1) \times (1.31 \times 10^{-22}\,\text{J})$$

The energies may be expressed in terms of equivalent frequencies with

$$\nu = \frac{E}{h} = (1.509 \times 10^{33}\,\text{J}^{-1}\,\text{s}^{-1})\,E.$$

Hence, the energies and equivalent frequencies are

l	0	1	2	3
$10^{22}E/J$	$\boxed{0}$	$\boxed{2.62}$	$\boxed{7.86}$	$\boxed{15.72}$
ν/GHz	0	396	1188	2376

P9.6 Treat the gravitational potential energy as a perturbation in the energy operator:

$$H^{(1)} = mgx.$$

The first-order correction to the ground-state energy, E_1, is:

$$E_1^{(1)} = \int_0^L \psi_1^{(0)*} H^{(1)} \psi_1^{(0)}\, \mathrm{d}x = \int_0^L \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) mgx \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) \mathrm{d}x,$$

$$E_1^{(1)} = \frac{2mg}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) \mathrm{d}x,$$

$$E_1^{(1)} = \frac{2mg}{L} \left(\frac{x^2}{4} - \frac{xL}{2\pi} \cos\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) - \frac{L^2}{4\pi^2} \cos^2\left(\frac{\pi x}{L}\right)\right)\Bigg|_0^L,$$

$$E_1^{(1)} = \boxed{\tfrac{1}{2}mgL}$$

Not surprisingly, this amounts to the energy perturbation evaluated at the midpoint of the box. For $m = m_e$, $E_1^{(1)}/L = 4.47 \times 10^{-30}\ \mathrm{J\ m^{-1}}$.

Solutions to theoretical problems

P9.8 The energy of any given molecule is

$$E = \frac{n^2h^2}{8mL^2} \text{ [9.12b with } n^2 = n_x^2 + n_y^2 + n_z^2 \text{ and equal lengths]}$$

(The lowest energy level is $n_x = n_y = n_z = 1$, so $n^2 = 3$; however, what follows applies to any allowed energy level.) So the internal energy of a sample of N molecules is

$$U = NE = \frac{Nn^2h^2}{8mL^2} = \frac{Nn^2h^2}{8mV^{2/3}}$$

In the last step we used $V = L^3$, because we are interested in how the energy changes with volume. Consider an adiabatic change of volume, that is, a change in which no heat enters or leaves the sample. In that case, the change in energy is entirely work (First Law with $q = 0$). Differentiate the expression for U:

$$\mathrm{d}w = \left(\frac{\partial U}{\partial V}\right)_{\text{adiabatic}} \mathrm{d}V = -\frac{Nn^2h^2}{12mV^{5/3}}\, \mathrm{d}V \qquad \text{(a)}$$

In Chapter 2, we learned that expansion work has the form $\mathrm{d}w = -p_{ex}\mathrm{d}V$. Can these expressions be reconciled, and if so, under what conditions? First, note that the expression that multiplies $\mathrm{d}V$ in equation (a) refers to the sample, so if it is some sort of pressure, it must be the sample pressure, and not an arbitrary external pressure, so if the expressions can be reconciled, it must be for *reversible* adiabatic expansion or compression. The expression that multiplies $\mathrm{d}V$ can be expressed as

$$\frac{Nn^2h^2}{12mV^{5/3}} = \frac{2}{3}\frac{N}{V}E.$$

In fact, the kinetic model of gases (Chapter 21) says that the pressure of a gas is equal to $\frac{2}{3}\frac{N}{V}E$ where E is the average kinetic energy of the gas molecules–completely consistent with interpreting it as the

average particle-in-a-box energy. To summarize, reversible adiabatic work for a gas of particle-in-a-box molecules is $dw = -pdV$, where the pressure is

$$p = \frac{Nn^2h^2}{12mL^5} = \frac{2}{3}\frac{N}{V}E$$

In expansion, the volume increases, meaning that the box gets bigger. Equation 9.12b tells us that the kinetic energy decreases, even as the quantum numbers remain constant. This is also consistent with what we know of adiabatic expansion and the kinetic model of gases: the temperature of the sample drops on expansion, and temperature is related to the kinetic energy ($T^2 \propto E$).

In isothermal expansion, energy must enter the system as heat to maintain the temperature. We can interpret this influx of heat as an increase in quantum numbers (an excitation of the molecules) that offsets the falling energy levels.

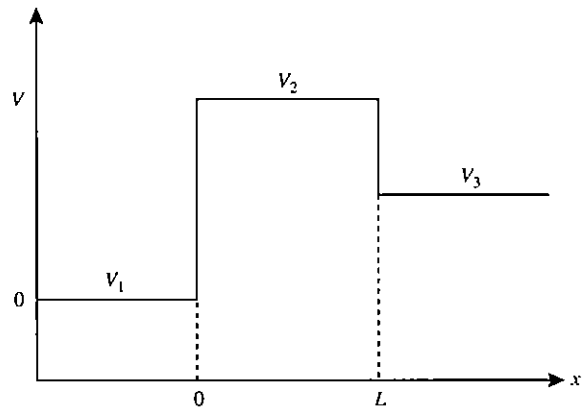


Figure 9.2a

P9.10 (a) The wavefunctions in each region (see Figure 9.2(a)) are (eqns 9.14, 9.16, and 9.17):

$$\psi_1(x) = e^{ik_1x} + B_1e^{-ik_2x}$$

$$\psi_2(x) = A_2e^{k_2x} + B_2e^{-k_2x}$$

$$\psi_3(x) = A_3e^{ik_3x}$$

With the above choice of $A_1 = 1$ the transmission probability is simply $T = |A_3|^2$. The wavefunction coefficients are determined by the criteria that both the wavefunctions and their first derivatives with respect to x be continuous at potential boundaries

$$\psi_1(0) = \psi_2(0); \quad \psi_2(L) = \psi_3(L)$$

$$\frac{d\psi_1(0)}{dx} = \frac{d\psi_2(0)}{dx}; \quad \frac{d\psi_2(L)}{dx} = \frac{d\psi_3(L)}{dx}$$

These criteria establish the algebraic relationships:

$$1 + B_1 - A_2 - B_2 = 0$$

$$(-ik_1 - k_2)A_2 + (-ik_1 + k_2)B_2 + 2ik_1 = 0$$

$$A_2e^{k_2L} + B_2e^{-k_2L} - A_3e^{ik_3L} = 0$$

$$A_2k_2e^{k_2L} - B_2k_2e^{-k_2L} - iA_3k_3e^{ik_3L} = 0$$

Solving the simultaneous equations for A_3 gives

$$A_3 = \frac{4k_1k_2e^{ik_3L}}{(ia+b)\,e^{k_2L} - (ia-b)\,e^{-k_2L}}$$

where $a = k_2^2 - k_1k_3$ and $b = k_1k_2 + k_2k_3$.

Since $\sinh(z) = (e^z - e^{-z})/2$ or $e^z = 2\sinh(z) + e^{-z}$, substitute $e^{k_2L} = 2\sinh(k_2L) + e^{-k_2L}$ giving:

$$A_3 = \frac{2k_1k_2e^{ik_3L}}{(ia+b)\sinh(k_2L) + be^{-k_2L}}$$

$$T = |A_3|^2 = A_3 \times A_3^* = \frac{4k_1^2k_2^2}{(a^2+b^2)\sinh^2(k_2L) + b^2}$$

where $a^2 + b^2 = (k_1^2 + k_2^2)(k_2^2 + k_3^2)$ and $b^2 = k_2^2(k_1 + k_3)^2$

(b) In the special case for which $V_1 = V_3 = 0$, eqns 9.14 and 9.17 require that $k_1 = k_3$. Additionally,

$$\left(\frac{k_1}{k_2}\right)^2 = \frac{E}{V_2 - E} = \frac{\varepsilon}{1-\varepsilon} \quad \text{where} \quad \varepsilon = E/V_2.$$

$$a^2 + b^2 = (k_1^2 + k_2^2)^2 = k_2^4\left\{1 + \left(\frac{k_1}{k_2}\right)^2\right\}^2$$

$$b^2 = 4k_1^2k_2^2$$

$$\frac{a^2+b^2}{b^2} = \frac{k_2^2\left\{1 + \left(\frac{k_1}{k_2}\right)^2\right\}^2}{4k_1^2} = \frac{1}{4\varepsilon(1-\varepsilon)}$$

$$T = \frac{b^2}{b^2 + (a^2+b^2)\sinh^2(k_2L)} = \frac{1}{1 + \left(\frac{a^2+b^2}{b^2}\right)\sinh^2(k_2L)}$$

$$T = \left\{1 + \frac{\sinh^2(k_2L)}{4\varepsilon(1-\varepsilon)}\right\}^{-1} = \left\{1 + \frac{(e^{k_2L} - e^{-k_2L})^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1}$$

This proves eqn 9.20a where $V_1 = V_3 = 0$.

In the high wide barrier limit $k_2L \gg 1$. This implies both that e^{-k_2L} is negligibly small compared to e^{k_2L} and that 1 is negligibly small compared to $e^{2k_2L}/\{16\varepsilon(1-\varepsilon)\}$. The previous equation simplifies to

$$T = 16\varepsilon(1-\varepsilon)e^{-2k_2L} \quad [9.20b]$$

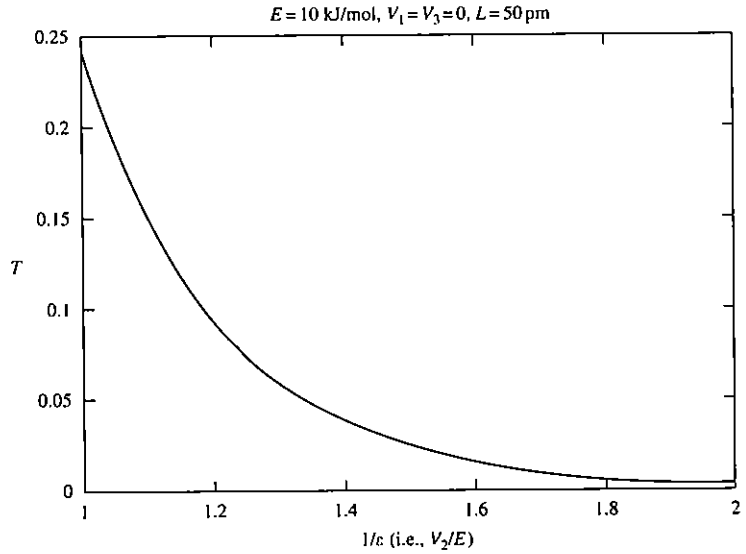


Figure 9.2(b)

P9.12 The Schrödinger equation is $-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \dfrac{1}{2}kx^2\psi = E\psi$

and we write $\psi = \mathrm{e}^{-gx^2}$, so $\dfrac{\mathrm{d}\psi}{\mathrm{d}x} = -2gx\mathrm{e}^{-gx^2}$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -2g\mathrm{e}^{-gx^2} + 4g^2x^2\mathrm{e}^{-gx^2} = -2g\psi + 4g^2x^2\psi$$

$$\left(\frac{\hbar^2 g}{m}\right)\psi - \left(\frac{2\hbar^2 g^2}{m}\right)x^2\psi + \frac{1}{2}kx^2\psi = E\psi$$

$$\left[\left(\frac{\hbar^2 g}{m}\right) - E\right]\psi + \left(\frac{1}{2}k - \frac{2\hbar^2 g^2}{m}\right)x^2\psi = 0$$

This equation is satisfied if

$$E = \frac{\hbar^2 g}{m} \quad \text{and} \quad 2\hbar^2 g^2 = \frac{1}{2}mk, \quad \text{or} \quad \boxed{g = \frac{1}{2}\left(\frac{mk}{\hbar^2}\right)^{1/2}}$$

Therefore,

$$E = \frac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \frac{1}{2}\hbar\omega \quad \text{if } \omega = \left(\frac{k}{m}\right)^{1/2}$$

P9.14

$$\langle x^n\rangle = \alpha^n\langle y^n\rangle = \alpha^n\int_{-\infty}^{+\infty}\psi y^n\psi\,\mathrm{d}x = \alpha^{n+1}\int_{-\infty}^{+\infty}\psi^2 y^n\,\mathrm{d}y \quad [x = \alpha y]$$

$$\langle x^3\rangle \propto \int_{-\infty}^{+\infty}\psi^2 y^3\,\mathrm{d}y = \boxed{0} \text{ by symmetry} \quad [y^3 \text{ is an odd function of } y]$$

$$\langle x^4\rangle = \alpha^5\int_{-\infty}^{+\infty}\psi y^4\psi\,\mathrm{d}y$$

$$y^4\psi = y^4 N H_v \mathrm{e}^{-y^2/2}$$

$$y^4H_v = y^3\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right) = y^2\left[\tfrac{1}{2}\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + v\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right]$$
$$= y^2\left[\tfrac{1}{4}H_{v+2} + \left(v + \tfrac{1}{2}\right)H_v + v(v-1)H_{v-2}\right]$$
$$= y\left[\tfrac{1}{4}\left(\tfrac{1}{2}H_{v+3} + (v+2)H_{v+1}\right) + \left(v + \tfrac{1}{2}\right) \times \left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right)\right.$$
$$\left. + v(v-1) \times \left(\tfrac{1}{2}H_{v-1} + (v-2)H_{v-3}\right)\right]$$
$$= y\left(\tfrac{1}{8}H_{v+3} + \tfrac{3}{4}(v+1)H_{v+1} + \tfrac{3}{2}v^2H_{v-1} + v(v-1) \times (v-2)H_{v-3}\right)$$

Only yH_{v+1} and yH_{v-1} lead to H_v and contribute to the expectation value (since H_v is orthogonal to all except H_v) [Table 9.1]; hence

$$y^4H_v = \tfrac{3}{4}y\{(v+1)H_{v+1} + 2v^2H_{v-1}\} + \cdots$$
$$= \tfrac{3}{4}\left[(v+1)\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + 2v^2\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right] + \cdots$$
$$= \tfrac{3}{4}\{(v+1)^2H_v + v^2H_v\} + \cdots$$
$$= \tfrac{3}{4}(2v^2 + 2v + 1)H_v + \cdots$$

Therefore

$$\int_{-\infty}^{+\infty} \psi y^4 \psi \, dy = \tfrac{3}{4}(2v^2 + 2v + 1)N^2 \int_{-\infty}^{+\infty} H_v^2 e^{-y^2} \, dy = \frac{3}{4\alpha}(2v^2 + 2v + 1)$$

and so

$$\langle x^4 \rangle = (\alpha^5) \times \left(\frac{3}{4\alpha}\right) \times (2v^2 + 2v + 1) = \boxed{\frac{3}{4}(2v^2 + 2v + 1)\alpha^4}$$

P9.16

$$\mu \equiv \int \psi_{v'} x \psi_v \, dx = \alpha^2 \int \psi_{v'} y \psi_v \, dy \quad [x = \alpha y]$$

$$y\psi_v = N_v\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right)e^{-y^2/2} \text{ [Table 9.1]}$$

Hence $\mu = \alpha^2 N_v N_{v'} \int \left(\frac{1}{2}H_{v'}H_{v+1} + vH_{v'}H_{v-1}\right)e^{-y^2} \, dy = 0$ unless $v' = v \pm 1$ [Table 9.1]

For $v' = v + 1$

$$\mu = \frac{1}{2}\alpha^2 N_v N_{v+1} \int H_{v+1}^2 e^{-y^2} \, dy = \frac{1}{2}\alpha^2 N_v N_{v+1} \pi^{1/2} 2^{v+1}(v+1)! = \boxed{\alpha\left(\frac{v+1}{2}\right)^{1/2}}$$

For $v' = v - 1$

$$\mu = v\alpha^2 N_v N_{v-1} \int H_{v-1}^2 e^{-y^2} \, dy = v\alpha^2 N_v N_{v-1} \pi^{1/2} 2^{v-1}(v-1)! = \boxed{\alpha\left(\frac{v}{2}\right)^{1/2}}$$

No other values of v' result in a non-zero value for μ; hence, no other transitions are allowed.

P9.18 To address this time-dependent problem, we need a time-dependent wavefunction, made up from solutions of the time-dependent Schrödinger equation

$$\hat{H}\Psi(x,t) = \mathrm{i}\hbar\frac{\partial\Psi(x,t)}{\partial t} \text{ [Table 8.1]}$$

If $\psi(x)$ is an eigenfunction of the energy operator with energy eigenvalue E, then

$$\Psi(x,t) = \psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar}$$

is a solution of the time-dependent Schrödinger equation (provided the energy operator is not itself time dependent). To verify this, evaluate both sides of the time-dependent Schrödinger equation. On the left we have

$$\hat{H}\Psi(x,t) = \hat{H}\psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar} = E\psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar} = E\Psi(x,t)$$

On the right we have

$$\mathrm{i}\hbar\frac{\partial\Psi(x,t)}{\partial t} = \mathrm{i}\hbar\psi(x)\frac{\partial}{\partial t}\mathrm{e}^{-\mathrm{i}Et/\hbar} = -\mathrm{i}^2E\psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar} = E\Psi(x,t),$$

the same as on the left. Our wavepacket is an arbitrary superposition of time-evolving harmonic oscillator states,

$$\Psi(x,t) = \sum_{v=0} c_v\psi_v(x)\mathrm{e}^{-\mathrm{i}E_vt/\hbar}$$

where $\psi_v(x)$ are time-independent harmonic-oscillator wavefunctions and

$$E_v = \left(v + \tfrac{1}{2}\right)\hbar\omega \quad [9.25]$$

Hence, the wavepacket is

$$\Psi(x,t) = \mathrm{e}^{-\mathrm{i}\omega t/2}\sum_{v=0} c_v\psi_v(x)\mathrm{e}^{-\mathrm{i}v\omega t}$$

The angular frequency ω is related to the period T by $T = 2\pi/\omega$, so we can evaluate the wavepacket at any whole number of periods after t, that is at a time $t + nT$, where n is any integer. (Note: n is not a quantum number.) Note that

$$t + nT = t + 2\pi n/\omega,$$

so

$$\begin{aligned}\Psi(x,t+nT) &= \mathrm{e}^{-\mathrm{i}\omega t/2}\mathrm{e}^{-\mathrm{i}\omega nT/2}\sum_{v=0} c_v\psi_v(x)\mathrm{e}^{-\mathrm{i}v\omega t}\mathrm{e}^{-\mathrm{i}v\omega nT}\\ &= \mathrm{e}^{-\mathrm{i}\omega t/2}\mathrm{e}^{-\mathrm{i}\pi n}\sum_{v=0} c_v\psi_v(x)\mathrm{e}^{-\mathrm{i}v\omega t}\mathrm{e}^{-2\pi\mathrm{i}vn}\end{aligned}$$

Noting that the exponential of ($2\pi\mathrm{i}$ × any integer) = 1, we note that the last factor inside the sum is 1 for every state. Also, since $\mathrm{e}^{-\mathrm{i}n\pi} = (-1)^n$, we have

$$\Psi(x,t+nT) = (-1)^n\Psi(x,t)$$

At any whole number of periods after time t, the wavefunction is either the same at time t or -1 times its value at time t. In any event, $|\Psi|^2$ returns to its original value each period, so the wavepacket returns to the same spatial distribution each period.

P9.20 In each case, if the function is an eigenfunction of the operator, the eigenvalue is also the expectation value; if it is not an eigenfunction we form

$$\langle\Omega\rangle = \int \psi^*\hat{\Omega}\psi \, d\tau \quad [8.34]$$

(a) $\hat{l}_z e^{i\phi} = \frac{\hbar}{i}\frac{d}{d\phi}e^{i\phi} = \hbar e^{i\phi}$; hence $l_z = \boxed{+\hbar}$

(b) $\hat{l}_z e^{-2i\phi} = \frac{\hbar}{i}\frac{d}{d\phi}e^{-2i\phi} = -2\hbar e^{-2i\phi}$; hence $l_z = \boxed{-2\hbar}$

(c) $\langle l_z\rangle \propto \int_0^{2\pi} \cos\phi \left(\frac{\hbar}{i}\frac{d}{d\phi}\cos\phi\right) d\phi \propto -\frac{\hbar}{i}\int_0^{2\pi} \cos\phi \, \sin\phi \, d\phi = \boxed{0}$

(d) $\langle l_z\rangle = N^2 \int_0^{2\pi} (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})^* \left(\frac{\hbar}{i}\frac{d}{d\phi}\right) \times (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})\, d\phi$

$$= \frac{\hbar}{i}N^2 \int_0^{2\pi} (\cos\chi e^{-i\phi} + \sin\chi e^{i\phi}) \times (i\cos\chi e^{i\phi} - \sin\chi e^{-i\phi})\, d\phi$$

$$= \hbar N^2 \int_0^{2\pi} (\cos^2\chi - \sin^2\chi + \cos\chi \, \sin\chi [e^{2i\phi} - e^{-2i\phi}])\, d\phi$$

$$= \hbar N^2(\cos^2\chi - \sin^2\chi) \times (2\pi) = 2\pi\hbar N^2 \cos 2\chi$$

We must evaluate the normalization constant:

$$N^2 \int_0^{2\pi} (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})^*(\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})\, d\phi = 1$$

$$1 = N^2 \int_0^{2\pi} (\cos^2\chi + \sin^2\chi + \cos\chi \sin\chi \, [e^{2i\phi} + e^{-2i\phi}])\, d\phi$$

$$= 2\pi N^2(\cos^2\chi + \sin^2\chi) = 2\pi N^2 \quad \text{so } N^2 = \frac{1}{2\pi}$$

Therefore

$$\langle l_z\rangle = \boxed{\hbar\cos 2\chi} \; [\chi \text{ is a parameter}]$$

For the kinetic energy we use $\hat{T} \equiv \hat{E}_K = \frac{\hat{J}_z^2}{2I}$ [9.36] $= -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$ [9.40]

(a) $\hat{T}e^{i\phi} = -\frac{\hbar^2}{2I}(i^2 e^{i\phi}) = \frac{\hbar^2}{2I}e^{i\phi}$; hence $\langle T\rangle = \boxed{\frac{\hbar^2}{2I}}$

(b) $\hat{T}e^{-2i\phi} = -\frac{\hbar^2}{2I}(2i)^2 e^{-2i\phi} = \frac{4\hbar^2}{2I}e^{-2i\phi}$; hence $\langle T\rangle = \boxed{\frac{2\hbar^2}{I}}$

(c) $\hat{T}\cos\phi = -\frac{\hbar^2}{2I}(-\cos\phi) = \frac{\hbar^2}{2I}\cos\phi$; hence $\langle T\rangle = \boxed{\frac{\hbar^2}{2I}}$

(d) $\hat{T}(\cos\chi e^{i\phi} + \sin\chi e^{-i\phi}) = -\frac{\hbar^2}{2I}(-\cos\chi e^{i\phi} - \sin\chi e^{-i\phi}) = \frac{\hbar^2}{2I}(\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})$

and hence $\langle T\rangle = \boxed{\frac{\hbar^2}{2I}}$

COMMENT. All of these functions are eigenfunctions of the kinetic energy operator, which is also the total energy or Hamiltonian operator, since the potential energy is zero for this system.

P9.22 Mathematical software can animate the real part or the imaginary part of $\Psi(\phi, t)$, or you may wish to have it display $|\Psi^2(\phi, t)|$. Try a "pure" state, that is, let $c = 1$ for one value of m_l and 0 for all others. This "packet" does not spread, but only circulates. Also try making all the coefficients in the sum equal (all 1, for example). Whatever your choice of coefficients, the pattern will repeat with a period T that makes all the time-dependent factors equal to the exponential of (2π i $\times$ an integer):

$$T = \frac{4\pi I}{\hbar}$$

making the exponent $iE_{m_l}t/\hbar$ equal to $2\pi i m_l^2$ when $t = T$ and at intervals of T thereafter. (See Problem 9.18.) An example of this approach using Mathcad is illustrated below:

Wavepacket on a Ring as a MathCad Document. Let $\tau = \frac{h \cdot t}{4 \cdot \pi \cdot I}$ and let each function in the superposition of $m + 1$ functions contribute with equal probability. The normalized angular functions are:

$$\psi(m, \phi) := \left(\frac{1}{2 \cdot \pi}\right)^{\frac{1}{2}} \cdot e^{i \cdot m \cdot \phi}$$ ([9.38b] where m is an integer.)

The normalized superposition is:

$$\Psi(m_{max}, \phi, \tau) := \left(\frac{1}{m+1}\right)^{\frac{1}{2}} \cdot \sum_{m=0}^{m_{max}} \psi(m, \phi) \cdot e^{-i \cdot m^2 \cdot \tau}$$

$N := 500 \quad j := 0..N \quad \phi_j := \frac{2 \cdot \pi \cdot j}{N} \quad m_{max} := 8 \quad \Delta\tau := .03$

The probability density of the superposition is: $P(\phi, \tau) := \Psi(m_{max}, \phi, \tau) \cdot \overline{\Psi(m_{max}, \phi, \tau)}$

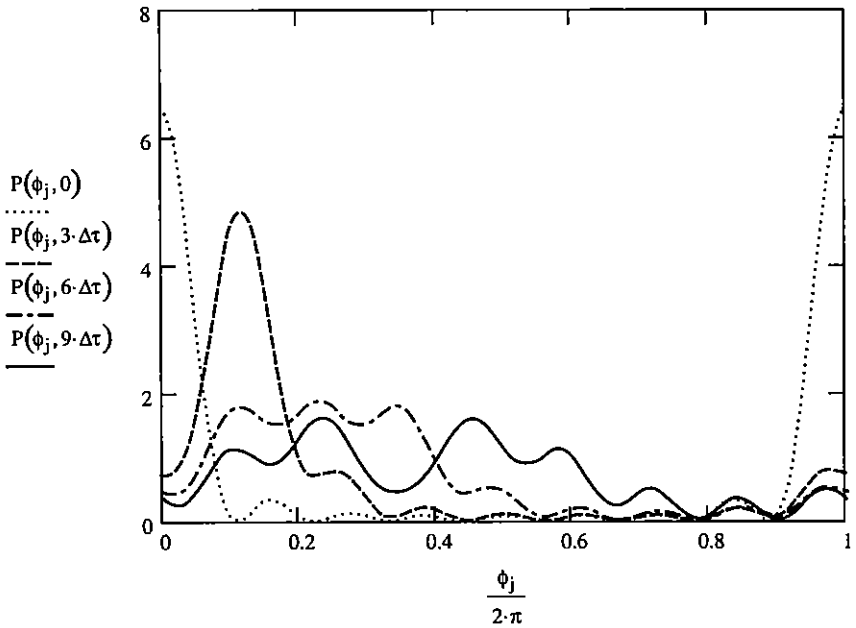


Figure 9.3

The above plot (Figure 9.3) shows that as the initially localized wave propagates around the ring it spreads with time and the uncertainty in knowing particle position increases. The effect of increasing or decreasing the energies accessible to the particle may be explored by increasing or decreasing the value of m_{max} in the MathCad document.

P9.24

$$\int_0^{\pi}\int_0^{2\pi} Y_{3,3}^* Y_{3,3} \sin\theta \, d\theta \, d\phi = \left(\frac{1}{64}\right) \times \left(\frac{35}{\pi}\right) \int_0^{\pi} \sin^6\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi \quad \text{[Table 9.3]}$$

$$= \left(\frac{1}{64}\right) \times \left(\frac{35}{\pi}\right) \times (2\pi) \int_{-1}^{1} (1 - \cos^2\theta)^3 \, d\cos\theta$$

$$[\sin\theta \, d\theta = d\cos\theta, \ \sin^2\theta = 1 - \cos^2\theta]$$

$$= \frac{35}{32} \int_{-1}^{1} (1 - 3x^2 + 3x^4 - x^6) \, dx \quad [x = \cos\theta]$$

$$= \frac{35}{32} \left(x - x^3 + \frac{3}{5}x^5 - \frac{1}{7}x^7\right)\Big|_{-1}^{1} = \frac{35}{32} \times \frac{32}{35} = \boxed{1}$$

P9.26

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\frac{\partial^2}{\partial x^2} f = -a^2 f \qquad \frac{\partial^2}{\partial y^2} f = -b^2 f \qquad \frac{\partial^2}{\partial y^2} f = -c^2 f$$

and f is an eigenfunction with eigenvalue $\boxed{-(a^2 + b^2 + c^2)}$

P9.28 Upon making the operator substitutions

$$p_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \quad \text{and} \quad p_y = \frac{\hbar}{i}\frac{\partial}{\partial y}$$

into $\hat{l}_z$ we find

$$\hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

But $\dfrac{\partial}{\partial\phi} = \dfrac{\partial x}{\partial\phi}\dfrac{\partial}{\partial x} + \dfrac{\partial y}{\partial\phi}\dfrac{\partial}{\partial y} + \dfrac{\partial z}{\partial\phi}\dfrac{\partial}{\partial z}$ which is the chain rule of partial differentiation.

$$\frac{\partial x}{\partial\phi} = \frac{\partial}{\partial\phi}(r\sin\theta\cos\phi) = -r\sin\theta\sin\phi = -y$$

$$\frac{\partial y}{\partial\phi} = \frac{\partial}{\partial\phi}(r\sin\theta\sin\phi) = r\sin\theta\cos\phi = x$$

$$\frac{\partial z}{\partial\phi} = 0$$

Thus, $\dfrac{\partial}{\partial\phi} = -y\dfrac{\partial}{\partial x} + x\dfrac{\partial}{\partial y}$

Upon substitution,

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} = -i\hbar\frac{\partial}{\partial\phi}$$

P9.30 **(a)** Suppose that a particle moves classically at the constant speed v. It starts at $x = 0$ at $t = 0$ and at $t = \tau$ is at position $x = L$. $v = L/\tau$ and $x = vt$.

$$\langle x \rangle = \frac{1}{\tau}\int_{t=0}^{\tau} x\,\mathrm{d}t = \frac{1}{\tau}\int_{t=0}^{\tau} vt\,\mathrm{d}t$$

$$= \frac{v}{\tau}\int_{t=0}^{\tau} t\,\mathrm{d}t = \frac{v}{2\tau}t^2\Big|_{t=0}^{\tau}$$

$$= \frac{v\tau^2}{2\tau} = \frac{v\tau}{2} = \boxed{\frac{L}{2} = \langle x \rangle}$$

$$\langle x^2 \rangle = \frac{1}{\tau}\int_{t=0}^{\tau} x^2\,\mathrm{d}t = \frac{v^2}{\tau}\int_{t=0}^{\tau} t^2\,\mathrm{d}t$$

$$= \frac{v^2}{3\tau}t^3\Big|_{t=0}^{\tau} = \frac{(v\tau)^2}{3} = \frac{L^2}{3}$$

$$\boxed{\langle x^2 \rangle^{1/2} = \frac{L}{3^{1/2}}}$$

(b) $$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } 0 \le x \le L \quad [9.4b]$$

$$\langle x \rangle_n = \int_{x=0}^{L} \psi_n^* x \psi_n\,\mathrm{d}x = \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

$$= \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin\left(\frac{2n\pi x}{L}\right)}{4(n\pi/L)} - \frac{\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2}\right]_{x=0}^{x=L}$$

$$= \frac{2}{L}\left[\frac{L^2}{4}\right] = \boxed{\frac{L}{2} = \langle x \rangle_n}$$

This agrees with the classical result.

$$\langle x^2 \rangle_n = \int_{x=0}^{L} \psi_n^* x^2 \psi_n\,\mathrm{d}x = \frac{2}{L}\int_{x=0}^{L} x^2 \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

$$= \frac{2}{L}\left[\frac{x^3}{6} - \left(\frac{x^2}{4(n\pi/L)} - \frac{1}{8(n\pi/L)^3}\right)\sin\left(\frac{2n\pi x}{L}\right) - \frac{x\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2}\right]_{x=0}^{x=L}$$

$$= \frac{2}{L}\left[\frac{L^3}{6} - \frac{L}{8(n\pi/L)^2}\right]$$

$$= \frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}$$

$$\boxed{\langle x^2 \rangle_n^{1/2} = \left(\frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}\right)^{1/2}}$$

This agrees with the classical result in the limit of large quantum numbers:

$$\lim_{n\to\infty} \langle x^2\rangle_n^{1/2} = \frac{L}{3^{1/2}}$$

Solutions to applications

P9.32 The rate of tunnelling is proportional to the transmission probability, so a ratio of tunnelling rates is equal to the corresponding ratio of transmission probabilities (given in eqn 9.20a). The desired factor is T_1/T_2, where the subscripts denote the tunnelling distances in nanometers:

$$\frac{T_1}{T_2} = \frac{1 + \dfrac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{16\varepsilon(1-\varepsilon)}}{1 + \dfrac{(e^{\kappa L_1} - e^{-\kappa L_1})^2}{16\varepsilon(1-\varepsilon)}}.$$

If $\dfrac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{16\varepsilon(1-\varepsilon)} \gg 1,$

then $\dfrac{T_1}{T_2} \approx \dfrac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{(e^{\kappa L_1} - e^{-\kappa L_1})^2} \approx e^{2\kappa(L_2 - L_1)} = e^{2(7/\text{nm})(2.0-1.0)\text{nm}} = \boxed{1.2 \times 10^6}.$

This is, the tunnelling rate increases about a million-fold. Note: if the first approximation does not hold, we need more information, namely $\varepsilon = E/V$. If the first approximation is valid, then the second is also likely to be valid, namely that the negative exponential is negligible compared to the positive one.

P9.34 Assuming that one can identify the CO peak in the infrared spectrum of the CO-myoglobin complex, taking infrared spectra of each of the isotopic variants of CO-myoglobin complexes can show which atom binds to the haem group and determine the C≡O force constant. Compare isotopic variants to $^{12}C^{16}O$ as the standard; when an isotope changes but the vibrational frequency does not, then the atom whose isotope was varied is the atom that binds to the haem. See table below, which includes predictions of the wavenumber of all isotopic variants compared to that of $\tilde{\nu}(^{12}C^{16}O)$. (As usual, the better the experimental results agree with the whole set of predictions, the more confidence one would have with the conclusion.)

Wavenumber for isotopic variant	If O binds	If C binds
$\tilde{\nu}(^{12}C^{18}O) =$	$\tilde{\nu}(^{12}C^{16}O)^{\dagger}$	$(16/18)^{1/2}\tilde{\nu}(^{12}C^{16}O)$
$\tilde{\nu}(^{13}C^{16}O) =$	$(12/13)^{1/2}\tilde{\nu}(^{12}C^{16}O)$	$\tilde{\nu}(^{12}C^{16}O)^{\dagger}$
$\tilde{\nu}(^{13}C^{18}O) =$	$(12/13)^{1/2}\tilde{\nu}(^{12}C^{16}O)$	$(16/18)^{1/2}\tilde{\nu}(^{12}C^{16}O)$

† That is, no change compared to the standard.

The wavenumber is related to the force constant as follows:

$$\omega = 2\pi c\tilde{\nu} = \left(\frac{k}{m}\right)^{1/2} \quad \text{so} \quad k = m(2\pi c\tilde{\nu})^2,$$

$$k = m(1.66 \times 10^{-27}\text{kg u}^{-1})[(2\pi)(2.998 \times 10^{10}\text{ cm s}^{-1})\tilde{\nu}(^{12}C^{16}O)]^2,$$

and $k/(\text{kg s}^{-1}) = (5.89 \times 10^{-5})(m/\text{u})[\tilde{\nu}(^{12}C^{16}O)/\text{cm}^{-1}]^2.$

Here m is the mass of the atom that is not bound, i.e. 12 u if O is bound and 16 u if C is bound. (Of course, one can compute k from any of the isotopic variants, and take k to be a mean derived from all the relevant data.)

P9.36 See solution to P2.38, parts (c) and (d). First, let $f = n/N$; therefore, f is the fraction of the totally stretched chain represented by the end-to-end distance.

$$F = -\frac{kT}{2l}\ln\left(\frac{N+n}{N-n}\right) = -\frac{kT}{2l}\ln\left(\frac{N(1+f)}{N(1-f)}\right) = -\frac{kT}{2l}\ln\left(\frac{1+f}{1-f}\right)$$
$$= -\frac{kT}{2l}[\ln(1+f) - \ln(1-f)]$$

When $n \ll N$, then $f \ll 1$, and the natural log can be expanded: $\ln(1+f) \approx f$ and $\ln(1-f) \approx -f$. Therefore

$$F \approx -\frac{kT}{2l}[f - (-f)] = -\frac{fkT}{l} = -\frac{nkT}{Nl} = -\frac{kT}{Nl^2}x.$$

In the last step, we note that the distance x between ends is equal to nl, so $n = x/l$. This is a Hooke's law force with force constant kT/Nl^2.

The root mean square displacement is $\langle x^2\rangle^{1/2}$. In part (b) of P9.15, $\langle x^2\rangle$ for a harmonic oscillator was evaluated and was found to be

$$\langle x^2\rangle = \left(v + \frac{1}{2}\right) \times \left(\frac{\hbar^2}{mk_{\text{force}}}\right)^{1/2}$$

Therefore, putting in the appropriate values for the ground state ($v = 0$) of this model

$$\langle x^2\rangle = \frac{1}{2} \times \left(\frac{\hbar^2}{Nm} \times \frac{Nl^2}{kT}\right)^{1/2} = \frac{\hbar l}{2} \times \left(\frac{1}{mkT}\right)^{1/2}$$

and $$\langle x^2\rangle^{1/2} = \boxed{\left(\frac{\hbar l}{2}\right)^{1/2} \times \left(\frac{1}{mkT}\right)^{1/4}}$$

P9.38 **(a)** In the box, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = E\psi$$

Assume that the solution is a product of three functions of a single variable; that is, let

$$\psi(x, y, z) = X(x)Y(y)Z(z).$$

Substituting into the Schrödinger equation gives

$$-\frac{\hbar^2}{2m}\left(YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2}\right) = EXYZ$$

Divide both sides by XYZ:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right)=E$$

For the purposes of illustration, isolate the terms that depend on x on the left side of the equation:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right)=E+\frac{\hbar^2}{2m}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}\right)$$

Note that the left side depends only on one variable, x, while the right side depends on two different and independent variables, y and z. The only way that the two sides can be equal to each other for all x, y, and z is if they are both equal to a constant. Call that constant E_x, and we have, from the left side of the equation:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right)=E_x \quad \text{so} -\frac{\hbar^2}{2m}\frac{\partial^2 X}{\partial x^2}=E_x X.$$

Note that this is just the Schrödinger equation for a particle in a one-dimensional box. Note also that we could just as easily have isolated y terms or z terms, leading to similar equations.

$$-\frac{\hbar^2}{2m}\frac{\partial^2 Y}{\partial y^2}=E_y Y \quad \text{and} \quad -\frac{\hbar^2}{2m}\frac{\partial^2 Z}{\partial z^2}=E_z Z$$

The assumption that the wavefunction can be written as a product of single-variable functions is a valid one, for we can find ordinary differential equations for the assumed factors. That is what it means for a partial differential equation to be separable.

(b) Since X, Y, and Z are particle-in-a-box wavefunctions of independent variables x,y, and z respectively, each of them has its own quantum number. The three-dimensional wavefunction is a product of the three, and therefore depends on all three quantum numbers:

$$\psi(x,y,z)=X(x)Y(y)Z(z)=\left(\frac{2}{L_1}\right)^{1/2}\sin\frac{n_x\pi x}{L_1}\times\left(\frac{2}{L_2}\right)^{1/2}\sin\frac{n_y\pi y}{L_2}\times\left(\frac{2}{L_3}\right)^{1/2}\sin\frac{n_z\pi z}{L_3}$$

Each constant of separation (E_x, E_y, and E_z) depends on its own quantum number. The three constants of separation add up to the total energy, which therefore depends on all three quantum numbers:

$$E=E_x+E_y+E_z=\frac{h^2}{8m}\left(\frac{n_x^2}{L_1^2}+\frac{n_y^2}{L_2^2}+\frac{n_z^2}{L_3^2}\right)$$

(c) For a cubic box, $L_1=L_2=L_3=L$, so

$$E=\frac{h^2(n_x^2+n_y^2+n_z^2)}{8mL^2}$$

The energy levels are shown in Figure 9.4.

(d) Compare this energy-level diagram to Figure 9.2 of the textbook. The energy levels here are much more closely spaced. In a one-dimensional box, the 15th energy level is not reached until

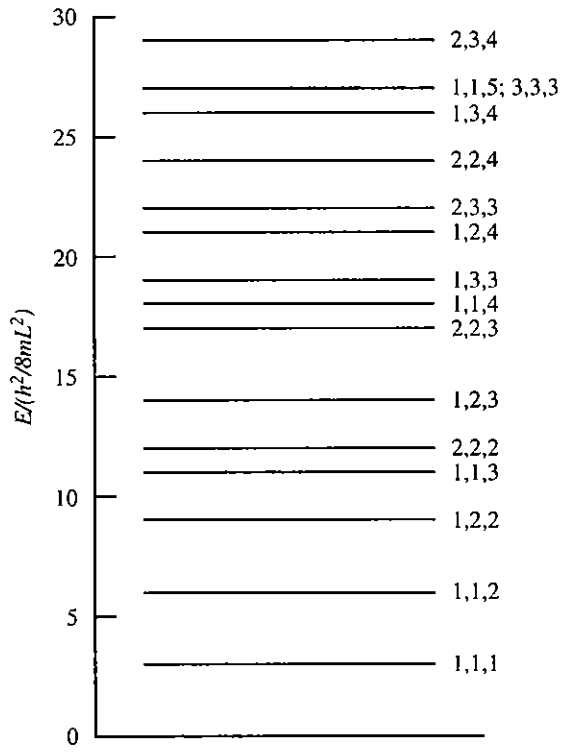
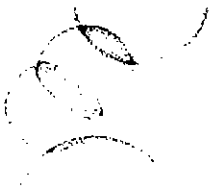


Figure 9.4

$\frac{E}{h^2/8mL^2} = 225$, and the previous level is 29 units below that. In the three-dimensional box, the first 15 energy levels fit within the range of 29 units. The energy levels in a one-dimensional box are sparse compared to those in a three-dimensional box.



10 Atomic structure and atomic spectra

Answers to discussion questions

D10.2 (1) The principal quantum number, n, determines the energy of a hydrogenic atomic orbital through eqn 10.11.

(2) The azimuthal quantum number, l, determines the magnitude of the angular momentum of a hydrogenic atomic orbital through the formula $\{l(l+1)\}^{1/2}\hbar$.

(3) The magnetic quantum number, m_l, determines the z-component of the angular momentum of a hydrogenic orbital through the formula $m_l\hbar$.

(4) The spin quantum number, s, determines the magnitude of the spin angular momentum through the formula $\{s(s+1)\}^{1/2}\hbar$. For hydrogenic atomic orbitals, s can only be $1/2$.

(5) The spin quantum number, m_s, determines the z-component of the spin angular momentum through the formula $m_s\hbar$. For hydrogenic atomic orbitals, m_s can only be $\pm 1/2$.

D10.4 (a) A boundary surface for a hydrogenic orbital is drawn so as to contain most (say 90%) of the probability density of an electron in that orbital. Its shape varies from orbital to orbital because the electron density distribution is different for different orbitals.

(b) The radial distribution function gives the probability that the electron will be found anywhere within a shell of radius r around the nucleus. It gives a better picture of where the electron is likely to be found with respect to the nucleus than the probability density which is the square of the wavefunction.

D10.6 The first ionization energies increase markedly from Li to Be, decrease slightly from Be to B, again increase markedly from B to N, again decrease slightly from N to O, and finally increase markedly from N to Ne. The general trend is an overall increase of I_1 with atomic number across the period. That is to be expected since the principal quantum number (electron shell) of the outer electron remains the same, while its attraction to the nucleus increases. The slight decrease from Be to B is a reflection of the outer electron being in a higher energy subshell (larger l value) in B than in Be. The slight decrease from N to O is due to the half-filled subshell effect; half-filled sub-shells have increased stability. O has one electron outside of the half-filled p subshell and that electron must pair with another resulting in strong electron–electron repulsions between them.

D10.8 An electron has a magnetic moment and magnetic field due to its orbital angular momentum. It also has a magnetic moment and magnetic field due to its spin angular momentum. There is an interaction energy between magnetic moments and magnetic fields. That between the spin magnetic moment and the magnetic field generated by the orbital motion is called spin–orbit coupling. The energy of interaction is proportional to the scalar product of the two vectors representing the spin and orbital angular momenta

and hence depends upon the orientation of the two vectors. See Figure 10.27. The total angular momentum of an electron in an atom is the vector sum of the orbital and spin angular momenta as illustrated in Figure 10.28 and expressed in eqn 10.46. The spin–orbit coupling results in a splitting of the energy levels associated with atomic terms as shown in Figures 10.29 and 10.30. This splitting shows up in atomic spectra as a fine structure as illustrated in Figure 10.30.

Solutions to exercises

E10.1(b) The energy of the photon that struck the Xe atom goes into liberating the bound electron and giving it any kinetic energy it now possesses

$$E_{\text{photon}} = I + E_{\text{kinetic}} \qquad I = \text{ionization energy}$$

The energy of a photon is related to its frequency and wavelength

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

and the kinetic energy of an electron is related to its mass and speed, s

$$E_{\text{kinetic}} = \tfrac{1}{2}m_e s^2$$

$$\text{So } \frac{hc}{\lambda} = I + \frac{1}{2}m_e s^2 \Rightarrow I = \frac{hc}{\lambda} - \frac{1}{2}m_e s^2$$

$$I = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{58.4 \times 10^{-9}\,\text{m}} - \frac{1}{2}\left(9.11 \times 10^{-31}\,\text{kg}\right) \times \left(1.79 \times 10^{6}\,\text{m s}^{-1}\right)^2$$

$$= \boxed{1.94 \times 10^{-18}\ \text{J}} = 12.1\,\text{eV}$$

E10.2(b) The radial wavefunction is [Table 10.1]

$$R_{3,0} = A\left(6 - 2\rho + \frac{1}{9}\rho^2\right)\mathrm{e}^{-\rho/6} \text{ where } \rho \equiv \frac{2Zr}{a_0}, \text{ and } A \text{ is a collection of constants.}$$

[Note: ρ defined here is $3 \times \rho$ as defined in Table 10.1]

Differentiating with respect to ρ yields

$$\frac{\mathrm{d}R_{3,0}}{\mathrm{d}\rho} = 0 = A\left(6 - 2\rho + \frac{1}{9}\rho^2\right) \times \left(-\frac{1}{6}\right)\mathrm{e}^{-\rho/6} + \left(-2 + \frac{2}{9}\rho\right)A\mathrm{e}^{-\rho/6}$$

$$= A\mathrm{e}^{-\rho/6}\left(-\frac{\rho^2}{54} + \frac{5}{9}\rho - 3\right)$$

This is a quadratic equation

$$0 = a\rho^2 + b\rho + c \qquad \text{where } a = -\frac{1}{54},\ b = \frac{5}{9},\ \text{and } c = -3.$$

The solution is

$$\rho = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = 15 \pm 3\sqrt{7}$$

so $r = \boxed{\left(\frac{15}{2} \pm \frac{3\,(7^{1/2})}{2}\right)\frac{a_0}{Z}}$.

Numerically, this works out to $\rho = 7.65$ and 2.35, so $r = \boxed{11.5a_0/Z}$ and $\boxed{3.53a_0/Z}$. Substituting $Z = 1$ and $a_0 = 5.292 \times 10^{-11}$ m, $r = \boxed{607 \text{ pm}}$ and $\boxed{187 \text{ pm}}$.

The other maximum in the wavefunction is at $\boxed{r = 0}$. It is a physical maximum, but not a calculus maximum: the first derivative of the wavefunction does not vanish there, so it cannot be found by differentiation.

E10.3(b) The complete radial wavefunction, $R_{4,1}$ is not given in Table 10.1; however in the statement of the exercise we are told that it is proportional to

$$(20 - 10\rho + \rho^2)\rho \quad \text{where} \quad \rho = \frac{2Zr}{a_0} \text{ [Note: } \rho \text{ defined here is } n \times \rho \text{ as defined in Table 10.1]}$$

The radial nodes occur where the radial wavefunction vanishes, namely where

$$(20 - 10\rho + \rho^2)\rho = 0.$$

The zeros of this function occur at

$$\rho = 0, \qquad \boxed{r = 0}$$

and when

$$(20 - 10\rho + \rho^2) = 0, \quad \text{with roots } \rho = 2.764, \quad \text{and } \rho = 7.236$$

then $r = \frac{\rho a_0}{2Z} = \frac{\rho a_0}{2} = \frac{2.764a_0}{2} = \boxed{1.382a_0}$ and $\frac{7.236a_0}{2} = \boxed{3.618a_0}$

or $r = \boxed{7.31 \times 10^{-11}\text{ m}}$ and $\boxed{1.917 \times 10^{-10}\text{ m}}$

E10.4(b) Normalization requires

$$\int |\psi|^2 \,\mathrm{d}\tau = 1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} [N(2 - r/a_0)\,\mathrm{e}^{-r/2a_0}]^2 \,\mathrm{d}\phi \,\sin\theta \,\mathrm{d}\theta \, r^2 \,\mathrm{d}r$$

$$1 = N^2 \int_0^\infty \mathrm{e}^{-r/a_0}(2 - r/a_0)^2 r^2 \,\mathrm{d}r \int_0^\pi \sin\theta \,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi$$

Integrating over angles yields

$$1 = 4\pi N^2 \int_0^\infty \mathrm{e}^{-r/a_0}(2 - r/a_0)^2 r^2 \,\mathrm{d}r$$

$$= 4\pi N^2 \int_0^\infty \mathrm{e}^{-r/a_0}(4 - 4r/a_0 + r^2/a_0^2) r^2 \,\mathrm{d}r = 4\pi N^2 (8a_0^3)$$

In the last step, we used

$$\int_0^\infty \mathrm{e}^{-r/k} r^2\,\mathrm{d}r = 2k^3,\ \int_0^\infty \mathrm{e}^{-r/k} r^3\,\mathrm{d}r = 6k^4, \text{ and } \int_0^\infty \mathrm{e}^{-r/k} r^4\,\mathrm{d}r = 24k^5,$$

So $\boxed{N = \dfrac{1}{4\sqrt{2\pi a_0^3}}}$

E10.5(b) The average kinetic energy is

$$\langle \hat{E}_\mathrm{K} \rangle = \int \psi^* \hat{E}_\mathrm{K} \psi\,\mathrm{d}\tau$$

where $\psi = N(2-\rho)\mathrm{e}^{-\rho/2}$ with $N = \dfrac{1}{4}\left(\dfrac{Z^3}{2\pi a_0^3}\right)^{1/2}$ and $\rho \equiv \dfrac{Zr}{a_0}$ here

$$\hat{E}_\mathrm{K} = -\frac{\hbar^2}{2m}\nabla^2 \qquad \mathrm{d}\tau = r^2 \sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi = \frac{a_0^3 \rho^2 \sin\theta\,\mathrm{d}\rho\,\mathrm{d}\theta\,\mathrm{d}\phi}{Z^3}$$

In spherical polar coordinates, three of the derivatives in ∇^2 are derivatives with respect to angles, so those parts of $\nabla^2\psi$ vanish. Thus

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} = \frac{\partial^2\psi}{\partial\rho^2}\left(\frac{\partial\rho}{\partial r^2}\right)^2 + \frac{2Z}{\rho a_0}\left(\frac{\partial\psi}{\partial\rho}\right)\frac{\partial\rho}{\partial r} = \left(\frac{Z}{a_0}\right)^2 \times \left(\frac{\partial^2\psi}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial\psi}{\partial\rho}\right)$$

$$\frac{\partial\rho}{\partial r} = N(2-\rho) \times \left(-\tfrac{1}{2}\right)\mathrm{e}^{-\rho/2} - N\,\mathrm{e}^{-\rho/2} = N\left(\tfrac{1}{2}\rho - 2\right)\mathrm{e}^{-\rho/2}$$

$$\frac{\partial^2\psi}{\partial\rho^2} = N\left(\tfrac{1}{2}\rho - 2\right) \times \left(-\tfrac{1}{2}\right)\mathrm{e}^{-\rho/2} + \tfrac{1}{2}N\,\mathrm{e}^{-\rho/2} = N\left(\tfrac{3}{2} - \tfrac{1}{4}\rho\right)\mathrm{e}^{-\rho/2}$$

$$\nabla^2\psi = \left(\frac{Z}{a_0}\right)^2 N\mathrm{e}^{-\rho/2}(-4/\rho + 5/2 - \rho/4)$$

and

$$\langle \hat{E}_\mathrm{K} \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} N(2-\rho)\mathrm{e}^{-\rho/2}\left(\frac{Z}{a_0}\right)^2 \times \left(\frac{-\hbar^2}{2m}\right) \times N\mathrm{e}^{-\rho/2}(-4/\rho + 5/2 - \rho/4)\frac{a_0^3\,\mathrm{d}\phi\sin\theta\,\mathrm{d}\theta\,\rho^2\,\mathrm{d}\rho}{Z^3}$$

The integrals over angles give a factor of 4π, so

$$\langle \hat{E}_\mathrm{K} \rangle = 4\pi N^2\left(\frac{a_0}{Z}\right) \times \left(-\frac{\hbar^2}{2m}\right)\int_0^\infty (2-\rho) \times \left(-4 + \frac{5}{2}\rho - \frac{1}{4}\rho^2\right)\rho\mathrm{e}^{-\rho}\,\mathrm{d}\rho$$

The integral in this last expression works out to -2, using $\displaystyle\int_0^\infty \mathrm{e}^{-\rho}\rho^n\,\mathrm{d}\rho = n!$ for $n = 1, 2$, and 3. So

$$\langle \hat{E}_\mathrm{K} \rangle = 4\pi\left(\frac{Z^3}{32\pi a_0^3}\right) \times \left(\frac{a_0}{Z}\right) \times \left(\frac{\hbar^2}{m}\right) = \boxed{\frac{\hbar^2 Z^2}{8ma_0^2}}$$

The average potential energy is

$$\langle V\rangle = \int \psi^* V \psi \, d\tau \text{ where } V = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{Z^2e^2}{4\pi\varepsilon_0 a_0 \rho}$$

$$\text{and } \langle V\rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} N(2-\rho)e^{-\rho/2}\left(-\frac{Z^2e^2}{4\pi\varepsilon_0 a_0\rho}\right)N(2-\rho)e^{-\rho/2}\frac{a_0^3\rho^2\sin\theta\, d\rho\, d\theta\, d\phi}{Z^3}$$

The integrals over angles give a factor of 4π, so

$$\langle V\rangle = 4\pi N^2\left(\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}\right)\times\left(\frac{a_0^3}{Z^3}\right)\int_0^\infty (2-\rho)^2\rho e^{-\rho}\, d\rho$$

The integral in this last expression works out to 2, using $\int_0^\infty e^{-\rho}\rho^n\, d\rho = n!$ for $n = 1, 2, 3$, and 4. So

$$\langle V\rangle = 4\pi\left(\frac{Z^3}{32\pi a_0^3}\right)\times\left(-\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}\right)\times\left(\frac{a_0^3}{Z^3}\right)\times(2) = \boxed{-\frac{Z^2e^2}{16\pi\varepsilon_0 a_0}}$$

E10.6(b) The radial distribution function is defined as

$$P = 4\pi r^2\psi^2 \text{ so } P_{3s} = 4\pi r^2(Y_{0,0}R_{3,0})^2,$$

$$\boxed{P_{3s} = 4\pi r^2\left(\frac{1}{4\pi}\right)\times\left(\frac{1}{243}\right)\times\left(\frac{Z}{a_0}\right)\times(6-6\rho+\rho^2)^2e^{-\rho}}$$

where $\rho \equiv \dfrac{2Zr}{na_0} = \dfrac{2Zr}{3a_0}$ here.

But we want to find the most likely radius, so it would help to simplify the function by expressing it in terms either of r or ρ, but not both. To find the most likely radius, we could set the derivative of P_{3s} equal to zero; therefore, we can collect all multiplicative constants together (including the factors of a_0/Z needed to turn the initial r^2 into ρ^2) since they will eventually be divided into zero

$$P_{3s} = C^2\rho^2(6-6\rho+\rho^2)^2\, e^{-\rho}$$

Note that not all the extrema of P are maxima; some are minima. But all the extrema of $(P_{3s})^{1/2}$ correspond to maxima of P_{3s}. So let us find the extrema of $(P_{3s})^{1/2}$

$$\frac{d(P_{3s})^{1/2}}{d\rho} = 0 = \frac{d}{d\rho}C\rho(6-6\rho+\rho^2)e^{-\rho/2}$$

$$= C[\rho(6-6\rho+\rho^2)\times\left(-\tfrac{1}{2}\right)+(6-12\rho+3\rho^2)]e^{-\rho/2}$$

$$0 = C\left(6-15\rho+6\rho^2-\tfrac{1}{2}\rho^3\right)e^{-\rho/2} \text{ so } 12-30\rho+12\rho^2-\rho^3 = 0$$

Numerical solution of this cubic equation yields

$$\rho = 0.49,\ 2.79,\ \text{and } 8.72$$

corresponding to

$$r = \boxed{0.74a_0/Z,\ 4.19a_0/Z,\ \text{and } 13.08a_0/Z}$$

COMMENT. If numerical methods are to be used to locate the roots of the equation which locates the extrema, then graphical/numerical methods might as well be used to locate the maxima directly. That is, the student may simply have a spreadsheet compute P_{3s} and examine or manipulate the spreadsheet to locate the maxima.

E10.7(b) The most probable radius occurs when the radial wavefunction is a maximum. At this point the derivative of the function wrt either r or ρ equals zero.

$$\left(\frac{dR_{31}}{d\rho}\right)_{max} = 0 = \left(\frac{d\left((4-\rho)\,\rho e^{-\rho/2}\right)}{d\rho}\right)_{max} \text{[Table 10.1]} = \left(4 - 4\rho + \frac{\rho^2}{2}\right)e^{-\rho/2}$$

The function is a maximum when the polynomial equals zero. The quadratic equation gives the roots $\rho = 4 + 2\sqrt{2} = 6.89$ and $\rho = 4 - 2\sqrt{2} = 1.17$. Since $\rho = (2Z/na_0)r$ and $n = 3$, these correspond to $r = 10.3 \times a_0/Z$ and $r = 1.76 \times a_0/Z$. However, $\left|\frac{R_{31}(\rho_1)}{R_{31}(\rho_2)}\right| = \left|\frac{R_{31}(1.17)}{R_{31}(10.3)}\right| = 4.90$. So, we conclude that the function is a maximum at $\rho = 1.17$ which corresponds to $\boxed{r = 1.76a_0/Z.}$

E10.8(b) Orbital angular momentum is

$$\langle \hat{L}^2 \rangle^{1/2} = \hbar(l(l+1))^{1/2}$$

There are l angular nodes and $n - l - 1$ radial nodes

(a) $n = 4, l = 2$, so $\langle \hat{L}^2 \rangle^{1/2} = 6^{1/2}\hbar = \boxed{2.45 \times 10^{-34}\,\text{J s}}$ $\boxed{2}$ angular nodes $\boxed{1}$ radial node

(b) $n = 2, l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34}\,\text{J s}}$ $\boxed{1}$ angular nodes $\boxed{0}$ radial nodes

(c) $n = 3, l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34}\,\text{J s}}$ $\boxed{1}$ angular node $\boxed{1}$ radial node

E10.9(b) For $l > 0$, $j = l \pm 1/2$, so

(a) $l = 1$, so $j = \boxed{1/2 \text{ or } 3/2}$

(b) $l = 5$, so $j = \boxed{9/2 \text{ or } 11/2}$

E10.10(b) Use the Clebsch–Gordan series in the form

$$J = j_1 + j_2,\ j_1 + j_2 - 1, \ldots, |j_1 - j_2|$$

Then, with $j_1 = 5$ and $j_2 = 3$

$$J = \boxed{8, 7, 6, 5, 4, 3, 2}$$

E10.11(b) The degeneracy g of a hydrogenic atom with principal quantum number n is $g = n^2$. The energy E of hydrogenic atoms is

$$E = -\frac{hcZ^2R_H}{n^2} = -\frac{hcZ^2R_H}{g}$$

so the degeneracy is

$$g = -\frac{hcZ^2R_H}{E}$$

(a) $$g = -\frac{hc\,(2)^2\,R_H}{-4hcR_H} = \boxed{1}$$

(b) $$g = -\frac{hc\,(4)^2\,R_H}{-\frac{1}{4}hcR_H} = \boxed{64}$$

(c) $$g = -\frac{hc(5)^2R_H}{-hcR_H} = \boxed{25}$$

E10.12(b) The letter F indicates that the total orbital angular momentum quantum number L is 3; the superscript 3 is the multiplicity of the term, $2S + 1$, related to the spin quantum number $S = 1$; and the subscript 4 indicates the total angular momentum quantum number J.

E10.13(b) The radial distribution function varies as

$$P = 4\pi r^2\psi^2 = \frac{4}{a_0^3}r^2e^{-2r/a_0}$$

The maximum value of P occurs at $r = a_0$ since

$$\frac{dP}{dr} \propto \left(2r - \frac{2r^2}{a_0}\right)e^{-2r/a_0} = 0 \text{ at } r = a_0 \text{ and } P_{max} = \frac{4}{a_0}e^{-2}$$

P falls to a fraction f of its maximum given by

$$f = \frac{(4r^2/a_0^3)e^{-2r/a_0}}{(4/a_0)e^{-2}} = \frac{r^2}{a_0^2}e^2e^{-2r/a_0}$$

and hence we must solve for r in

$$\frac{f^{1/2}}{e} = \frac{r}{a_0}e^{-r/a_0}$$

(a) $f = 0.50$

$0.260 = \frac{r}{a_0}e^{-r/a_0}$ solves to $r = 2.08a_0 = \boxed{110\text{ pm}}$ and to $r = 0.380a_0 = \boxed{20.1\text{ pm}}$

(b) $f = 0.75$

$0.319 = \frac{r}{a_0}e^{-r/a_0}$ solves to $r = 1.63a_0 = \boxed{86\text{ pm}}$ and to $r = 0.555a_0 = \boxed{29.4\text{ pm}}$

In each case the equation is solved numerically (or graphically) with readily available personal computer software. The solutions above are easily checked by substitution into the equation for f. The radial distribution function is readily plotted and is shown in Figure 10.1.

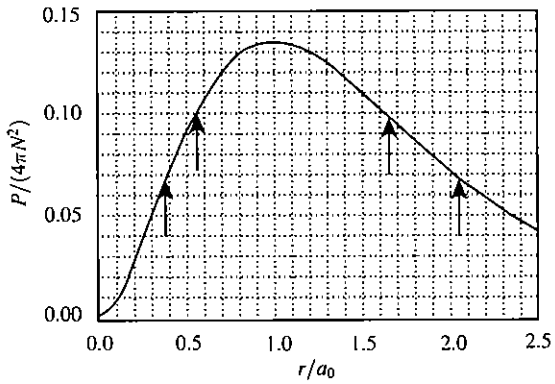


Figure 10.1

E10.14(b) (a) $5d \rightarrow 2s$ is [not] an allowed transition, for $\Delta l = -2$ (Δl must equal ± 1).

(b) $5p \rightarrow 3s$ is [allowed], since $\Delta l = -1$.

(c) $5p \rightarrow 3f$ is [not] allowed, for $\Delta l = +2$ (Δl must equal ± 1).

(d) $6h$: $l = 5$; maximum occupancy = [22]

E10.15(b) V^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 = [Ar]3d^3$

The only unpaired electrons are those in the $3d$ subshell. There are three.

$S =$ [$\frac{3}{2}$] and $\frac{3}{2} - 1 =$ [$\frac{1}{2}$].

For $S = \frac{3}{2}$, $M_S =$ [$\pm\frac{1}{2}$ and $\pm\frac{3}{2}$]

for $S = \frac{1}{2}$, $M_S =$ [$\pm\frac{1}{2}$]

E10.16(b) (a) Possible values of S for four electrons in different orbitals are [2, 1, and 0]; the multiplicity is $2S + 1$, so multiplicities are [5, 3, and 1] respectively.

(b) Possible values of S for five electrons in different orbitals are [5/2, 3/2 and 1/2]; the multiplicity is $2S + 1$, so multiplicities are [6, 4, and 2] respectively.

E10.17(b) The coupling of a p electron ($l = 1$) and a d electron ($l = 2$) gives rise to $L = 3$ (F), 2 (D), and 1 (P) terms. Possible values of S include 0 and 1. Possible values of J (using Russell–Saunders coupling) are 3, 2, and 1 ($S = 0$) and 4, 3, 2, 1, and 0 ($S = 1$). The term symbols are

[$^1F_3; {}^3F_4, {}^3F_3, {}^3F_2; {}^1D_2; {}^3D_3, {}^3D_2, {}^3D_1; {}^1P_1, {}^3P_2, {}^3P_1, {}^3P_0$].

Hund's rules state that the lowest energy level has maximum multiplicity. Consideration of spin–orbit coupling says the lowest energy level has the lowest value of $J(J + 1) - L(L + 1) - S(S + 1)$. So the lowest energy level is [$^3F_2$].

E10.18(b) (a) ^3D has $S = 1$ and $L = 2$, so $J =$ [3, 2, and 1] are present. $J = 3$ has [7] states, with $M_J = 0, \pm 1, \pm 2,$ or ± 3; $J = 2$ has [5] states, with $M_J = 0, \pm 1,$ or ± 2; $J = 1$ has [3] states, with $M_J = 0,$ or ± 1.

(b) ^{4}D has $S = 3/2$ and $L = 2$, so $J =$ $\boxed{7/2, 5/2, 3/2, \text{and } 1/2}$ are present. $J = 7/2$ has $\boxed{8}$ possible states, with $M_J = \pm 7/2, \pm 5/2, \pm 3/2$ or $\pm 1/2$; $J = 5/2$ has $\boxed{6}$ possible states, with $M_J = \pm 5/2, \pm 3/2$ or $\pm 1/2$; $J = 3/2$ has $\boxed{4}$ possible states, with $M_J = \pm 3/2$ or $\pm 1/2$; $J = 1/2$ has $\boxed{2}$ possible states, with $M_J = \pm 1/2$.

(c) ^{2}G has $S = 1/2$ and $L = 4$, so $J = 9/2$ and $7/2$ are present. $J = 9/2$ has $\boxed{10}$ possible states, with $M_J = \pm 9/2, \pm 7/2, \pm 5/2, \pm 3/2$, or $\pm 1/2$; $J = 7/2$ has $\boxed{8}$ possible states, with $M_J = \pm 7/2$, $\pm 5/2, \pm 3/2$, or $\pm 1/2$.

E10.19(b) Closed shells and subshells do not contribute to either L or S and thus are ignored in what follows.

(a) Sc[Ar]$3d^1 4s^2$: $S = \frac{1}{2}, L = 2; J = \frac{5}{2}, \frac{3}{2}$, so the terms are $^2D_{5/2}$ and $^2D_{3/2}$.

(b) Br[Ar]$3d^{10}4s^2 4p^5$. We treat the missing electron in the $4p$ subshell as equivalent to a single "electron" with $l = 1$, $s = \frac{1}{2}$. Hence $L = 1$, $S = \frac{1}{2}$, and $J = \frac{3}{2}, \frac{1}{2}$, so the terms are $\boxed{^2P_{3/2} \text{ and } ^2P_{1/2}}$.

Solutions to problems

Solutions to numerical problems

P10.2 All lines in the hydrogen spectrum fit the Rydberg formula

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \left[10.1, \text{ with } \tilde{\nu} = \frac{1}{\lambda}\right] \qquad R_H = 109\,677\,\text{cm}^{-1}$$

Find n_1 from the value of λ_{max}, which arises from the transition $n_1 + 1 \rightarrow n_1$

$$\frac{1}{\lambda_{max} R_H} = \frac{1}{n_1^2} - \frac{1}{(n_1+1)^2} = \frac{2n_1 + 1}{n_1^2(n_1+1)^2}$$

$$\lambda_{max} R_H = \frac{n_1^2(n_1+1)^2}{2n_1+1} = (656.46 \times 10^{-9}\,\text{m}) \times (109\,677 \times 10^2\,\text{m}^{-1}) = 7.20$$

and hence $n_1 = 2$, as determined by trial and error substitution. Therefore, the transitions are given by

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677\,\text{cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{n_2^2}\right), \quad n_2 = 3, 4, 5, 6$$

The next line has $n_2 = 7$, and occurs at

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677\,\text{cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{49}\right) = \boxed{397.13\,\text{nm}}$$

The energy required to ionize the atom is obtained by letting $n_2 \rightarrow \infty$. Then

$$\tilde{\nu} = \frac{1}{\lambda_\infty} = (109\,677\,\text{cm}^{-1}) \times \left(\frac{1}{4} - 0\right) = 27\,419\,\text{cm}^{-1}, \quad \text{or} \quad \boxed{3.40\,\text{eV}}$$

(The answer, 3.40 eV, is the ionization energy of an H atom that is already in an excited state, with $n = 2$.)

COMMENT. The series with $n_1 = 2$ is the Balmer series.

P10.4 The lowest possible value of n in $1s^2nd^1$ is 3; thus the series of ^{2}D terms correspond to $1s^23d$, $1s^24d$, etc. Figure 10.2 is a description consistent with the data in the problem statement.

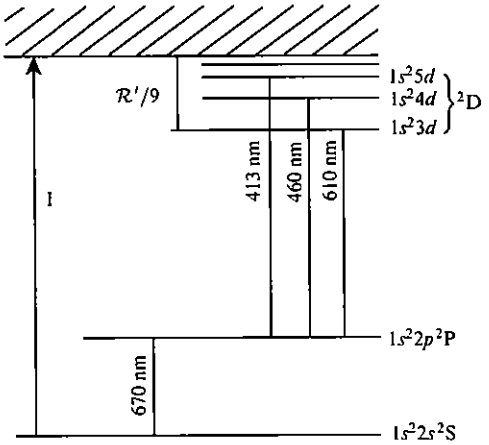


Figure 10.2

If we assume that the energies of the d orbitals are hydrogenic we may write

$$E(1s^2nd^1, {}^2\mathrm{D}) = -\frac{hcR'}{n^2} \quad [n = 3, 4, 5, \mathrm{L}]$$

Then for the ^{2}D $\rightarrow$ ^{2}P transitions

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{|E(1s^22p^1, {}^2\mathrm{P})|}{hc} - \frac{R'}{n^2} \qquad \left[\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu},\ \tilde{\nu} = \frac{\Delta E}{hc}\right]$$

from which we can write

$$\frac{|E(1s^22p^1, {}^2\mathrm{P})|}{hc} = \frac{1}{\lambda} + \frac{R'}{n^2} = \begin{cases} \dfrac{1}{610.36 \times 10^{-7}\,\mathrm{cm}} + \dfrac{R'}{9} & \text{(a)} \\ \dfrac{1}{460.29 \times 10^{-7}\,\mathrm{cm}} + \dfrac{R'}{16} & \text{(b)} \\ \dfrac{1}{413.23 \times 10^{-7}\,\mathrm{cm}} + \dfrac{R'}{25} & \text{(c)} \end{cases}$$

Then
$$\left.\begin{array}{l} \text{(b) } - \text{ (a) solves to } R' = 109\,886\,\mathrm{cm}^{-1} \\ \text{(a) } - \text{ (c) solves to } R' = 109\,910\,\mathrm{cm}^{-1} \\ \text{(b) } - \text{ (c) solves to } R' = 109\,963\,\mathrm{cm}^{-1} \end{array}\right\} \text{ Mean } = 109\,920\,\mathrm{cm}^{-1}$$

The binding energies are therefore

$$E(1s^23d^1, {}^2\mathrm{D}) = \frac{R'}{9} = -12\,213\,\mathrm{cm}^{-1}$$

$$E(1s^22p, {}^2\mathrm{P}) = -\frac{1}{610.36 \times 10^{-7}\,\mathrm{cm}} - 12\,213\,\mathrm{cm}^{-1} = -28\,597\mathrm{cm}^{-1}$$

$$E(1s^22s^1, {}^2\mathrm{S}) = -\frac{1}{670.78 \times 10^{-7}\,\mathrm{cm}} - 28\,597\,\mathrm{cm}^{-1} = -43\,505\,\mathrm{cm}^{-1}$$

Therefore, the ionization energy is

$$I(1s^2 2s^1, {}^2\mathrm{S}) = 43\,505\,\mathrm{cm}^{-1}, \quad \text{or} \quad \boxed{5.39\,\mathrm{eV}}$$

P10.6 The ground term is $[\mathrm{Ar}]4s^1\,{}^2\mathrm{S}_{1/2}$ and the first excited is $[\mathrm{Ar}]4p^1\,{}^2\mathrm{P}$. The latter has two levels with $J = 1 + \frac{1}{2} = \frac{3}{2}$ and $J = 1 - \frac{1}{2} = \frac{1}{2}$ which are split by spin–orbit coupling (Section 10.8). Therefore, ascribe the transitions to $\boxed{{}^2\mathrm{P}_{3/2} \rightarrow {}^2\mathrm{S}_{1/2}}$ and $\boxed{{}^2\mathrm{P}_{1/2} \rightarrow {}^2\mathrm{S}_{1/2}}$ (since both are allowed). For these values of J, the splitting is equal to $\frac{3}{2}A$ (Example 10.5). Hence, since

$$(766.70 \times 10^{-7}\,\mathrm{cm})^{-1} - (770.11 \times 10^{-7}\,\mathrm{cm})^{-1} = 57.75\,\mathrm{cm}^{-1}$$

we can conclude that $A = \boxed{38.50\ \mathrm{cm}^{-1}}$

P10.8 The Rydberg constant for positronium (R_{Ps}) is given by

$$R_{\mathrm{Ps}} = \frac{R}{1 + \dfrac{m_e}{m_e}} = \frac{R}{1+1} = \frac{1}{2}R \quad [10.16; \text{ also Problem } 10.7;\ m\ (\text{positron}) = m_e]$$

$$= 54\,869\,\mathrm{cm}^{-1}\ [R = 109\,737\,\mathrm{cm}^{-1}]$$

Hence

$$\tilde{\nu} = \frac{1}{\lambda} = (54\,869\,\mathrm{cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{n^2}\right), \quad n = 3, 4, \ldots$$

$$= \boxed{7621\,\mathrm{cm}^{-1}}, \boxed{10\,288\,\mathrm{cm}^{-1}}, \boxed{11\,522\,\mathrm{cm}^{-1}}, \ldots$$

The binding energy of Ps is

$$E = -hc\mathrm{R}_{\mathrm{Ps}}, \text{ corresponding to } (-)54\,869\,\mathrm{cm}^{-1}$$

The ionization energy is therefore $54\,869\,\mathrm{cm}^{-1}$, or $\boxed{6.80\,\mathrm{eV}}$.

P10.10 If we assume that the innermost electron is a hydrogen-like $1s$ orbital we may write

$$r^* = \frac{a_0}{Z}\,[\text{Example } 10.3] = \frac{52.92\,\mathrm{pm}}{126} = \boxed{0.420\,\mathrm{pm}}$$

Solutions to theoretical problems

P10.12 In each case we need to show that

$$\int_{\text{all space}} \psi_1^* \psi_2\,\mathrm{d}\tau = 0$$

(a)
$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{1s}\psi_{2s} r^2\,\mathrm{d}r \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = 0$$

$$\left.\begin{aligned}\psi_{1s} &= R_{1,0}Y_{0,0}\\ \psi_{2s} &= R_{2,0}Y_{0,0}\end{aligned}\right\} Y_{0,0} = \left(\frac{1}{4\pi}\right)^{1/2} \quad [\text{Table } 9.3]$$

Since $Y_{0,0}$ is a constant, the integral over the radial functions determines the orthogonality of the functions.

$$\int_0^\infty R_{1,0}R_{2,0}r^2\,\mathrm{d}r$$

$$R_{1,0} \propto \mathrm{e}^{-\rho/2} = \mathrm{e}^{-Zr/a_0} \quad \left[\rho = \frac{2Zr}{a_0}\right]$$

$$R_{2,0} \propto (2-\rho/2)\mathrm{e}^{-\rho/4} = \left(2 - \frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0} \quad \left[\rho = \frac{2Zr}{a_0}\right]$$

$$\int_0^\infty R_{1,0}, R_{2,0}r^2\,\mathrm{d}r \propto \int_0^\infty \mathrm{e}^{-Zr/a_0}\left(2 - \frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0}r^2\,\mathrm{d}r$$

$$= \int_0^\infty 2\mathrm{e}^{-(3/2)Zr/a_0}r^2\,\mathrm{d}r - \int_0^\infty \frac{Z}{a_0}\mathrm{e}^{-(3/2)Zr/a_0}r^3\,\mathrm{d}r$$

$$= \frac{2 \times 2!}{\left(\frac{3}{2}\frac{z}{a_0}\right)^3} - \left(\frac{Z}{a_0}\right) \times \frac{3!}{\left(\frac{3}{2}\frac{z}{a_0}\right)^4} = \boxed{0}$$

Hence, the functions are orthogonal.

(b) We use the p_x and p_y orbitals in the form given in Section 10.2(f), eqn 10.24

$$p_x \propto x, \qquad p_y \propto y$$

Thus

$$\int_{\text{all space}} p_x\,p_y\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \propto \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} xy\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

This is an integral of an odd function of x and y over the entire range of variable from $-\infty$ to $+\infty$, therefore, the $\boxed{\text{integral is zero}}$. More explicitly we may perform the integration using the orbitals in the form (Section 10.2(f), eqn 10.24)

$$p_x = f(r)\sin\theta\cos\phi \quad p_y = f(r)\sin\theta\sin\phi$$

$$\int_{\text{all space}} p_x\,p_y\,r^2\,\mathrm{d}r\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \int_0^\infty f(r)^2r^2\,\mathrm{d}r\int_0^\pi \sin^2\theta\,\mathrm{d}\theta\int_0^{2\pi}\cos\phi\sin\phi\,\mathrm{d}\phi$$

The first factor is nonzero since the radial functions are normalized. The second factor is $\pi/2$. The third factor is zero. Therefore, the product of the integrals is $\boxed{\text{zero}}$ and the functions are orthogonal.

P10.14 We use the p_x and p_y orbitals in the form (Section 10.2(f))

$$p_x = rf(r)\sin\theta\cos\phi \qquad p_y = rf(r)\sin\theta\sin\phi$$

and use $\cos\phi = \frac{1}{2}(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi})$ and $\sin\phi = \frac{1}{2\mathrm{i}}(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi})$ then

$$p_x = \frac{1}{2}rf(r)\sin\theta(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}) \qquad p_y = \frac{1}{2\mathrm{i}}rf(r)\sin\theta(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi})$$

$\hat{l}_z = \dfrac{\hbar}{\mathrm{i}}\dfrac{\partial}{\partial\phi}$ [Problem 9.28 and Section 9.6 and eqn 9.46]

$$\hat{l}_z p_x = \frac{\hbar}{2} r f(r) \sin\theta\, \mathrm{e}^{\mathrm{i}\phi} - \frac{\hbar}{2} r f(r) \sin\theta\, \mathrm{e}^{-\mathrm{i}\phi} = \mathrm{i}\hbar p_y \neq \text{ constant } \times p_x$$

$$\hat{l}_z p_y = \frac{\hbar}{2\mathrm{i}} r f(r) \sin\theta\, \mathrm{e}^{\mathrm{i}\phi} + \frac{\hbar}{2\mathrm{i}} r f(r) \sin\theta\, \mathrm{e}^{-\mathrm{i}\phi} = -\mathrm{i}\hbar p_x \neq \text{ constant } \times p_y$$

Therefore, neither p_x nor p_y are eigenfunctions of $\hat{l}_z$. However, $\boxed{p_x + \mathrm{i}p_y \text{ and } p_x - \mathrm{i}p_y}$ are eigenfunctions

$$p_x + \mathrm{i}p_y = r f(r) \sin\theta\, \mathrm{e}^{\mathrm{i}\phi} \qquad p_x - \mathrm{i}p_y = r f(r) \sin\theta\, \mathrm{e}^{-\mathrm{i}\phi}$$

since both $\mathrm{e}^{\mathrm{i}\phi}$ and $\mathrm{e}^{-\mathrm{i}\phi}$ are eigenfunctions of $\hat{l}_z$ with eigenvalues $+h$ and $-h$.

P10.16 $$\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \mathrm{e}^{-r/a_0} \text{ [10.18]}$$

The probability of the electron being within a sphere of radius r' is

$$\int_0^{r'} \int_0^{\pi} \int_0^{2\pi} \psi_{1s}^2 r^2 \,\mathrm{d}r \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi$$

We set this equal to 0.90 and solve for r'. The integral over θ and ϕ gives a factor of 4π; thus

$$0.90 = \frac{4}{a_0^3} \int_0^{r'} r^2 \mathrm{e}^{-2r/a_0} \,\mathrm{d}r$$

$\displaystyle\int_0^{r'} r^2 \mathrm{e}^{-2r/a_0} \,\mathrm{d}r$ is integrated by parts to yield

$$-\frac{a_0 r^2 \mathrm{e}^{-2r/a_0}}{2}\bigg|_0^{r'} + a_0 \left[-\frac{a_0 r \mathrm{e}^{-2r/a_0}}{2}\bigg|_0^{r'} + \frac{a_0}{2}\left(-\frac{a_0 \mathrm{e}^{-2r/a_0}}{2} \right)\bigg|_0^{r'} \right]$$

$$= -\frac{a_0 (r')^2 \mathrm{e}^{-2r'/a_0}}{2} - \frac{a_0^2 r'}{2}\mathrm{e}^{-2r'/a_0} - \frac{a_0^3}{4}\mathrm{e}^{-2r'/a_0} + \frac{a_0^3}{4}$$

Multiplying by $4/a_0^3$ and factoring e^{-2r'/a_0}

$$0.90 = \left[-2\left(\frac{r'}{a_0}\right)^2 - 2\left(\frac{r'}{a_0}\right) - 1 \right] \mathrm{e}^{-2r'/a_0} + 1 \text{ or } 2\left(\frac{r'}{a_0}\right)^2 + 2\left(\frac{r'}{a_0}\right) + 1 = 0.10\,\mathrm{e}^{2r'/a_0}$$

It is easiest to solve this numerically. It is seen that $\boxed{r' = 2.66 a_0}$ satisfies the above equation.

Mathematical software has powerful features for handling this type of problem. Plots are very convenient to both make and use. Solve blocks can be used as functions. Both features are demonstrated

below using Mathcad.

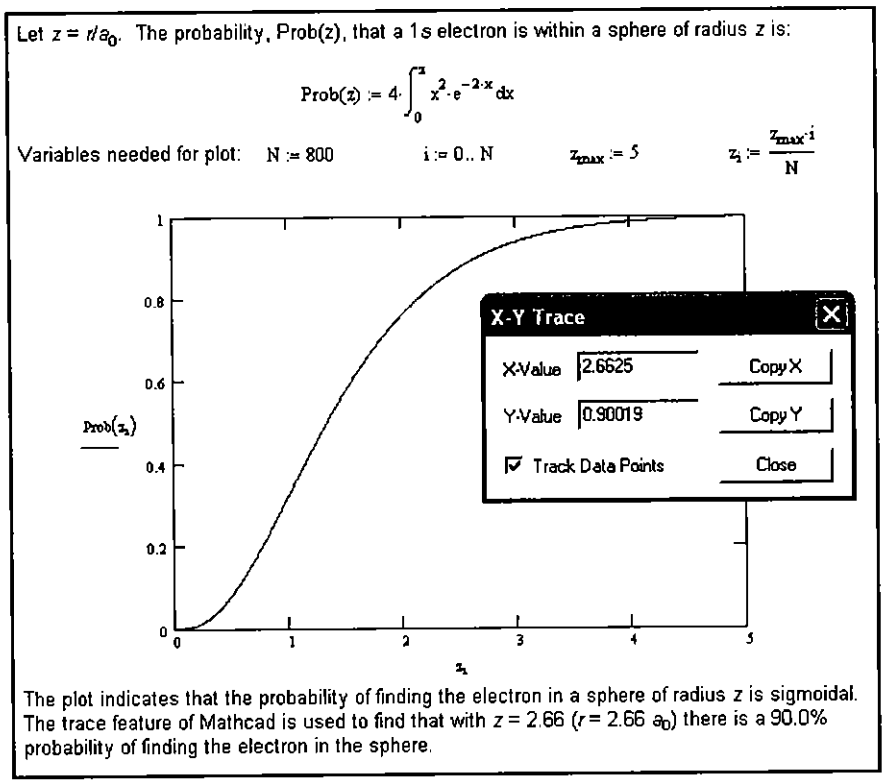


Figure 10.3(a)

The following Mathcad document develops a function for calculating the radius for any desired probability. The probability is presented to the function as an argument

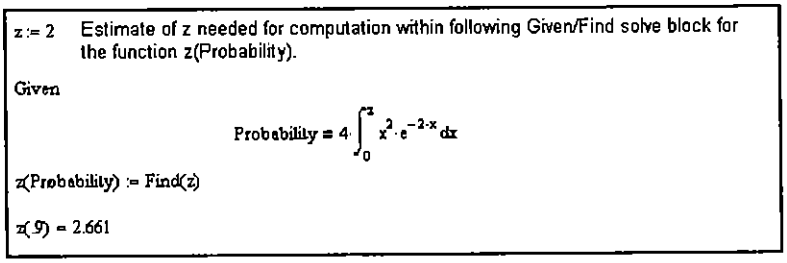


Figure 10.3(b)

P10.18 The attractive Coulomb force $= \dfrac{Ze^2}{4\pi\varepsilon_0} \cdot \dfrac{1}{r^2}$

The repulsive centrifugal force $= \dfrac{(\text{angular momentum})^2}{m_e r^3} = \dfrac{(n\hbar)^2}{m_e r^3}$ [postulated]

The two forces balance when

$$\frac{Ze^2}{4\pi\varepsilon_0} \times \frac{1}{r^2} = \frac{n^2\hbar^2}{m_e r^3}, \text{ implying that } r = \frac{4\pi n^2 \hbar^2 \varepsilon_0}{Ze^2 m_e}$$

The total energy is

$$E = E_K + V = \frac{(\text{angular momentum})^2}{2I} - \frac{Ze^2}{4\pi\varepsilon_0} \times \frac{1}{r} = \frac{n^2\hbar^2}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r} \text{ [postulated]}$$

$$= \left(\frac{n^2\hbar^2}{2m_e}\right) \times \left(\frac{Ze^2 m_e}{4\pi n^2\hbar^2\varepsilon_0}\right)^2 - \left(\frac{Ze^2}{4\pi\varepsilon_0}\right) \times \left(\frac{Ze^2 m_e}{4\pi n^2\hbar^2\varepsilon_0}\right) = \boxed{\frac{Z^2 e^4 m_e}{32\pi^2\varepsilon_0^2\hbar^2} \times \frac{1}{n^2}}$$

P10.20 Refer to Problems 10.8 and 10.18 and their solutions.

$$\mu_H = \frac{m_e m_p}{m_e + m_p} \approx m_e \quad [m_p = \text{mass of proton}]$$

$$\mu_{Ps} = \frac{m_e m_{pos}}{m_e + m_{pos}} = \frac{m_e}{2} \quad [m_{pos} = \text{mass of proton} = m_e]$$

$$a_0 = r(n = 1) = \frac{4\pi\hbar^2\varepsilon_0}{e^2 m_e} \text{ [10.13 and Problem 10.18]}$$

To obtain a_{Ps} the radius of the first Bohr orbit of positronium, we replace m_e with $\mu_{Ps} = m_e/2$; hence,

$$\boxed{a_{Ps} = 2a_0} = \frac{\pi\hbar^2\varepsilon_0}{e^2 m_e}$$

The energy of the first Bohr orbit of positronium is

$$E_{1,Ps} = -hcR_{Ps} = -\frac{hc}{2}R_\infty \text{ [Problem 10.8]}$$

Thus, $\boxed{E_{1,Ps} = \frac{1}{2}E_{1,H}}$

Question. What modifications are required in these relations when the finite mass of the hydrogen nucleus is recognized?

P10.22 **(a)** The speed distribution in the molecular beam is related to the speed distribution within the chamber by a factor of $v\cos\theta$ as shown in Figure 10.4. Since an integration over all possible θ must be performed, the $\cos\theta$ factor may be absorbed into the constant of proportionality.

$$f_{beam}(v) = Cvf_{chamber}(v) \quad \text{where } C \text{ is to be determined}$$

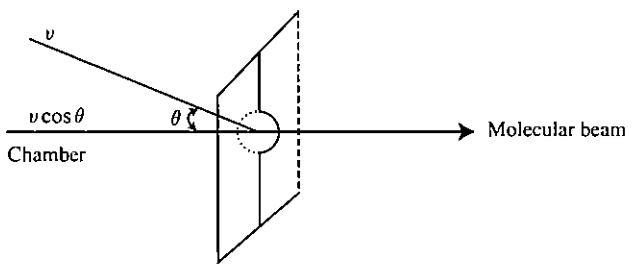


Figure 10.4

By normalization over the possible beam speeds ($0 < v_{\text{beam}} < \infty$)

$$f_{\text{beam}} = Cv\left(v^2 e^{-(mv^2/2kT)}\right)$$
$$= Cv^3 e^{-(mv^2/2kT)}$$
$$\int_{v=0}^{\infty} f_{\text{beam}}\,dv = 1 = C\int_{v=0}^{\infty} v^3 e^{-(mv^2/2kT)}\,dv = C\left\{\frac{1}{2(m/2kT)^2}\right\}$$
$$C = 2(m/2kT)^2$$
$$\langle v^2\rangle = \int_{v=0}^{\infty} v^2 f_{\text{beam}}(v)\,dv = C\int v^5 e^{-(mv^2/2kT)}\,dv$$
$$= C\left\{\frac{1}{(m/2kT)^3}\right\} = 2\frac{(m/2kT)^2}{(m/2kT)^3}$$
$$= \frac{4kT}{m}$$
$$\langle E_K\rangle = \frac{m}{2}\langle v^2\rangle = \frac{m}{2}\left(\frac{4kT}{m}\right) = \boxed{2kT}$$

(b)
$$\Delta x = \left(\frac{2\mu_B L^2}{4E_K}\right)\frac{dB}{dz}$$
$$\frac{dB}{dz} = \frac{4E_K\Delta x}{2\mu_B L^2} = \frac{4(2kT)\Delta x}{2\mu_B L^2}$$
or
$$= \frac{4kT\Delta x}{\mu_B L^2}$$
$$= \frac{4(1.3807\times10^{-23}\,\text{J K}^{-1})\times(1000\,\text{K})\times(1.00\times10^{-3}\,\text{m})}{(9.27402\times10^{-24}\,\text{J T}^{-1})\times(50\times10^{-2}\,\text{m})^2}$$
$$\frac{dB}{dz} = \boxed{23.8\,\text{T m}^{-1}}$$

Solutions to applications

P10.24 A stellar surface temperature of 3000–4000 K (a "red star") doesn't have the energetic particles and photons that are required for either the collisional or radiation excitation of a neutral hydrogen atom. Atomic hydrogen affects neither the absorption nor the emission lines of red stars in the absence of excitation. "Blue stars" have surface temperature of 15 000–20 000 K. Both the kinetic energy and the blackbody emissions display energies great enough to completely ionize hydrogen. Lacking an electron, the remaining proton cannot affect absorption and emission lines either.

In contrast, a star with a surface temperature of 8000–10 000 K has a temperature low enough to avoid complete hydrogen ionization but high enough for blackbody radiation to cause electronic transitions of atomic hydrogen. Hydrogen spectral lines are intense for these stars.

Simple kinetic energy and radiation calculations confirm these assertions. For example, a plot of blackbody radiation against the radio photon energy and the ionization energy, I, is shown below. It is clearly

seen that at 25 000 K a large fraction of the radiation is able to ionize the hydrogen ($h\nu/I$). It is likely that at such high surface temperatures all hydrogen is ionized and, consequently, unable to affect spectra.

Alternatively, consider the equilibrium between hydrogen atoms and their component charged particles:

$$H = H^+ + e^-$$

The equilibrium constant is:

$$K = \frac{p_+ p_-}{p_H p^\ominus} = \exp\left(\frac{-\Delta G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta H^\ominus}{RT}\right) \times \exp\left(\frac{-\Delta S^\ominus}{R}\right).$$

Clearly $\Delta S^\ominus$ is positive for ionization, which makes two particles out of one, and $\Delta H^\ominus$, which is close to the ionization energy, is also positive. At a sufficiently high temperature, ions will outnumber neutral molecules. Using concepts developed in Chapters 16 and 17, one can compute the equilibrium constant; it turns out to be 60. Hence, there are relatively few undissociated H atoms in the equilibrium mixture that is consistent with the weak spectrum of neutral hydrogen observed.

The details of the calculation of the equilibrium constant based on the methods of Chapter 17 follows. Consider the equilibrium between hydrogen atoms and their component charged particles:

$$H = H^+ + e^-.$$

The equilibrium constant is:

$$K = \frac{p_+ p_-}{p_H p^\ominus} = \exp\left(\frac{-\Delta G^\ominus}{RT}\right).$$

Jump ahead to Section 17.7(b) to use the statistical thermodynamic analysis of a dissociation equilibrium:

$$K = \frac{q_+^\ominus q_-^\ominus}{q_H^\ominus N_A} e^{-\Delta_r E_0/RT}.$$

where $q^\ominus = \dfrac{RT}{gp^\ominus \Lambda^3}$ and $\Lambda = \left(\dfrac{h^2}{2\pi kTm}\right)^{1/2}$

and where g is the degeneracy of the species. Note that $g_+ = 2$, $g_- = 2$, and $g_H = 4$. Consequently, these factors cancel in the expression for K.

$$\text{So } K = \frac{RT}{p^\ominus N_A}\left(\frac{2\pi kT}{h^2}\right)^{3/2}\left(\frac{m_- m_+}{m_H}\right)^{3/2} e^{-\Delta_r E_0/RT}$$

Note that the Boltzmann, Avogadro, and perfect gas constants are related ($R = N_A k$), and collect powers of kT; note also that the product of masses is the reduced mass, which is approximately equal to the mass of the electron; note finally that the molar energy $\Delta_r E_0$ divided by R is the same as the atomic

ionization energy (2.179×10^{-18} J from Chapter 10.2(b)) divided by k:

$$K = \frac{(kT)^{5/2}(2\pi m_e)^{3/2}}{p^{\ominus}h^3} e^{-E/kT},$$

$$K = \frac{\left[(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}})\,(25\,000\,\mathrm{K})\right]^{5/2}\left[2\pi\,(9.11 \times 10^{-31}\,\mathrm{Kg})\right]^{3/2}}{(10^5\,\mathrm{Pa})\,(6.626 \times 10^{-34}\,\mathrm{J\,s})^3}$$

$$\times \exp\left(\frac{-2.179 \times 10^{-18}\,\mathrm{J}}{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}})\,(25\,000\,\mathrm{K})}\right).$$

$$K = 60.$$

Thus, the equilibrium favors the ionized species, even though the ionization energy is greater than kT.

P10.26 $E_n = -\dfrac{hcR_H}{n^2}$ where $R_H = 109\,677\,\mathrm{cm^{-1}}$ [10.11 with 10.15]

For $n = 100$

$$\Delta E = E_{n+1} - E_n = -hcR_H\left(\frac{1}{101^2} - \frac{1}{100^2}\right) = 1.97 \times 10^{-6} hcR$$

$$\tilde{\nu} = \frac{\Delta E}{hc} = 1.97 \times 10^{-6} R = \boxed{0.216\,\mathrm{cm^{-1}}}$$

$$\langle r\rangle_{n,l} = n^2\left\{1 + \frac{1}{2} + \left(1 - \frac{l(l+1)}{n^2}\right)\right\}\frac{a_0}{Z}\ [10.19]$$

$$\langle r\rangle_{100} \approx \frac{n^2 a_0}{Z} = 100^2 a_0 = 10^4 a_0 = \boxed{529\,\mathrm{nm}}$$

$$I = E_\infty - E_n = -E_n = \frac{hcR_H}{n^2}$$

$$I_{100} = 10^{-4} hcR_H \text{ so } \boxed{\frac{I_{100}}{hc} = 10.9677\,\mathrm{cm^{-1}}}$$

At T

$$\frac{kT}{hc} = \frac{(1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})\left(\dfrac{\mathrm{m}}{10^2\,\mathrm{cm}}\right)}{(6.63 \times 10^{-34}\,\mathrm{J\,s}) \times (3.00 \times 10^8\,\mathrm{m\,s^{-1}})} = 207\,\mathrm{cm^{-1}}$$

so the thermal energy is readily available to ionize the state $n = 100$. Let v_{min} be the minimum speed required for collisional ionization. Then

$$\frac{1}{2}\frac{m_H v_{min}^2}{hc} = \frac{I_{100}}{hc}$$

$$v_{min} = \left[\frac{2hc}{m_H}\left(\frac{I_{100}}{hc}\right)\right]^{1/2}$$

$$= \sqrt{\frac{2(6.63 \times 10^{-34}\,\mathrm{J\,s}) \times (3.00 \times 10^8\,\mathrm{m\,s^{-1}}) \times (10.97\,\mathrm{cm^{-1}})}{(1.008 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})^{-1} \times \left(\dfrac{\mathrm{m}}{10^2\,\mathrm{cm}}\right)}}$$

$\boxed{v_{min} = 511\,\mathrm{m\,s^{-1}}}$ [very slow for an H atom]

The radius of a Bohr orbit is $a_n \approx n^2 a_0$; hence the geometric cross-section $\pi a_n^2 \approx n^4 \pi a_0^2$. For $n = 1$ this is 8.8×10^{-21} m^2; for $n = 100$, it is $\boxed{8.8 \times 10^{-13} \text{ m}^2}$. Thus a neutral H atom in its ground state is likely to pass right by the $n = 100$ Rydberg atom, leaving it undisturbed, since it is largely empty space.

The radial wavefunction for $n = 100$ will have 99 radial nodes and an extremely small amplitude above $r/a_0 \approx 20$. For large values of n we expect the radial wavefunction [10.14] to be governed largely by the product of ρ^{n-1} and $e^{-\rho/2n}$ and thus to approach a smoothly decreasing function of distance, as the exponential will predominate over the power term.

P10.28 Electronic configurations of neutral, fourth period transition atoms in the ground state are summarized in the following table along with observed, positive oxidation states. The most common, positive oxidation states are indicated with bright boxing.

Group	3	4	5	6	7	8	9	10	11	12
Oxidation State	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0	$3d4s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s$	$3d^{10}4s^2$
+1					☺		☺	☺	☺	
+2					☺	☺	☺	☺	☺	☺
+3	☺	☺		☺	☺	☺	☺	☺		
+4		☺	☺		☺					
+5			☺							
+6				☺						
+7					☺					

Toward the middle of the first transition series (Cr, Mn, and Fe) elements exhibit the widest ranges of oxidation states. This phenomenon is related to the availability of both electrons and orbitals favorable for bonding. Elements to the left (Sc and Ti) of the series have few electrons and relatively low effective nuclear charge leaves d orbitals at high energies that are relatively unsuitable for bonding. To the far right (Cu and Zn) effective nuclear charge may be higher but there are few, if any, orbitals available for bonding. Consequently, it is more difficult to produce a range of compounds that promote a wide range of oxidation states for elements at either end of the series. At the middle and right of the series the +2 oxidation state is very commonly observed because normal reactions can provide the requisite ionization energies for the removal of $4s$ electrons. The readily available +2 and +3 oxidation states of Mn, Fe, and the +1 and +2 oxidation states of Cu make these cations useful in electron transfer processes occurring chains of specialized protein within biological cells. The special size and charge of the Zn^{2+} cation makes it useful for the function of some enzymes. The tendency of Fe^{2+} and Cu^{+} to bind oxygen proves very useful in hemoglobin and electron transport (respiratory) chain, respectively.

11 Molecular structure

Answers to discussion questions

D11.2 Consider the case of the carbon atom. Mentally we break the process of hybridization into two major steps. The first is promotion, in which we imagine that one of the electrons in the $2s$ orbital of carbon ($2s^2 2p^2$) is promoted to the empty $2p$ orbital giving the configuration $2s2p^3$. In the second step we mathematically mix the four orbitals by way of the specific linear combinations in eqn 11.3 corresponding to the sp^3 hybrid orbitals. There is a principle of conservation of orbitals that enters here. If we mix four unhybridized atomic orbitals we must end up four hybrid orbitals. In the construction of the sp^2 hybrids we start with the $2s$ orbital and two of the $2p$ orbitals, and after mixing we end up with three sp^2 hybrid orbitals. In the sp case we start with the $2s$ orbital and one of the $2p$ orbitals. The justification for all of this is in a sense the First Law of thermodynamics. Energy is a state function and therefore its value is determined only by the final state of the system, not by the path taken to achieve that state, and the path can even be imaginary.

D11.4 It can be proven that if an arbitrary wavefunction is used to calculate the energy of a system, the value calculated is never less than the true energy. This is the variation principle. This principle allows us an enormous amount of latitude in constructing wavefunctions. We can continue modifying the wavefunctions in any arbitrary manner until we find a set that we feel provides an energy close to the true minimum in energy. Thus we can construct wavefunctions containing many parameters and then minimize the energy with respect to those parameters. These parameters may or may not have some chemical or physical significance. Of course, we might strive to construct trial wavefunctions that provide some chemical and physical insight and an interpretation that we can perhaps visualize, but that is not essential. Examples of the mathematical steps involved are illustrated in Sections 11.5(c) and (d), *Justification* 11.3, and Section 11.6.

D11.6 These are all terms originally associated with the Hückel approximation used in the treatment of conjugated π-electron molecules, in which the π-electrons are considered independent of the σ-electrons. π-electron binding energy is the sum of the energies of each π-electron in the molecule. The delocalization energy is the difference in energy between the conjugated molecule with n double bonds and the energy of n ethene molecules, each of which has one double bond. The π-bond formation energy is the energy released when a π-bond is formed. It is obtained from the total π-electron binding energy by subtracting the contribution from the Coulomb integrals, α.

D11.8 In *ab initio* methods an attempt is made to evaluate all integrals that appear in the secular determinant. Approximations are still employed, but these are mainly associated with the construction of the wavefunctions involved in the integrals. In semi-empirical methods, many of the integrals are expressed in terms of spectroscopic data or physical properties. Semi-empirical methods exist at several levels. At some levels, in order to simplify the calculations, many of the integrals are set equal to zero. Density functional theory (DFT) is considered an *ab initio* method, but it is different from the Hartree–Fock (HF) or self-consistent field (SCF) approach in that DFT focuses on the electron density while HF/SCF methods focus on the wavefunction. They are both iterative self consistent methods in that the calculations are repeated until the energy and wavefunctions (HF) or energy and electron density (DFT) are unchanged to within some acceptable tolerance.

Solutions to exercises

E11.1(b) Use Figure 11.23 for H_2^-, 11.33 for N_2, and 11.31 for O_2.

(a) H_2^- (3 electrons) : $\boxed{1\sigma^2 2\sigma^{*1}}$ $b = 0.5$

(b) N_2 (10 electrons) : $\boxed{1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2}$ $b = 3$

(c) O_2 (12 electrons) : $\boxed{1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}}$ $b = 2$

E11.2(b) ClF is isoelectronic with F_2, CS with N_2.

(a) ClF (14 electrons) : $\boxed{1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}}$ $b = 1$

(b) CS (10 electrons) : $\boxed{1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2}$ $b = 3$

(c) O_2^- (13 electrons) : $\boxed{1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*3}}$ $b = 1.5$

E11.3(b) Decide whether the electron added or removed increases or decreases the bond order. The simplest procedure is to decide whether the electron occupies or is removed from a bonding or antibonding orbital. We can draw up the following table, which denotes the orbital involved

	N_2	NO	O_2	C_2	F_2	CN
(a) AB^-	$2\pi^*$	$2\pi^*$	$2\pi^*$	3σ	$4\sigma^*$	3σ
Change in bond order	$-1/2$	$-1/2$	$-1/2$	$+1/2$	$-1/2$	$+1/2$
(b) AB^+	3σ	$2\pi^*$	$2\pi^*$	1π	$2\pi^*$	3σ
Change in bond order	$-1/2$	$+1/2$	$+1/2$	$-1/2$	$+1/2$	$-1/2$

(a) Therefore, $\boxed{C_2 \text{ and CN}}$ are stabilized (have lower energy) by anion formation.

(b) $\boxed{\text{NO, } O_2 \text{ and } F_2}$ are stabilized by cation formation; in each of these cases the bond order increases.

E11.4(b) Figure 11.1 is based on Figure 11.31 of the text but with Cl orbitals lower than Br orbitals. BrCl is likely to have a shorter bond length than $BrCl^-$; it has a bond order of 1, while $BrCl^-$ has a bond order of 1/2.

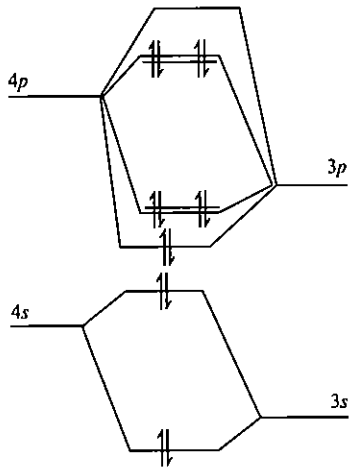


Figure 11.1

E11.5(b) O_2^+(11 electrons): $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*1}$ $b = 5/2$

O_2(12 electrons): $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$ $b = 2$

O_2^-(13 electrons): $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*3}$ $b = 3/2$

O_2^{2-}(14 electrons): $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$ $b = 1$

Each electron added to O_2^+ is added to an antibonding orbital, thus increasing the length. So the sequence $\boxed{O_2^+, O_2, O_2^-, O_2^{2-}}$ has progressively longer bonds.

E11.6(b) $$\int \psi^2 \,\mathrm{d}\tau = N^2 \int (\psi_A + \lambda\psi_B)^2 \,\mathrm{d}\tau = 1 = N^2 \int (\psi_A^2 + \lambda^2\psi_B^2 + 2\lambda\psi_A\psi_B)\,\mathrm{d}\tau = 1$$

$$= N^2(1 + \lambda^2 + 2\lambda S) \quad \left[\int \psi_A\psi_B \mathrm{d}\tau = S\right]$$

Hence $\boxed{N = \left(\frac{1}{1 + 2\lambda S + \lambda^2}\right)^{1/2}}$

E11.7(b) We seek an orbital of the form $aA + bB$, where a and b are constants, which is orthogonal to the orbital $N(0.145A + 0.844B)$. Orthogonality implies

$$\int (aA + bB)N(0.145A + 0.844B)\,\mathrm{d}\tau = 0$$

$$N\int [0.145aA^2 + (0.145b + 0.844a)AB + 0.844bB^2]\,\mathrm{d}\tau = 0$$

The integrals of squares of orbitals are 1 and the integral $\int AB\,\mathrm{d}\tau$ is the overlap integral S, so

$$0 = (0.145 + 0.844S)a + (0.145S + 0.844)b \quad \text{so} \quad a = \boxed{-\frac{0.145S + 0.844}{0.145 + 0.844S}b}$$

This would make the orbitals orthogonal, but not necessarily normalized. If $S = 0$, the expression simplifies to

$$a = -\frac{0.844}{0.145}b$$

and the new orbital would be normalized if $a = 0.844N$ and $b = -0.145N$. That is

$$\boxed{N(0.844A - 0.145B)}$$

E11.8(b) The trial function $\psi = x^2(L - 2x)$ does not obey the boundary conditions of a particle in a box, so it is $\boxed{\text{not appropriate}}$. In particular, the function does not vanish at $x = L$.

E11.9(b) The variational principle says that the minimum energy is obtained by taking the derivative of the trial energy with respect to adjustable parameters, setting it equal to zero, and solving for the parameters:

$$E_{\text{trial}} = \frac{3a\hbar^2}{2\mu} - \frac{e^2}{\varepsilon_0}\left(\frac{a}{2\pi^3}\right)^{1/2} \quad \text{so} \quad \frac{dE_{\text{trial}}}{da} = \frac{3\hbar^2}{2\mu} - \frac{e^2}{2\varepsilon_0}\left(\frac{1}{2\pi^3 a}\right)^{1/2} = 0.$$

Solving for a yields:

$$\frac{3\hbar^2}{2\mu} = \frac{e^2}{2\varepsilon_0}\left(\frac{1}{2\pi^3 a}\right)^{1/2} \quad \text{so} \quad a = \left(\frac{\mu e^2}{3\hbar^2\varepsilon_0}\right)^2\left(\frac{1}{2\pi^3}\right) = \frac{\mu^2 e^4}{18\pi^3\hbar^4\varepsilon_0^2}.$$

Substituting this back into the trial energy yields the minimum energy:

$$E_{\text{trial}} = \frac{3\hbar^2}{2\mu}\left(\frac{\mu^2 e^4}{18\pi^3\hbar^4\varepsilon_0^2}\right) - \frac{e^2}{\varepsilon_0}\left(\frac{\mu^2 e^4}{18\pi^3\hbar^4\varepsilon_0^2 \cdot 2\pi^3}\right)^{1/2} = \boxed{\frac{-\mu e^4}{12\pi^3\varepsilon_0^2\hbar^2}}$$

E11.10(b) Energy is conserved, so when the photon is absorbed, its energy is transferred to the electron. Part of it overcomes the binding energy (ionization energy) and the remainder is manifest as the now freed electron's kinetic energy.

$$E_{\text{photon}} = I + E_{\text{kinetic}}$$

$$\text{so} \quad E_{\text{kinetic}} = E_{\text{photon}} - I = \frac{hc}{\lambda} - I = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^8\,\text{m s}^{-1})}{(584 \times 10^{-12}\,\text{m}) \times (1.602 \times 10^{-19}\,\text{J eV}^{-1})} - 4.69\,\text{eV}$$

$$= \boxed{2.11\overline{9}\,\text{eV}} = \boxed{3.39 \times 10^{-16}\,\text{J}}$$

E11.11(b) The molecular orbitals of the fragments and the molecular orbitals that they form are shown in Figure 11.2.

E11.12(b) We use the molecular orbital energy level diagram in Figure 11.41. As usual, we fill the orbitals starting with the lowest energy orbital, obeying the Pauli principle and Hund's rule. We then write

(a) $C_6H_6^-$ (7 electrons) : $\boxed{a_{2u}^2 e_{1g}^4 e_{2u}^1}$

$$E = 2(\alpha + 2\beta) + 4(\alpha + \beta) + (\alpha - \beta) = \boxed{7\alpha + 7\beta}$$

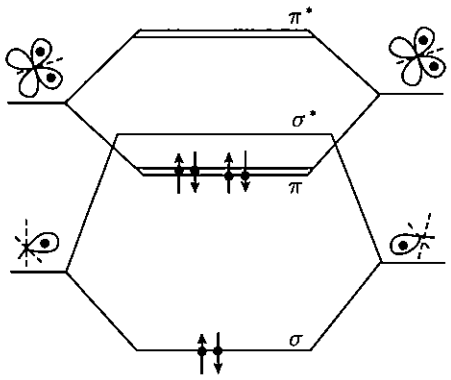


Figure 11.2

(b) $C_6H_6^+$ (5 electrons) : $\boxed{a_{2u}^2 e_{1g}^3}$

$$E = 2(\alpha + 2\beta) + 3(\alpha + \beta) = \boxed{5\alpha + 7\beta}$$

E11.13(b) The secular determinants from E11.13(a) can be diagonalized with the assistance of general-purpose mathematical software. Alternatively, programs specifically designed for Hückel calculations (such as the one at Australia's Northern Territory University, http://www.smps.ntu.edu.au/modules/mod3/interface.html) can be used. In both molecules, 14 π-electrons fill seven orbitals.

(a) In anthracene, the energies of the filled orbitals are $\alpha + 2.414\,21\beta$, $\alpha + 2.000\,00\beta$, $\alpha + 1.414\,21\beta$ (doubly degenerate), $\alpha + 1.000\,00\beta$ (doubly degenerate), and $\alpha + 0.414\,21\beta$, so the total energy is $14\alpha + 19.313\,68\beta$ and the π energy is $\boxed{19.313\,68\beta}$.

(b) For phenanthrene, the energies of the filled orbitals are $\alpha + 2.434\,76\beta$, $\alpha + 1.950\,63\beta$, $\alpha + 1.516\,27\beta$, $\alpha + 1.305\,80\beta$, $\alpha + 1.142\,38\beta$, $\alpha + 0.769\,05\beta$, $\alpha + 0.605\,23\beta$, so the total energy is $14\alpha + 19.448\,24\beta$ and the π energy is $\boxed{19.448\,24\beta}$.

Solutions to problems

Solutions to numerical problems

P11.2 Draw up the following table

R/a_0	0	1	2	3	4	5	6	7	8	9	10
S	1.000	0.858	0.586	0.349	0.189	0.097	0.047	0.022	0.010	0.005	0.002

The points are plotted in Figure 11.3.

P11.4 Quantitatively correct values of the total amplitude require the properly normalized functions

$$\psi_\pm = \left(\frac{1}{2(1 \pm S)}\right)^{1/2} (A \pm B) \text{ [11.7 and Example 11.1]}$$

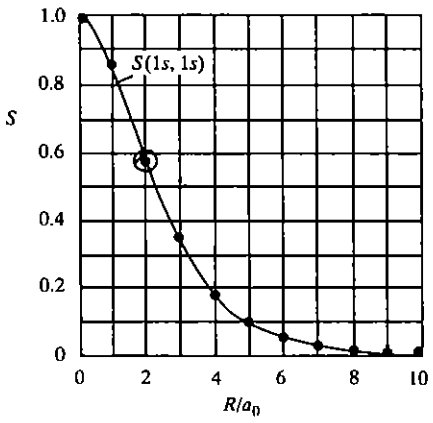


Figure 11.3

We first calculate the overlap integral at $R = 106$ pm $= 2a_0$. (The expression for the overlap integral, S is given in Problem 11.2.)

$$S = \left(1 + 2 + \frac{1}{3}(2)^2\right) e^{-2} = 0.586$$

Then $N_+ = \left(\dfrac{1}{2(1+S)}\right)^{1/2} = \left(\dfrac{1}{2(1+0.586)}\right)^{1/2} = 0.561$

$$N_- = \left(\frac{1}{2(1-S)}\right)^{1/2} = \left(\frac{1}{2(1-0.586)}\right)^{1/2} = 1.09\bar{9}$$

We then calculate with $\psi = \left(\dfrac{1}{\pi a_0^3}\right)^{1/2} e^{-r_A/a_0}$, $\psi_\pm = N_\pm \left(\dfrac{1}{\pi a_0^3}\right)^{1/2} \{e^{-r_A/a_0} \pm e^{-r_B/a_0}\}$ with r_A and r_B both measured from nucleus A, that is

$$\psi_\pm = N_\pm \left(\frac{1}{\pi a_0^3}\right)^{1/2} \{e^{-|z|/a_0} \pm e^{-|z-R|/a_0}\}$$

with z measured from A along the axis toward B. We draw up the following table with $R = 106$ pm and $a_0 = 52.9$ pm.

z/pm	−100	−80	−60	−40	−20	0	20	40
$\dfrac{\psi_+}{(1/\pi a_0^3)^{1/2}}$	0.096	0.14	0.20	0.30	0.44	0.64	0.49	0.42
$\dfrac{\psi_-}{(1/\pi a_0^3)^{1/2}}$	0.14	0.21	0.31	0.45	0.65	0.95	0.54	0.20

z/pm	60	80	100	120	140	160	180	200
$\dfrac{\psi_+}{(1/\pi a_0^3)^{1/2}}$	0.42	0.47	0.59	0.49	0.33	0.23	0.16	0.11
$\dfrac{\psi_-}{(1/\pi a_0^3)^{1/2}}$	−0.11	−0.43	−0.81	−0.73	−0.50	−0.34	−0.23	−0.16

The points are plotted in Figure 11.4.

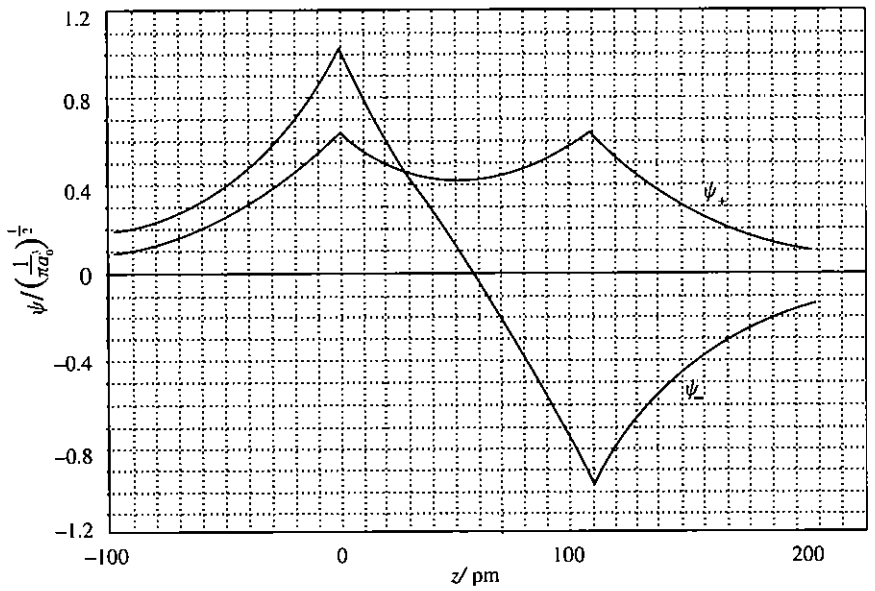
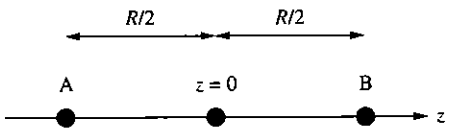


Figure 11.4

P11.6



(a) With spatial dimensions in units (multiples) of a_0, the atomic orbitals of atom A and atom B may be written in the form

$$p_{z,\mathrm{A}} = \frac{1}{4(2\pi)^{1/2}}(z + R/2)\mathrm{e}^{-[x^2+y^2+(z+R/2)^2]^{1/2}/2}$$

and

$$p_{z,\mathrm{B}} = \frac{1}{4(2\pi)^{1/2}}(z - R/2)\mathrm{e}^{-[x^2+y^2+(z-R/2)^2]^{1/2}/2}$$

Following eqn 11.7 and Example 11.1, we form LCAO-MOs of the form:

$$\psi_{\sigma_u} = \frac{p_{z,A} + p_{z,B}}{\{2(1+S)\}^{1/2}} \text{ [antibonding]} \quad \text{and} \quad \psi_{\sigma_g} = \frac{p_{z,A} - p_{z,B}}{\{2(1-S)\}^{1/2}} \text{ [bonding]}$$

$$\text{where } S = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_{z,A}p_{z,B}\, dx\, dy\, dz \text{ [11.17]}$$

Computations and plots are readily prepared with mathematical software such as Mathcad.

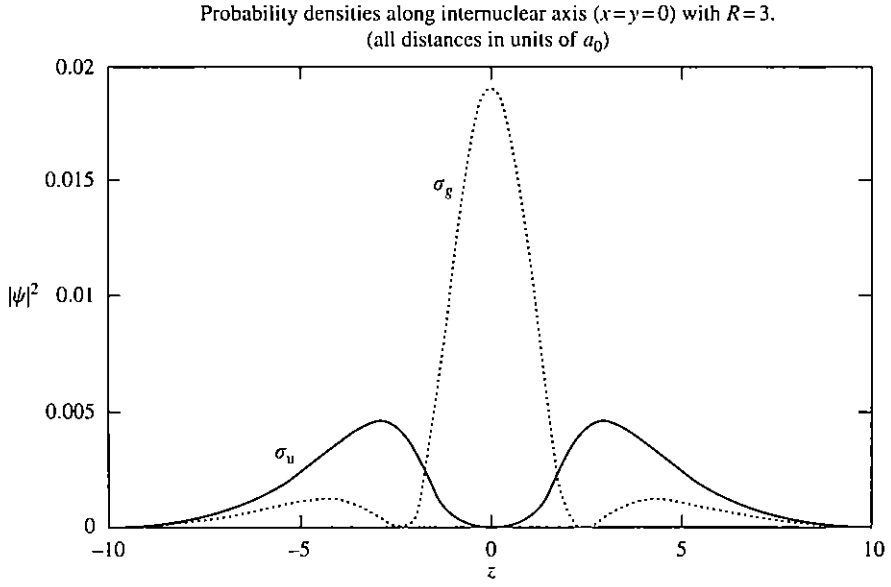


Figure 11.5(a)

(b) With spatial dimensions in units of a_0, the atomic orbitals for the construction of π molecular orbitals are:

$$p_{x,A} = \frac{1}{4(2\pi)^{1/2}} x e^{-[x^2+y^2+(z+R/2)^2]^{1/2}/2}$$

$$p_{x,B} = \frac{1}{4(2\pi)^{1/2}} x e^{-[x^2+y^2+(z-R/2)^2]^{1/2}/2}$$

The π-MOs are:

$$\psi_{\pi_u} = \frac{p_{x,A} + p_{x,B}}{\{2(1+S)\}^{1/2}} \text{ [bonding]} \quad \text{and} \quad \psi_{\pi_g} = \frac{p_{x,A} - p_{x,B}}{\{2(1-S)\}^{1/2}} \text{ [antibonding]}$$

$$\text{where } S = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_{x,A}p_{x,B}\, dx\, dy\, dz$$

The plots clearly show the constructive interference that makes a bonding molecular orbital. Nodal planes created by destructive interference are clearly seen in the antibonding molecular orbitals.

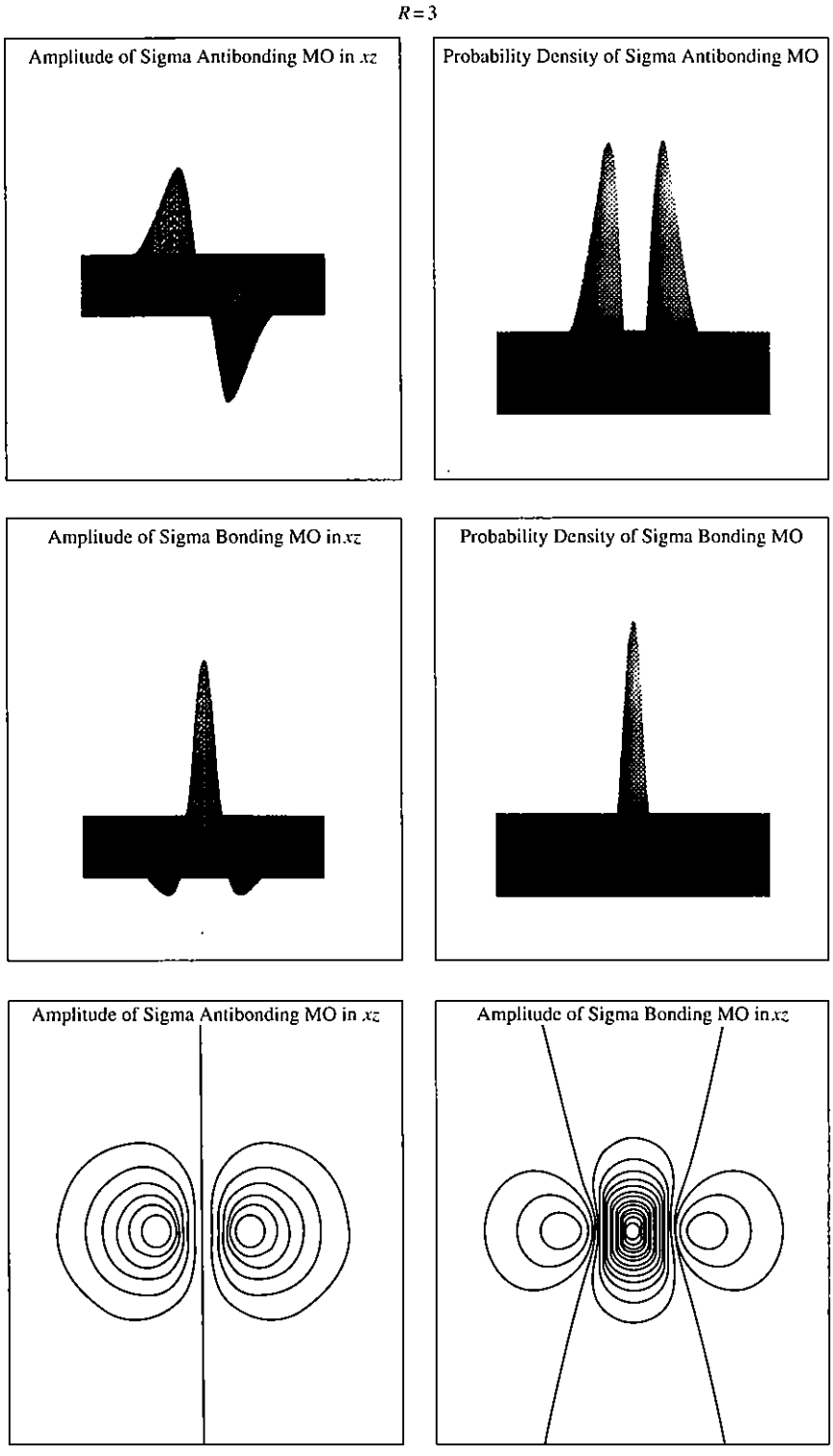

R = 3
Amplitude of Sigma Antibonding MO in xz
Probability Density of Sigma Antibonding MO
Amplitude of Sigma Bonding MO in xz
Probability Density of Sigma Bonding MO
Amplitude of Sigma Antibonding MO in xz
Amplitude of Sigma Bonding MO in xz

Figure 11.5(b)

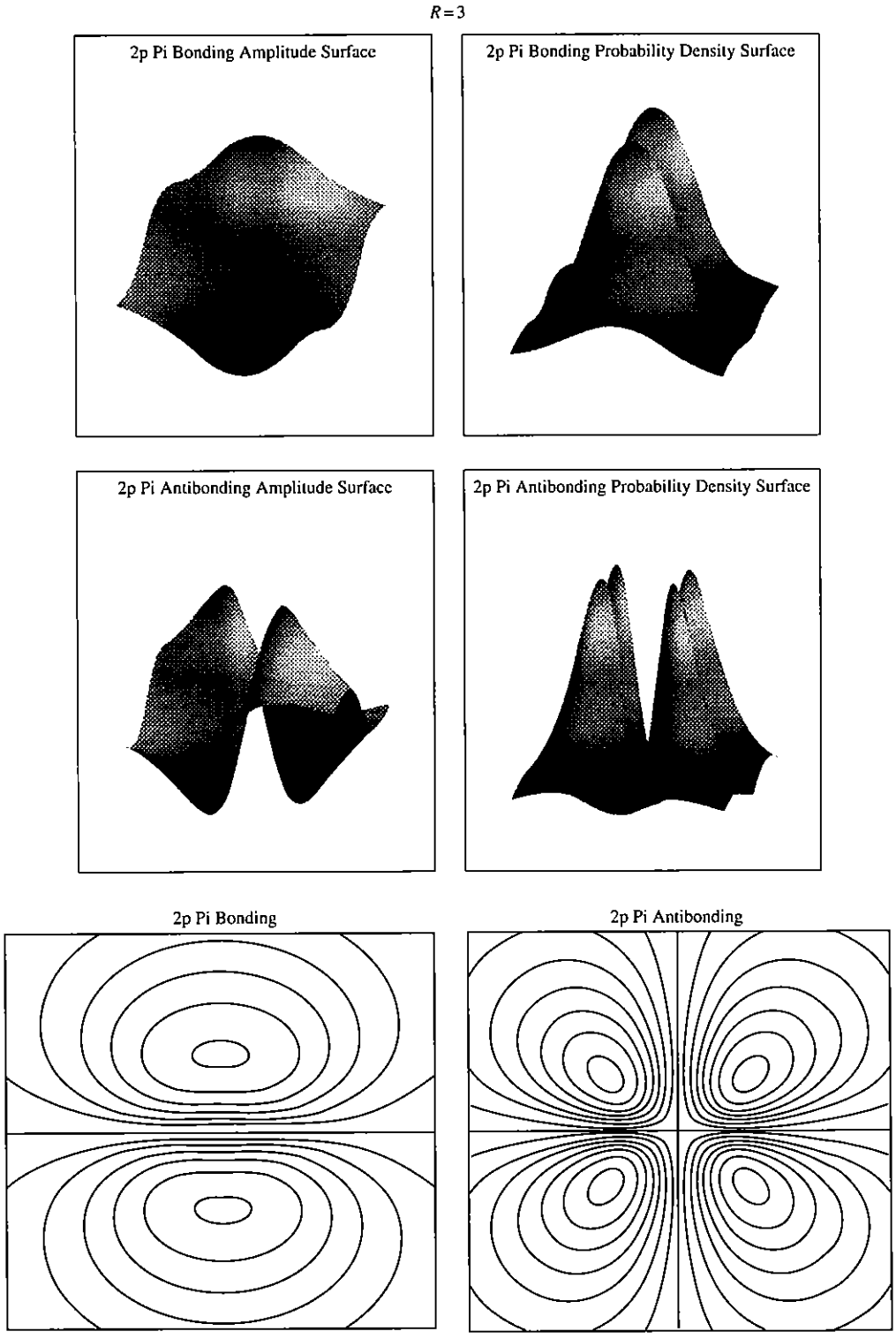

R = 3
2p Pi Bonding Amplitude Surface
2p Pi Bonding Probability Density Surface
2p Pi Antibonding Amplitude Surface
2p Pi Antibonding Probability Density Surface
2p Pi Bonding
2p Pi Antibonding

Figure 11.5(c)

When calculations and plots are produced for the $R = 10$ case, constructive and destructive interference is seen to be much weaker because of the weak atomic orbital overlap.

P11.8 $E_H = E_I = -hcR_H$ [Section 10.2(b)]

Draw up the following table using the data in question and using

$$\frac{e^2}{4\pi\varepsilon_0 R} = \frac{e^2}{4\pi\varepsilon_0 a_0} \times \frac{a_0}{R} = \frac{e^2}{4\pi\varepsilon_0 \times (4\pi\varepsilon_0\hbar^2/m_e e^2)} \times \frac{a_0}{R}$$

$$= \frac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2} \times \frac{a_0}{R} = E_h \times \frac{a_0}{R} \quad \left[E_h \equiv \frac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2} = 2hcR_H\right]$$

so that $\dfrac{\left(\dfrac{e^2}{4\pi\varepsilon_0 R}\right)}{E_h} = \dfrac{a_0}{R}$.

R/a_0	0	1	2	3	4	∞
$(e^2/4\pi\varepsilon_0 R)/E_h$	∞	1	0.500	0.333	0.250	0
$(V_1 + V_2)/E_h$	2.000	1.465	0.843	0.529	0.342	0
$(E - E_H)/E_h$	∞	0.212	−0.031	−0.059	−0.038	0

The points are plotted in Figure 11.6.

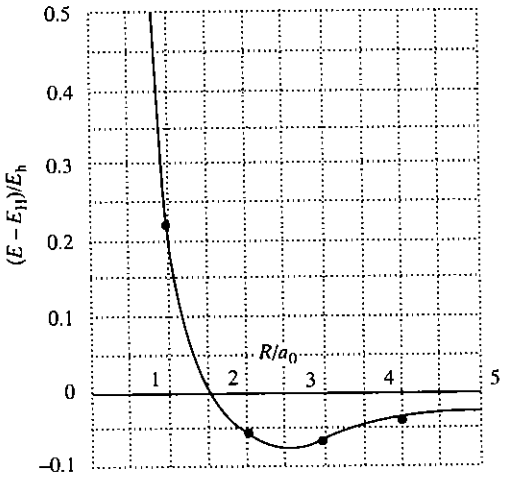


Figure 11.6

The minimum occurs at $R = 2.5a_0$, so $R = 130$ pm. At that bond length

$$E - E_H = -0.07E_h = -1.91\text{ eV}$$

Hence, the dissociation energy is predicted to be about 1.9 eV and the equilibrium bond length about 130 pm.

P11.10 The electron configuration of F_2 is $1\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 2\pi_g^{*4}$; that of F_2^- is $1\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 2\pi_g^{*4} 4\sigma_u^{*1}$. So F_2^- has one more antibonding electron than does F_2, suggesting a lower bond order (1/2 versus 1) and therefore a weaker bond. By definition a weaker bond has a smaller dissociation energy (hence the difference in D_e). Weaker bonds tend to be longer (hence the difference in R_e) and less stiff (hence the difference in $\tilde{\nu}$, reflecting a difference in the force constant k) than stronger bonds between similar atoms.

P11.12 Energy is conserved, so when the photon is absorbed, its energy is transferred to the electron. Part of it overcomes the binding energy (ionization energy) and the remainder is manifest as the now freed electron's kinetic energy.

$$E_{\text{photon}} = I + E_{\text{kinetic}} \quad \text{so} \quad I = E_{\text{photon}} - E_{\text{kinetic}}$$

so the first three ionization energies are:

$$I_1 = 21.21\,\text{eV} - 11.01\,\text{eV} = \boxed{10.20\,\text{eV}}$$

$$I_2 = 21.21\,\text{eV} - 8.23\,\text{eV} = \boxed{12.98\,\text{eV}}$$

and $$I_3 = 21.21\,\text{eV} - 5.22\,\text{eV} = \boxed{15.99\,\text{eV}}$$

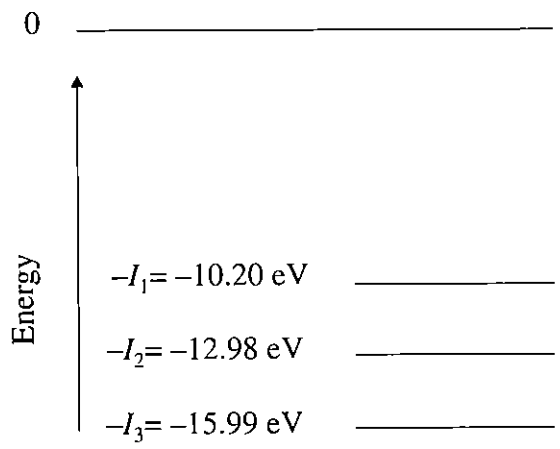


Figure 11.7

P11.14 $E_n = \dfrac{n^2h^2}{8mL^2}$, $n = 1, 2, \ldots$ and $\psi_n = \left(\dfrac{2}{L}\right)^{1/2} \sin\left(\dfrac{n\pi x}{L}\right)$ [Section 9.1]

Two electrons occupy each level (by the Pauli principle), and so butadiene (in which there are four π electrons) has two electrons in ψ_1 and two electrons in ψ_2

$$\psi_1 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) \quad \text{and} \quad \psi_2 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{2\pi x}{L}\right)$$

These orbitals are sketched in Figure 11.8(a).

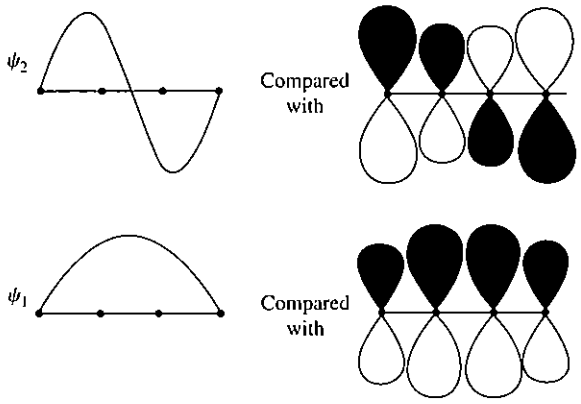


Figure 11.8(a)

The minimum excitation energy is

$$\Delta E = E_3 - E_2 = 5\left(\frac{h^2}{8m_eL^2}\right)$$

In $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$ there are eight π electrons to accommodate, so the HOMO will be ψ_4 and the LUMO ψ_5. From the particle-in-a-box solutions

$$\Delta E = E_5 - E_4 = (25 - 16)\frac{h^2}{8m_eL^2} = \frac{9h^2}{8m_eL^2}$$

$$= \frac{(9) \times (6.626 \times 10^{-34}\,\text{J s})^2}{(8) \times (9.109 \times 10^{-31}\,\text{kg}) \times (1.12 \times 10^{-9}\,\text{m})^2} = 4.3 \times 10^{-19}\,\text{J}$$

which corresponds to $\boxed{2.7\ \text{eV}}$. The HOMO and LUMO are

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$$

with $n = 4, 5$ respectively; the two wavefunctions are sketched in Figure 11.8(b).

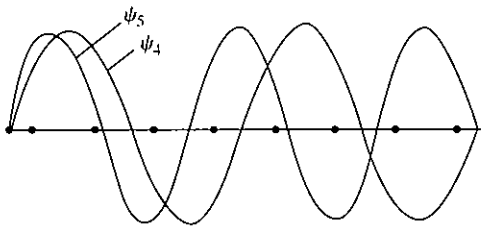


Figure 11.8(b)

COMMENT. It follows that

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{4.3 \times 10^{-19}\,\text{J}} = 4.6 \times 10^{-7}\,\text{m, or } \boxed{460\,\text{nm.}}$$

The wavelength 460 nm corresponds to blue light; so the molecule is likely to appear $\boxed{\text{orange}}$ in white light (since blue is subtracted).

P11.16 (a) In the absence of numerical values for α and β, we express orbital energies as $(E_k - \alpha)/\beta$ for the purpose of comparison. Recall that β is negative (as is α for that matter), so the orbital with the greatest value of $(E_k - \alpha)/\beta$ has the lowest energy. Draw up the following table, evaluating

$$\frac{E_k - \alpha}{\beta} = 2\cos\frac{2k\pi}{N}$$

	energy $(E_k - \alpha)/\beta$	
orbital, k	C_6H_6	C_8H_8
± 4		-2.000
± 3	-2.000	-1.414
± 2	-1.000	0
± 1	1.000	1.414
0	2.000	2.000

In each case, the lowest and highest energy levels are non-degenerate, while the other energy levels are doubly degenerate. The degeneracy is clear for all energy levels except, perhaps, the highest: each value of the quantum number k corresponds to a separate MO, and positive and negative values of k therefore give rise to a pair of MOs of the same energy. This is not the case for the highest energy level, though, because there are only as many MOs as there were AOs input to the calculation, which is the same as the number of carbon atoms; having a doubly-degenerate top energy level would yield one extra MO.

(b) The total energy of the π electron system is the sum of the energies of occupied orbitals weighted by the number of electrons that occupy them. In C_6H_6, each of the first three orbitals is doubly occupied, but the second level ($k = \pm 1$) is doubly degenerate, so

$$E_\pi = 2E_0 + 2 \times 2E_1 = 2(\alpha + 2\beta\cos 0) + 4\left(\alpha + 2\beta\cos\frac{2\pi}{6}\right) = 6\alpha + 8\beta$$

The delocalization energy is the difference between this quantity and that of three isolated double bonds:

$$E_{\text{deloc}} = E_\pi - 6(\alpha + \beta) = 6\alpha + 8\beta - 6(\alpha + \beta) = \boxed{2\beta}$$

For linear hexatriene, $E_{\text{deloc}} = 0.988\beta$, so benzene has considerably more delocalization energy (assuming that β is similar in the two molecules). This extra stabilization is an example of the special stability of aromatic compounds.

(c) In C_8H_8, each of the first three orbitals is doubly occupied, but the second level ($k = \pm 1$) is doubly degenerate. The next level is also doubly degenerate, with a single electron occupying each orbital. So the energy is

$$\begin{aligned} E_\pi &= 2E_0 + 2 \times 2E_1 + 2 \times 1E_2 \\ &= 2(\alpha + 2\beta\cos 0) + 4\left(\alpha + 2\beta\cos\frac{2\pi}{8}\right) + 2\left(\alpha + 2\beta\cos\frac{4\pi}{8}\right) \\ &= 8\alpha + 9.657\,\beta \end{aligned}$$

The delocalization energy is the difference between this quantity and that of four isolated double bonds:

$$E_{\text{deloc}} = E_\pi - 8(\alpha + \beta) = 8\alpha + 9.657\beta - 8(\alpha + \beta) = \boxed{1.657\beta}$$

This delocalization energy is not much different from that of linear octatetraene (1.518β), so cyclooctatetraene does not have much additional stabilization over the linear structure. Once again, though, we do see that the delocalization energy stabilizes the π orbitals of the closed ring conjugated system to a greater extent than what is observed in the open chain conjugated system. However, the benzene/hexatriene comparison shows a much greater stabilization than does the cyclooctatetraene/octatetraene system. This is a demonstration of the Hückel $4n + 2$ rule, which states that any planar, cyclic, conjugated system exhibits unusual aromatic stabilization if it contains $4n + 2$ π electrons where "n" is an integer. Benzene with its six π electrons has this aromatic stabilization whereas cyclooctatetraene with eight π electrons doesn't have this unusual stabilization. We can say that it is **not aromatic**, consistent with indicators of aromaticity such as the Hückel $4n + 2$ rule.

P11.18 **(a)** The table displays computed orbital energies and experimental $\pi^* \leftarrow \pi$ wavenumbers of ethene and the first few conjugated linear polyenes.

Species	E_{LUMO}/eV*	E_{HOMO}/eV*	ΔE/eV*	$\tilde{\nu}/\text{cm}^{-1}$
C_2H_4	1.2282	−10.6411	11.8693	61500
C_4H_6	0.2634	−9.4671	9.7305	46080
C_6H_8	−0.2494	−8.8993	8.6499	39750
C_8H_{10}	−0.5568	−8.5767	8.0199	32900
$C_{10}H_{12}$	−0.7556	−8.3755	7.6199	

* Semi-empirical, PM3 level, PC Spartan Pro™

(b) A plot of the computed energy difference vs. experimental wavenumbers appears in Figure 11.9. The computed points fall on a rather good straight line. Of course a better fit can be obtained to a quadratic and a perfect fit to a cubic polynomial; however, the improvement would be slight and the justification even more slight. The linear least-squares best fit is:

$$\boxed{\Delta E/\text{eV} = 3.3534 + 1.3791 \times 10^{-4}\, \tilde{\nu}/\text{cm}^{-1}} \quad (r^2 = 0.994)$$

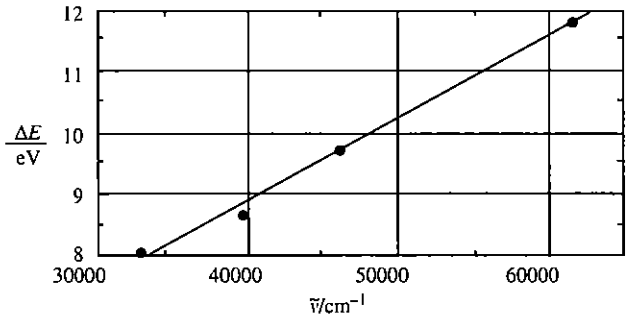


Figure 11.9

(c) Invert the fit equation obtained in (b) above:

$$\tilde{\nu}/\text{cm}^{-1} = \frac{\Delta E/\text{eV} - 3.3534}{1.3791 \times 10^{-4}}.$$

So for $C_{10}H_{12}$, we expect a transition at:

$$\tilde{\nu}/\text{cm}^{-1} = \frac{7.6199 - 3.3534}{1.3791 \times 10^{-4}} = \boxed{30937\,\text{cm}^{-1}}$$

(d) The fitting procedure is necessary because the orbital energies are only approximate. Remember that an orbital wavefunction is itself an approximation. A semi-empirical computation is a further approximation. If the orbitals were exact, then we would expect the energy difference to be directly proportional to the spectroscopic wavenumbers with the following proportionality:

$$\Delta E = hc\tilde{\nu} = \frac{(6.626 \times 10^{-34}\,\text{J s})(2.998 \times 10^{10}\,\text{cm s}^{-1})\tilde{\nu}}{1.602 \times 10^{-19}\,\text{J/eV}},$$

so $\Delta E/\text{eV} = 1.240 \times 10^{-4}\,\tilde{\nu}/\text{cm}^{-1}$.

Clearly this is different than the fit reported above. A further illustration of why the fitting procedure is necessary can be discerned by comparing the table from part (a) to a corresponding table based on a different computational model, namely Hartree–Fock computations with an STO-3G basis set:

Species	E_{LUMO}/eV*	E_{HOMO}/eV*	ΔE/eV*
C_2H_4	8.9335	−9.1288	18.0623
C_4H_6	6.9667	−7.5167	14.4834
C_6H_8	6.0041	−6.6783	12.6824
C_8H_{10}	5.4488	−6.1811	11.6299
$C_{10}H_{12}$	5.0975	−5.8621	10.9596

* *Ab initio*, STO-3G, PC Spartan Pro™

Obviously these energy differences are not the same as the PM3 differences computed above. Nor are they energy differences that correspond to the experimental frequencies.

COMMENT. The STO-3G data also fit a straight line. That fit can also be used to estimate the transition in $C_{10}H_{12}$:

$$\tilde{\nu}/\text{cm}^{-1} = \frac{\Delta E/\text{eV} - 3.8311}{2.3045 \times 10^{-4}},$$

so for $C_{10}H_{12}$ we expect a transition at

$$\tilde{\nu}/\text{cm}^{-1} = \frac{10.9596 - 3.8311}{2.3045 \times 10^{-4}} = 30933.$$

Even though the computations differed considerably in detail, with the calibration procedure they result in nearly identical predictions.

P11.20 **(a)** The standard enthalpy of formation ($\Delta_f H^\ominus$/kJ mol^{-1}) of ethene and the first few linear polyenes is listed below.

Species	Computed*	Experimental†	% error
C_2H_4	69.580	52.46694	32.6
C_4H_6	129.834	108.8 ± 0.79	19.3
		111.9 ± 0.96	16.0
C_6H_8	188.523	$168. \pm 3$	12.2
C_8H_{10}	246.848	295.9‡	16.6

* Semi-empirical, PM3 level, PC Spartan Pro™

† http://webbook.nist.gov/chemistry/

‡ Pedley, Naylor, and Kirby, *Thermodynamic Data of Organic Compounds*.

(b) The % error, shown in the table, is defined by:

$$\%\text{error} = \frac{\Delta_f H^\ominus(\text{calc}) - \Delta_f H^\ominus(\text{expt})}{\Delta_f H^\ominus(\text{expt})} \times 100\%.$$

(c) For all of the molecules, the computed enthalpies of formation exceed the experimental values by much more than the uncertainty in the experimental value. This observation serves to illustrate that molecular modeling software is not a substitute for experimentation when it comes to quantitative measures. It is also worth noting, however, that the experimental uncertainty can vary a great deal. The NIST database reports $\Delta_f H^\ominus$ for C_2H_4 to seven significant figures (with no explicit uncertainty). Even if the figure is not accurate to 1 part in 5000 000, it is clearly a very precisely known quantity—as one should expect in such a familiar and well studied substance. The database lists two different determinations for $\Delta_f H^\ominus(C_4H_6)$, and the experimental values differ by more than the uncertainty claimed for each; a critical evaluation of the experimental data is called for. The uncertainty claimed

for $\Delta_f H^\ominus(C_6H_8)$ is greater still (but still only about 2%). Finally, it should go without saying that not all of the figures reported by the molecular modeling software are physically significant.

Solutions to theoretical problems

P11.22 We need to determine whether $E_- + E_+ > 2E_H$

$$\begin{aligned} E_- + E_+ &= -\frac{V_1 - V_2}{1 - S} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{V_1 + V_2}{1 + S} + \frac{e^2}{4\pi\varepsilon_0 R} + 2E_H \\ &= -\frac{\{(V_1 - V_2) \times (1 + S) + (1 - S) \times (V_1 + V_2)\}}{(1 - S) \times (1 + S)} + \frac{2e^2}{4\pi\varepsilon_0 R} + 2E_H \\ &= \frac{2(SV_2 - V_1)}{1 - S^2} + \frac{2e^2}{4\pi\varepsilon_0 R} + 2E_H \end{aligned}$$

The nuclear repulsion term is always positive, and always tends to raise the mean energy of the orbitals above E_H. The contribution of the first term is difficult to assess. If $S \approx 0$, $SV_2 \approx 0$ and $V_1 \approx 0$, then the first term is small compared to the nuclear repulsion term. If $S \approx 1$ and $SV_2 \approx V_1$, then once again the nuclear repulsion term is dominant. At intermediate values of S, the first term is negative, but of smaller magnitude than the nuclear repulsion term. Thus in all cases $E_- + E_+ > 2E_H$.

P11.24 (a) $\psi = e^{-kr} \qquad H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$

$$\int \psi^2 \, d\tau = \int_0^\infty r^2 e^{-2kr} \, dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi = \frac{\pi}{k^3}$$

$$\int \psi \frac{1}{r} \psi \, d\tau = \int_0^\infty r e^{-2kr} \, dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi = \frac{\pi}{k^2}$$

$$\int \psi \nabla^2 \psi \, d\tau = \int \psi \frac{1}{r} \frac{d^2}{dr^2}(re^{-kr}) \, d\tau = \int \psi \left(k^2 - \frac{2k}{r}\right) \psi \, d\tau$$

$$= \frac{\pi}{k} - \frac{2\pi}{k} = -\frac{\pi}{k}$$

Therefore

$$\int \psi H \psi \, d\tau = \frac{\hbar^2}{2\mu} \times \frac{\pi}{k} - \frac{e^2}{4\pi\varepsilon_0} \times \frac{\pi}{k^2}$$

and

$$E = \frac{\left(\frac{\hbar^2\pi}{2\mu k}\right) - \left(\frac{e^2\pi}{4\pi\varepsilon_0 k^2}\right)}{\pi/k^3} = \frac{\hbar^2 k^2}{2\mu} - \frac{e^2 k}{4\pi\varepsilon_0}$$

$$\frac{dE}{dk} = 2\left(\frac{\hbar^2}{2\mu}\right)k - \frac{e^2}{4\pi\varepsilon_0} = 0 \quad \text{when} \quad k = \frac{e^2\mu}{4\pi\varepsilon_0\hbar^2}$$

The optimum energy is therefore

$$E = -\frac{e^4\mu}{32\pi^2\varepsilon_0^2\hbar^2} = \boxed{-hcR_H} \text{ the exact value.}$$

(b) $\psi = \mathrm{e}^{-kr^2}$, H as before.

$$\int \psi^2 \,\mathrm{d}\tau = \int_0^\infty \mathrm{e}^{-2kr^2} r^2 \,\mathrm{d}r \int_0^\pi \sin\theta \,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = \frac{\pi}{2}\left(\frac{\pi}{2k^3}\right)^{1/2}$$

$$\int \psi \frac{1}{r}\psi \,\mathrm{d}\tau = \int_0^\infty r\mathrm{e}^{-2kr^2} \,\mathrm{d}r \int_0^\pi \sin\theta \,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = \frac{\pi}{k}$$

$$\begin{aligned}\int \psi\nabla^2\psi \,\mathrm{d}\tau &= -2\int \psi(3k - 2k^2r^2)\psi \,\mathrm{d}\tau \\ &= -2\int_0^\infty (3kr^2 - 2k^2r^4)\mathrm{e}^{-2kr^2} \,\mathrm{d}r \int_0^\pi \sin\theta \,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \\ &= -8\pi\left\{\left(\frac{3k}{8}\right) \times \left(\frac{\pi}{2k^3}\right)^{1/2} - \frac{3k^2}{16}\left(\frac{\pi}{2k^5}\right)^{1/2}\right\}\end{aligned}$$

Therefore

$$E = \frac{3\hbar^2 k}{2\mu} - \frac{e^2 k^{1/2}}{\varepsilon_0(2\pi)^{1/2}}$$

$$\frac{\mathrm{d}E}{\mathrm{d}k} = 0 \quad \text{when} \quad k = \frac{e^4\mu^2}{18\pi^3\varepsilon_0^2\hbar^4}$$

and the optimum energy is therefore

$$E = -\frac{e^4\mu}{12\pi^3\varepsilon_0^2\hbar^2} = \boxed{-\frac{8}{3\pi} \times hcR_H}$$

Since $8/3\pi < 1$, the energy in (a) is lower than in (b), and so the exponential wavefunction is better than the Gaussian.

Solutions to applications

P11.26 **(a)**

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$

$$(\alpha - E)\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} - \beta\begin{vmatrix} \beta & \beta \\ \beta & \alpha - E \end{vmatrix} + \beta\begin{vmatrix} \beta & \alpha - E \\ \beta & \beta \end{vmatrix} = 0$$

$$(\alpha - E) \times \{(\alpha - E)^2 - \beta^2\} - \beta\{\beta(\alpha - E) - \beta^2\} + \beta\{\beta^2 - (\alpha - E)\beta\} = 0$$

$$(\alpha - E) \times \{(\alpha - E)^2 - \beta^2\} - 2\beta^2\{\alpha - E - \beta\} = 0$$

$$(\alpha - E) \times (\alpha - E - \beta) \times (\alpha - E + \beta) - 2\beta^2(\alpha - E - \beta) = 0$$

$$(\alpha - E - \beta) \times \{(\alpha - E) \times (\alpha - E + \beta) - 2\beta^2\} = 0$$

$$(\alpha - E - \beta) \times \{(\alpha - E) \times (\alpha - E + 2\beta) - \beta(\alpha - E) - 2\beta^2\} = 0$$

$$(\alpha - E - \beta) \times \{(\alpha - E) \times (\alpha - E + 2\beta) - \beta(\alpha - E + 2\beta)\} = 0$$

$$(\alpha - E - \beta) \times (\alpha - E + 2\beta) \times (\alpha - E - \beta) = 0$$

Therefore, the desired roots are $E = \boxed{\alpha - \beta,\ \alpha - \beta, \text{ and } \alpha + 2\beta}$. The energy level diagram is shown in Figure 11.10.

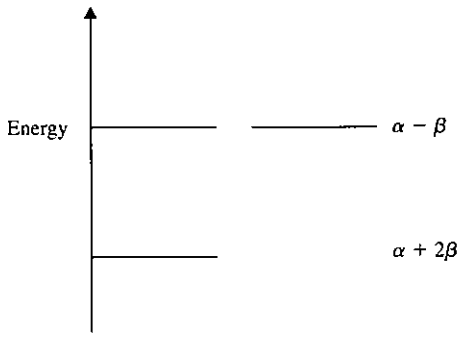


Figure 11.10

The binding energies are shown in the following table.

Species	Number of e^-	Binding energy
H_3^+	2	$2(\alpha + 2\beta) = 2\alpha + 4\beta$
H_3	3	$2(\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta$
H_3^-	4	$2(\alpha + 2\beta) + 2(\alpha - \beta) = 4\alpha + 2\beta$

(b)

$H_3^+(g)$	$\rightarrow 2H(g) + H^+(g)$	$\Delta H_1 = 849\,\text{kJ mol}^{-1}$
$H^+(g) + H_2(g)$	$\rightarrow H_3^+(g)$	$\Delta H_2 = ?$
$H_2(g)$	$\rightarrow 2H(g)$	$\Delta H_3 = [2(217.97) - 0]\,\text{kJ mol}^{-1}$

$$\Delta H_2 = \Delta H_3 - \Delta H_1 = 2[(217.97) - 849]\,\text{kJ mol}^{-1}$$

$$\Delta H_2 = \boxed{-413\,\text{kJ mol}^{-1}}$$

This is only slightly less than the binding energy of H_2 ($435.94\,\text{kJ mol}^{-1}$)

(c) $2\alpha + 4\beta = -\Delta H_1 = -849\,\text{kJ mol}^{-1}$

$$\beta = \frac{-\Delta H_1 - 2\alpha}{4} \quad \text{where } \Delta H_1 = 849\,\text{kJ mol}^{-1}$$

Species	Binding energy
H_3^+	$2\alpha + 4\beta = -\Delta H_I = \boxed{-849\ \text{kJ mol}^{-1}}$
H_3	$3\alpha + 3\beta = 3\left(\alpha - \dfrac{\Delta H_I + 2\alpha}{4}\right) = 3\left(\dfrac{1}{2}\alpha - \dfrac{\Delta H_I}{4}\right) = \boxed{3(\alpha/2) - 212\ \text{kJ mol}^{-1}}$
H_3^-	$4\alpha + 2\beta = 4\alpha - \dfrac{\Delta H_I + 2\alpha}{2} = 3\alpha - \dfrac{\Delta H_I}{2} = \boxed{3\alpha - 425\ \text{kJ mol}^{-1}}$

As α is a negative quantity, all three of these species are expected to be stable.

P11.28 **(a)** The orbitals are sketched in Figure 11.11(a). ψ_1 is a bonding orbital, showing no nodes between adjacent atoms, and ψ_3 is antibonding with respect to all three atoms. ψ_2 is non-bonding, with neither constructive nor destructive interaction of the atomic orbitals of adjacent atoms.

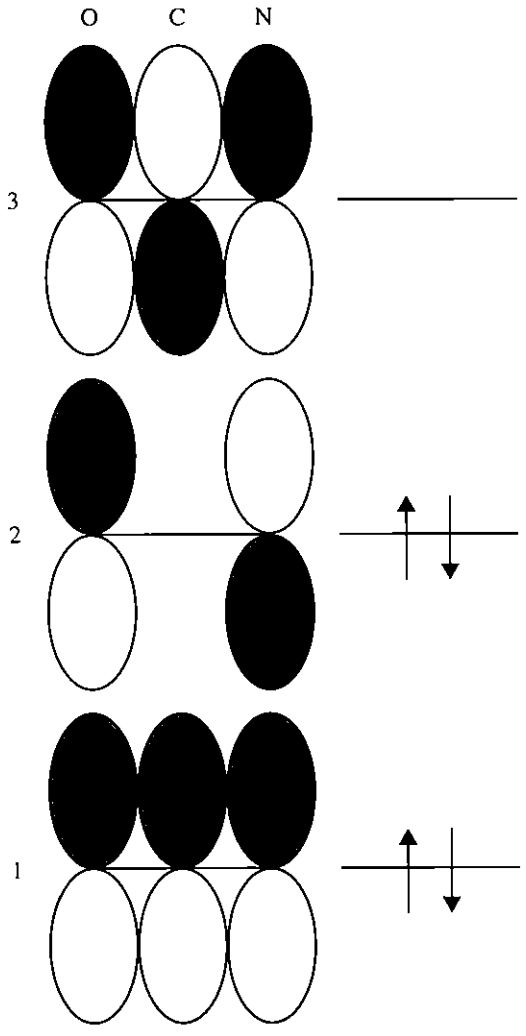


Figure 11.11(a)

(b) This arrangement only works if the entire peptide link is coplanar. Let us call the plane defined by the O, C, and N atoms the *xy* plane; therefore, the *p* orbitals used to make the three MOs sketched above are p_z orbitals. If the p_z orbital of N is used in the π system, then the σ bonds it makes must be in the *xy* plane. Hence the H atom and the atom labeled $C_{\alpha 2}$ must also be in the *xy* plane. Likewise, if the p_z orbital of the C atom in the peptide link is used in the π system, then its σ bonds must also lie in the *xy* plane, putting the atom labeled $C_{\alpha 1}$ in that plane as well.

(c) The relative energies of the orbitals and their occupancy are shown in Figure 11.11a. There are four electrons to be distributed. If we look at the conventional representation of the peptide link (**10** in the text), the two electrons represented by the C=O π bond are obviously part of the π system, leaving the two lone pairs on O, the C—O σ bond, and the two other σ bonds of C as part of the σ system. Turning now to the Lewis octet of electrons around the N atom, we must assign two electrons to

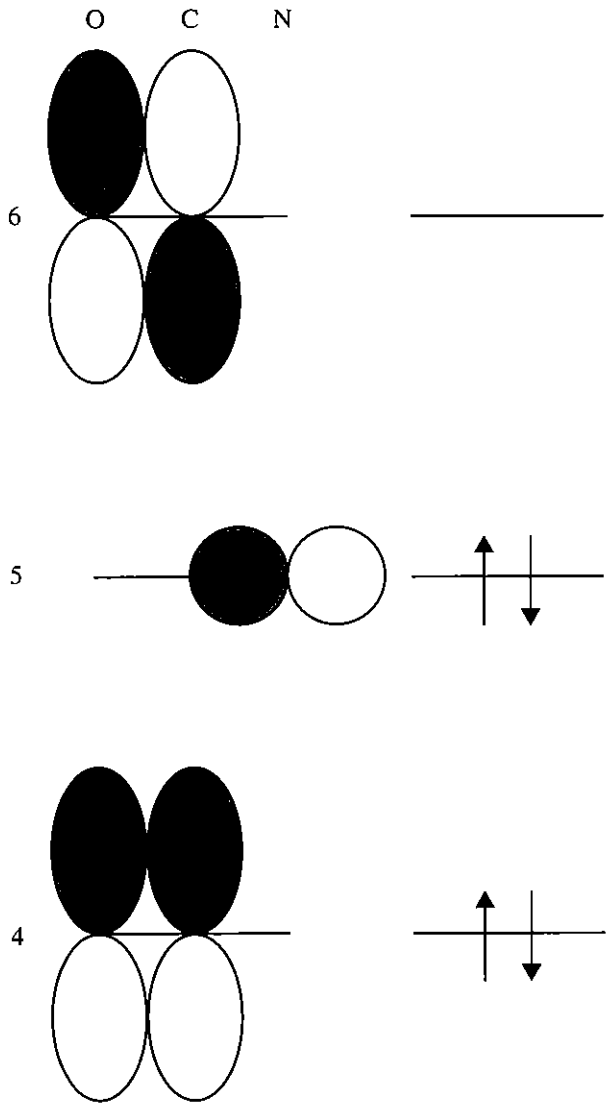


Figure 11.11(b)

each of the σ bonds involving N; clearly they cannot be part of the π system. That leaves the lone pair on N, which must occupy the other orbital that N contributes to the molecule, namely the p_z orbital that is part of the π system.

(d) The orbitals are sketched in Figure 11.11(b). ψ_4 is a bonding orbital with respect to C and O, and ψ_6 is antibonding with respect to C and O. ψ_5 is non-bonding, involving only the N atom. There are four electrons to be placed in this system, as before, two each in a bonding and non-bonding orbital.

(e) This system cannot be planar. As before, the atom labeled $C_{\alpha 1}$ must be in the xy plane. As before, the atoms bound to N must be in a plane perpendicular to the orbital that N contributes to this system, which is itself in the xy plane; the bonding partners of N are therefore forced out of the xy plane.

(f) The bonding MO ψ_1 must have a lower energy than the bonding MO ψ_4, for ψ_1 is bonding (stabilizing) with respect to all three atoms, while ψ_4 is bonding with respect to only two of them. Likewise, the antibonding MO ψ_3 must have a higher energy than the antibonding MO ψ_6, for ψ_3 is antibonding (destabilizing) with respect to all three atoms pairwise, while ψ_6 is antibonding only with respect to two of them. The non-bonding MOs ψ_2 and ψ_5 must have similar energies, not much different than the parameter α, for there is no significant constructive or destructive interference between adjacent atoms in either one.

(g) Because bonding orbital ψ_1 has a lower energy than ψ_4, the planar arrangement has a lower energy than the non-planar one. The total energy of the planar arrangement is

$$E_{\text{planar}} = 2E_1 + 2E_2.$$

Compare this to the energy of the non-planar arrangement:

$$E_{\text{non-planar}} = 2E_4 + 2E_5 > 2E_1 + 2E_2 = E_{\text{planar}}.$$

The fact that $E_3 > E_6$ is immaterial, for neither of those orbitals is occupied.

12 Molecular symmetry

Answers to discussion questions

D12.2

Symmetry operations	Symmetry elements
1. Identity, E	1. The entire object
2. n-fold rotation	2. n-fold axis of symmetry, C_n
3. Reflection	3. Mirror plane, σ
4. Inversion	4. Centre of symmetry, i
5. n-fold improper rotation	5. n-fold improper rotation axis, S_n

D12.4 A molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation, S_n. An improper rotation is a rotation followed by a reflection and this combination of operations always converts a right-handed object into a left-handed object and *vice versa*; hence an S_n axis guarantees that a molecule cannot exist in chiral forms.

D12.6 See Sections 12.4(a) and (b).

D12.8 The direct sum is the decomposition of the direct product. The procedure for the decomposition is the set of steps outlined in Section 12.5(a) and demonstrated in *Illustration* 12.1.

Solutions to exercises

E12.1(b) CCl_4 has $\boxed{4\,C_3 \text{ axes}}$ (each C—Cl axis), $\boxed{3\,C_2 \text{ axes}}$ (bisecting Cl—C—Cl angles), $\boxed{3S_4 \text{ axes}}$ (the same as the C_2 axes), and $\boxed{6 \text{ dihedral mirror planes}}$ (each Cl—C—Cl plane).

E12.2(b) Only molecules belonging to C_s, C_n, and C_{nv} groups may be polar, so . . .

(a) $CH_3Cl(C_{3v})$ $\boxed{\text{may be polar}}$ along the C—Cl bond;

(b) $HW_2(CO)_{10}(D_{4h})$ $\boxed{\text{may not be polar}}$

(c) $SnCl_4(T_d)$ $\boxed{\text{may not be polar}}$

E12.3(b) The factors of the integrand have the following characters under the operations of D_{6h}

	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
p_x	2	1	−1	−2	0	0	−2	−1	1	2	0	0
Z	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1
p_z	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1
Integrand	2	1	−1	−2	0	0	−2	−1	1	2	0	0

The integrand has the same set of characters as species E_{1u}, so it does not include A_{1g}; therefore the integral vanishes.

E12.4(b) We need to evaluate the character sets for the product $A_{1g}E_{2u}q$, where $q = x, y$, or z

	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0
(x, y)	2	1	−1	−2	0	0	−2	−1	1	2	0	0
Integrand	4	−1	1	−4	0	0	4	−1	1	−4	0	0

To see whether the totally symmetric species A_{1g} is present, we form the sum over classes of the number of operations times the character of the integrand

$$c(A_{1g}) = (4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) + (4)$$
$$+ 2(-1) + 2(1) + (-4) + 3(0) + 3(0) = 0$$

Since the species A_{1g} is absent, the transition is forbidden for x- or y-polarized light. A similar analysis leads to the conclusion that A_{1g} is absent from the product $A_{1g}E_{2uz}$; therefore the transition is forbidden.

E12.5(b) The classes of operations for D_2 are: $E, C_2(x)$, $C_2(y)$, and $C_2(z)$. How does the function xyz behave under each kind of operation? E leaves it unchanged. $C_2(x)$ leaves x unchanged and takes y to $-y$ and z to $-z$, leaving the product xyz unchanged. $C_2(y)$ and $C_2(z)$ have similar effects, leaving one axis unchanged and taking the other two into their negatives. These observations are summarized as follows

	E	$C_2(x)$	$C_2(y)$	$C_2(z)$
xyz	1	1	1	1

A look at the character table shows that this set of characters belong to symmetry species A_1.

E12.6(b) A molecule cannot be chiral if it has an axis of improper rotation. The point group T_d has S_4 axes and mirror planes ($= S_1$), which preclude chirality. The T_h group has, in addition, a center of inversion ($= S_2$).

E12.7(b) The group multiplication table of group C_{4v} is

	E	C_4^+	C_4^-	C_2	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$
E	E	C_4^+	C_4^-	C_2	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$
C_4^+	C_4^+	C_2	E	C_4^-	$\sigma_d(xy)$	$\sigma_d(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$
C_4^-	C_4^-	E	C_2	C_4^+	$\sigma_d(-xy)$	$\sigma_d(xy)$	$\sigma_v(x)$	$\sigma_v(y)$
C_2	C_2	C_4^-	C_4^+	E	$\sigma_v(y)$	$\sigma_v(x)$	$\sigma_d(-xy)$	$\sigma_d(xy)$
$\sigma_v(x)$	$\sigma_v(x)$	$\sigma_d(-xy)$	$\sigma_d(xy)$	$\sigma_v(y)$	E	C_2	C_4^-	C_4^+
$\sigma_v(y)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$	$\sigma_v(x)$	C_2	E	C_4^+	C_4^-
$\sigma_d(xy)$	$\sigma_d(xy)$	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(-xy)$	C_4^+	C_4^-	E	C_2
$\sigma_d(-xy)$	$\sigma_d(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$	$\sigma_d(xy)$	C_4^-	C_4^+	C_2	E

E12.8(b) See Figure 12.1.

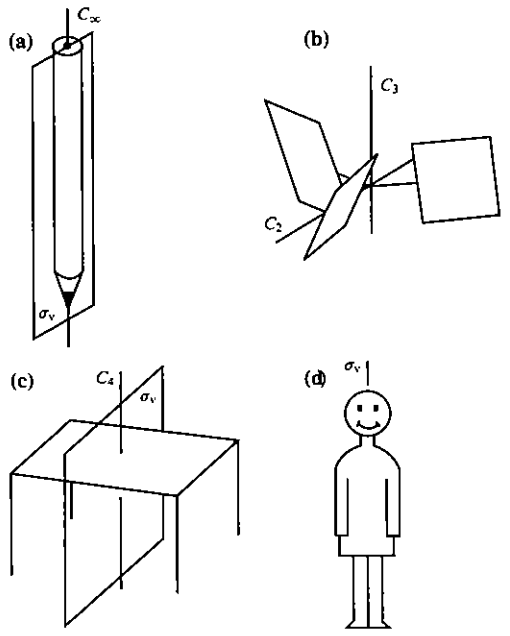


Figure 12.1

(a) Sharpened pencil: E, C_∞, σ_v; therefore $\boxed{C_{\infty v}}$

(b) Propellor: $E, C_3, 3C_2$; therefore $\boxed{D_3}$

(c) Square table: $E, C_4, 4\sigma_v$; therefore $\boxed{C_{4v}}$; Rectangular table: $E, C_2, 2\sigma_v$; therefore $\boxed{C_{2v}}$

(d) Person: E, σ_v (approximately); therefore $\boxed{C_s}$.

E12.9(b) We follow the flow chart in the text (Figure 12.7). The symmetry elements found in order as we proceed down the chart and the point groups are

(a) Naphthalene: E, C_2, C_2', C_2'', $3\sigma_h, i$; $\boxed{D_{2h}}$

(b) Anthracene: E, C_2, C_2', C_2'', $3\sigma_h, i$; $\boxed{D_{2h}}$

(c) Dichlorobenzenes:

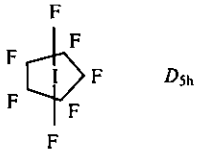
(i) 1,2-dichlorobenzene: E, C_2, σ_v, σ_v'; $\boxed{C_{2v}}$

(ii) 1,3-dichlorobenzene: E, C_2, σ_v, σ_v'; $\boxed{C_{2v}}$

(iii) 1,4-dichlorobenzene: E, C_2, C_2', C_2'', $3\sigma_h, i$; $\boxed{D_{2h}}$.

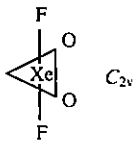
E12.10(b) (a) H–F $C_{\infty v}$

(b)



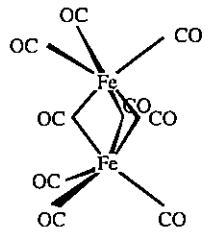
D_{5h}

(c)

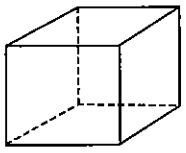


C_{2v}

(d) D_{3h}

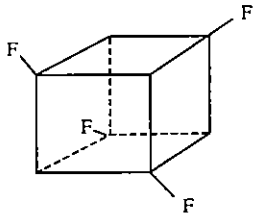


(e)



O_h

(f) T_d



The following responses refer to the text flow chart (Figure 12.7) for assigning point groups.

(a) HF: linear, no i, so $\boxed{C_{\infty v}}$

(b) IF_7: nonlinear, fewer than $2C_n$ with $n > 2$, $C_5, 5C_2'$ perpendicular to C_5, σ_h, so $\boxed{D_{5h}}$

(c) XeO_2F_2: nonlinear, fewer than $2C_n$ with $n > 2$, C_2, no C_2' perpendicular to C_2, no σ_h, $2\sigma_v$, so $\boxed{C_{2v}}$

(d) $Fe_2(CO)_9$: nonlinear, fewer than $2C_n$ with $n > 2$, C_3, $3C_2$ perpendicular to C_3, σ_h, so $\boxed{D_{3h}}$

(e) cubane (C_8H_8): nonlinear, more than $2C_n$ with $n > 2, i$, no C_5, so $\boxed{O_h}$

(f) tetrafluorocubane (**23**): nonlinear, more than $2C_n$ with $n > 2$, no i, so $\boxed{T_d}$.

E12.11(b) **(a)** Only molecules belonging to C_s, C_n, and C_{nv} groups may be polar. In Exercise 12.9(b) $\boxed{\textit{ortho}\text{-dichlorobenzene}}$ and $\boxed{\textit{meta}\text{-dichlorobenzene}}$ belong to C_{2v} and so may be polar; in Exercise 12.6(b), $\boxed{\text{HF and } XeO_2F_2}$ belong to C_{nv} groups, so they may be polar.

(b) A molecule cannot be chiral if it has an axis of improper rotation – including disguised or degenerate axes such as an inversion centre (S_2) or a mirror plane (S_1). In Exercises 12.5(b) and 12.6(b), all the molecules have mirror planes, so $\boxed{\text{none}}$ can be chiral.

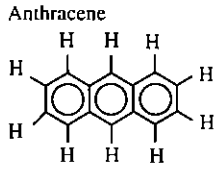
E12.12(b) In order to have nonzero overlap with a combination of orbitals that spans E, an orbital on the central atom must itself have some E character, for only E can multiply E to give an overlap integral with a totally symmetric part. A glance at the character table shows that $\boxed{p_x \text{ and } p_y}$ orbitals available to a bonding N atom have the proper symmetry. If d orbitals are available (as in SO_3), $\boxed{\text{all } d \text{ orbitals except } d_{z^2}}$ could have nonzero overlap.

E12.13(b) The product $\Gamma_f \times \Gamma(\mu) \times \Gamma_i$ must contain A_1 (Example 12.7). Then, since $\Gamma_i = B_1$, $\Gamma(\mu) = \Gamma(y) = B_2$ (C_{2v} character table), we can draw up the following table of characters

	E	C_2	σ_v	σ_v'	
B_2	1	−1	−1	1	
B_1	1	−1	1	−1	
B_1B_2	1	1	−1	−1	$= A2$

Hence, the upper state is $\boxed{A_2}$, because $A_2 \times A_2 = A_1$.

E12.14(b) (a)



D_{2h}

The components of μ span $B_{3u}(x)$, $B_{2u}(y)$, and $B_{1u}(z)$. The totally symmetric ground state is A_g. Since $A_g \times \Gamma = \Gamma$ in this group, the accessible upper terms are $\boxed{B_{3u}}$ (x-polarized), $\boxed{B_{2u}}$ (y-polarized), and $\boxed{B_{1u}}$ (z-polarized).

(b) Coronene, like benzene, belongs to the D_{6h} group. The integrand of the transition dipole moment must be or contain the A_{1g} symmetry species. That integrand for transitions from the ground state is $A_{1g}qf$, where q is x, y, or z and f is the symmetry species of the upper state. Since the ground state is already totally symmetric, the product qf must also have A_{1g} symmetry for the entire integrand to have A_{1g} symmetry. Since the different symmetry species are orthogonal, the only way qf can have A_{1g} symmetry is if q and f have the same symmetry. Such combinations include zA_{2u}, xE_{1u}, and yE_{1u}. Therefore, we conclude that transitions are allowed to states with $\boxed{A_{2u} \text{ or } E_{1u}}$ symmetry.

E12.15(b)

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
$\sin\theta$	1	Linear combinations of	1
$\cos\theta$	1	$\sin\theta$ and $\cos\theta$	−1
Product	1	1	−1

The product does not contain A_1, so $\boxed{\text{yes}}$ the integral vanishes.

Solutions to problems

P12.2 The operations are illustrated in Figure 12.2. Note that $R^2 = E$ for all the operations of the groups, that $ER = RE = R$ always, and that $RR' = R'R$ for this group. Since $C_2\sigma_h = i$, $\sigma_h i = C_2$, and $iC_2 = \sigma_h$ we

can draw up the following group multiplication table

	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E

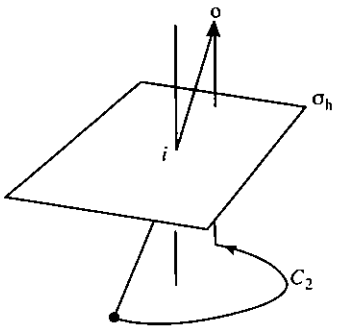


Figure 12.2

The *trans*-CHCl=CHCl molecule belongs to the group C_{2h}.

COMMENT. Note that the multiplication table for C_{2h} can be put into a one-to-one correspondence with the multiplication table of D_2 obtained in Exercise 12.5. We say that they both belong to the same abstract group and are isomorphous.

Question. Can you find another abstract group of order 4 and obtain its multiplication table? There is only one other.

P12.4 Refer to Figure 12.3 of the text. Place orbitals h_1 and h_2 on the H atoms and s, p_x, p_y, and p_z on the O atom. The z-axis is the C_2 axis; x lies perpendicular to σ_v', y lies perpendicular to σ_v. Then draw up the following table of the effect of the operations on the basis

	E	C_2	σ_v	σ_v'
h_1	h_1	h_2	h_2	h_1
h_2	h_2	h_1	h_1	h_2
s	s	s	s	s
p_x	p_x	$-p_x$	p_x	$-p_x$
p_y	p_y	$-p_y$	$-p_y$	p_y
p_z	p_z	p_z	p_z	p_z

Express the columns headed by each operation R in the form

$$\text{(new)} = D(R)\text{(original)}$$

where $D(R)$ is the 6×6 representative of the operation R. We use the rules of matrix multiplication set out in *Justification* 12.1.

(i) $E : (h_1, h_2, s, p_x, p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by the 6×6 unit matrix
(ii) $C_2 : (h_2, h_1, s, -p_x, -p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$\boldsymbol{D}(C2) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

(iii) $\sigma_v : (h_2, h_1, s, p_x, -p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$\boldsymbol{D}(\sigma_v) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

(iv) $\sigma_v' : (h_1, h_2, s, -p_x, p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$\boldsymbol{D}(\sigma_v') = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

(a) To confirm the correct representation of $C_2\sigma_v = \sigma_v'$, we write

$$\boldsymbol{D}(C_2)\boldsymbol{D}(\sigma_v) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{D}(\sigma_v')$$

(b) Similarly, to confirm the correct representation of $\sigma_v\sigma_v' = C_2$, we write

$$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{D}(C_2)$$

(a) The characters of the representatives are the sums of their diagonal elements:

E	C_2	σ_v	σ_v'
6	0	2	4

(b) The characters are not those of any one irreducible representation, so the representation is reducible.

(c) The sum of the characters of the specified sum is

	E	C_2	σ_v	σ_v'
$3A_1$	3	3	3	3
B_1	1	−1	1	−1
$2B_2$	2	−2	−2	2
$3A_1 + B_1 + 2B_2$	6	0	2	4

which is the same as the original. Therefore the representation is $3A_1 + B_1 + 2B_2$.

P12.6 *Representation 1*

$$\boldsymbol{D}(C_3)\boldsymbol{D}(C_2) = 1 \times 1 = 1 = \boldsymbol{D}(C_6)$$

and from the character table is either A_1 or A_2. Hence, either $\boldsymbol{D}(\sigma_v) = \boldsymbol{D}(\sigma_d) = \boxed{+1 \text{ or } -1}$ respectively.

Representation 2

$$\boldsymbol{D}(C_3)\boldsymbol{D}(C_2) = 1 \times (-1) = -1 = \boldsymbol{D}(C_6)$$

and from the character table is either B_1 or B_2. Hence, either $\boldsymbol{D}(\sigma_v) = -\boldsymbol{D}(\sigma_d) = \boxed{1}$ or $\boldsymbol{D}(\sigma_v) = -\boldsymbol{D}(\sigma_d) = \boxed{-1}$ respectively.

P12.8 A quick rule for determining the character without first having to set up the matrix representation is to count 1 each time a basis function is left unchanged by the operation, because only these functions give a nonzero entry on the diagonal of the matrix representative. In some cases there is a sign change, $(\ldots -f \ldots) \leftarrow (\ldots f \ldots)$; then -1 occurs on the diagonal, and so count -1. The character of the identity is always equal to the dimension of the basis since each function contributes 1 to the trace.

E: all four orbitals are left unchanged; hence $\chi = 4$

C_3: One orbital is left unchanged; hence $\chi = 1$

C_2: No orbitals are left unchanged; hence $\chi = 0$

S_4: No orbitals are left unchanged; hence $\chi = 0$

σ_d: Two orbitals are left unchanged; hence $\chi = 2$

The character set 4, 1, 0, 0, 2 spans $\boxed{A_1 + T_2}$. Inspection of the character table of the group T_d shows that s spans A_1 and that the three p orbitals on the C atom span T_2. Hence, the $\boxed{s \text{ and } p}$ orbitals of the C atom may form molecular orbitals with the four H1s orbitals. In T_d, the d orbitals of the central atom span E + T_2 (character table, final column), and so only the T_2 set $\boxed{(d_{xy}, d_{yz}, d_{zx})}$ may contribute to molecular orbital formation with the H orbitals.

P12.10 The most distinctive symmetry operation is the $\boxed{S_4}$ axis through the central atom and aromatic nitrogens on both ligands. That axis is also a $\boxed{C_2}$ axis. The group is $\boxed{S_4}$.

P12.12 (a) Working through the flow diagram (Figure 12.7) in the text, we note that there are no C_n axes with $n > 2$ (for the C_3 axes present in a tetrahedron are not symmetry axes any longer), but it does have C_2 axes; in fact it has 2 C_2 axes perpendicular to whichever C_2 we call principal; it has no σ_h, but it has 2 σ_d. So the point group is $\boxed{D_{2d}}$.

(b) Within this point group, the distortion belongs to the fully symmetric species $\boxed{A_1}$ for its motion is unchanged by the S_4 operation, either class of C_2, or σ_d.

(c) The resulting structure is a square bipyramid, but with one pyramid's apex farther from the base than the other's. Working through the flow diagram in Figure 12.7, we note that there is only one C_n axis with $n > 2$, namely a C_4 axis; it has no C_2 axes perpendicular to the C_4, and it has no σ_h, but it has $4\sigma_v$. So the point group is $\boxed{C_{4v}}$.

(d) Within this point group, the distortion belongs to the fully symmetric species $\boxed{A_1}$. The translation of atoms along the given axis is unchanged by any symmetry operation for the motion is contained within each of the group's symmetry elements.

P12.14 (a) xyz changes sign under the inversion operation (one of the symmetry elements of a cube); hence it does not span A_{1g} and its integral $\boxed{\text{must be zero}}$

(b) xyz spans A_1 in T_d [Problem 12.13] and so its integral $\boxed{\text{need not be zero}}$

(c) $xyz \rightarrow -xyz$ under $z \rightarrow -z$ (the σ_h operation in D_{6h}), and so its integral $\boxed{\text{must be zero}}$

P12.16 We shall adapt the simpler subgroup C_{6v} of the full D_{6h} point group. The six π-orbitals span $A_1 + B_1 + E_1 + E_2$, and are

$$a_1 = \frac{1}{\sqrt{6}}(\pi_1 + \pi_2 + \pi_3 + \pi_4 + \pi_5 + \pi_6)$$

$$b_1 = \frac{1}{\sqrt{6}}(\pi_1 - \pi_2 + \pi_3 - \pi_4 + \pi_5 - \pi_6)$$

$$e_2 = \begin{cases} \frac{1}{\sqrt{12}}(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6) \\ \frac{1}{2}(\pi_2 - \pi_3 + \pi_5 - \pi_6) \end{cases}$$

$$e_1 = \begin{cases} \frac{1}{\sqrt{12}}(2\pi_1 + \pi_2 - \pi_3 - 2\pi_4 - \pi_5 + \pi_6) \\ \frac{1}{2}(\pi_2 + \pi_3 - \pi_5 - \pi_6) \end{cases}$$

The hamiltonian transforms as A_1; therefore all integrals of the form $\int \psi' H \psi \, d\tau$ vanish unless ψ' and ψ belong to the same symmetry species. It follows that the secular determinant factorizes into four determinants

$$A_1: \quad H_{a_1 a_1} = \frac{1}{6}\int (\pi_1 + \cdots + \pi_6) H (\pi_1 + \cdots + \pi_6)\, d\tau = \alpha + 2\beta$$

$$B_1: \quad H_{b_1 b_1} = \frac{1}{6}\int (\pi_1 - \pi_2 + \cdots) H (\pi_1 - \pi_2 + \cdots)\, d\tau = \alpha - 2\beta$$

$$E_1: \quad H_{e_1(a)e_1(a)} = \alpha - \beta, \quad H_{e_1(b)e_1(b)} = \alpha - \beta, \quad H_{e_1(a)e_1(b)} = 0$$

$$\text{Hence} \begin{vmatrix} \alpha - \beta - \varepsilon & 0 \\ 0 & \alpha - \beta - \varepsilon \end{vmatrix} = 0 \text{ solves to } \varepsilon = \alpha - \beta \text{ (twice)}$$

$$E_2: \quad H_{e_2(a)e_2(a)} = \alpha + \beta, \quad H_{e_2(b)e_2(b)} = \alpha + \beta, \quad H_{e_2(a)e_2(b)} = 0$$

$$\text{Hence} \begin{vmatrix} \alpha + \beta - \varepsilon & 0 \\ 0 & \alpha + \beta - \varepsilon \end{vmatrix} = 0 \text{ solves to } \varepsilon = \alpha + \beta \text{ (twice)}$$

P12.18 (a) For a photon to induce a spectroscopic transition, the transition moment (μ) must be nonzero. The transition moment is the integral $\int \psi_f^* \mu \psi_i \, d\tau$, where the dipole moment operator has components proportional to the Cartesian coordinates. The integral vanishes unless the integrand, or at least some part of it, belongs to the totally symmetric representation of the molecule's point group. We can answer the first part of the question without reference to the character table, by considering the character of the integrand under inversion. Each component of μ has u character, but each state has g character; the integrand is g × g × u = u, so the integral vanishes and the transition is not allowed.

(b) However, if a vibration breaks the inversion symmetry, a look at the *I* character table shows that the components of μ have T_1 character. To find the character of the integrand, we multiply together the characters of its factors. For the transition to T_1

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
A_1	1	1	1	1	1
$\mu(T_1)$	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	-1
T_1	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	-1
Integrand	9	$\frac{1}{2}(3+\sqrt{5})$	$\frac{1}{2}(3-\sqrt{5})$	0	1

The decomposition of the characters of the integrand into those of the irreducible representations is difficult to do by inspection, but when accomplished it is seen to contain A_1. Therefore the transition to T_1 would become allowed. It is easier to use the formula below which is obtained from what is referred to as the "little orthogonality theorem" of group theory. (See the *Justification* in Section 15.5 of the 5th edition of this text.) The coefficient of A_1 in the integrand is given as

$$c_{A_1} = \frac{1}{h}\sum_C g(C)\chi(C) = \frac{\left\{9 + 12\left[\frac{1}{2}(3+\sqrt{5})\right] + 12\left[\frac{1}{2}(3-\sqrt{5})\right] + 20(0) + 15(1)\right\}}{60} = 1$$

So the integrand contains A_1, and the transition to T_1 would become allowed. For the transition to G

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
A_1	1	1	1	1	1
$\mu(T_1)$	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	-1
G	4	-1	-1	1	0
Integrand	12	$-\frac{1}{2}(1+\sqrt{5})$	$-\frac{1}{2}(1-\sqrt{5})$	0	0

The little orthogonality theorem gives the coefficient of A_1 in the integrand as

$$c_{A_1} = \frac{1}{h}\sum_C g(C)\chi(C) = \frac{\left\{12 + 12\left[-\frac{1}{2}(1+\sqrt{5})\right] + 12\left[-\frac{1}{2}(1-\sqrt{5})\right] + 20(0) + 15(0)\right\}}{60} = 0$$

So the integrand does not contain A_1, and the transition to G would still be forbidden.

Solutions to applications

P12.20 The point group for the square H_4 molecule is D_{4h} with $h = 16$ symmetry species. To find the irreducible representations or symmetry species spanned by four s orbitals, we use the methodology of Section 12.5c.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Number of unchanged basis members	4	0	0	2	0	0	0	4	2	0

The basis representation is obviously a linear combination of the D_{4h} symmetry species; it is reducible. Only the $E, 2C_2', \sigma_h$ and $2\sigma_v$ symmetry elements contribute (The others have factors of zero) to the number of times symmetry species Γ contributes ($a(\Gamma)$) to the representation of the basis.

E	$2C_2'$	σ_h	$2\sigma_v$	
$a(A_{1g}) = \frac{1}{16}\{4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot 1$	$+ 4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot 1\}$	$= 1$
$a(A_{2g}) = \frac{1}{16}\{4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot (-1)$	$+ 4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot (-1)\}$	$= 0$
$a(B_{1g}) = \frac{1}{16}\{4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot 1$	$+ 4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot 1\}$	$= 1$
$a(B_{2g}) = \frac{1}{16}\{4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot (-1)$	$+ 4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot (-1)\}$	$= 0$
$a(E_g) = \frac{1}{16}\{4\cdot 1\cdot 2$	$+ 2\cdot 2\cdot 0$	$+ 4\cdot 1\cdot (-2)$	$+ 2\cdot 2\cdot 0\}$	$= 0$
$a(A_{1u}) = \frac{1}{16}\{4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot 1$	$+ 4\cdot 1\cdot (-1)$	$+ 2\cdot 2\cdot (-1)\}$	$= 0$
$a(A_{2u}) = \frac{1}{16}\{4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot (-1)$	$+ 4\cdot 1\cdot (-1)$	$+ 2\cdot 2\cdot 1\}$	$= 0$
$a(B_{1u}) = \frac{1}{16}\{4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot 1$	$+ 4\cdot 1\cdot (-1)$	$+ 2\cdot 2\cdot (-1)\}$	$= 0$
$a(B_{2u}) = \frac{1}{16}\{4\cdot 1\cdot 1$	$+ 2\cdot 2\cdot (-1)$	$+ 4\cdot 1\cdot (-1)$	$+ 2\cdot 2\cdot 1\}$	$= 0$
$a(E_u) = \frac{1}{16}\{4\cdot 1\cdot 2$	$+ 2\cdot 2\cdot 0$	$+ 4\cdot 1\cdot 2$	$+ 2\cdot 2\cdot 0\}$	$= 1$

The basis spans $\boxed{A_{1g} + B_{1g} + E_u}$.

P12.22 Can the E_u excited state be reached by a dipole transition from the A_{1g} ground state? Only if the representation of the product $\psi_f^* \mu \psi_i$ includes the totally symmetric species A_{1g}. The z component of the dipole operator belongs to symmetry species A_{2u}, and the x and y components belong to E_u. So

the products we must consider are $E_u A_{2u} A_{1g}$ and $E_u E_u A_{1g}$. For z-polarized transitions, the relevant characters are:

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
E_u	2	0	−2	0	0	−2	0	2	0	0
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
A_{1g}	1	1	1	1	1	1	1	1	1	1
$E_u A_{2u} A_{1g}$	2	0	−2	0	0	2	0	−2	0	0

To see whether $E_u A_{2u} A_{1g}$ contains A_{1g}, we would multiply the characters of the $E_u A_{2u} A_{1g}$ by the characters of A_{1g}, sum those products, and divide the sum by the order h of the group; since the characters of A_{1g} are all 1, we can simply sum the characters of $E_u A_{2u} A_{1g}$. Since they sum to zero, the product $E_u A_{2u} A_{1g}$ does not contain A_{1g}, and the z-polarized transition is not allowed.

For x- or y-polarized transitions:

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
E_u	2	0	−2	0	0	−2	0	2	0	0
E_u	2	0	−2	0	0	−2	0	2	0	0
A_{1g}	1	1	1	1	1	1	1	1	1	1
$E_u E_u A_{1g}$	4	0	4	0	0	4	0	4	0	0

Summing the characters of $E_u E_u A_{1g}$, yields 16, the order of the group. Therefore the product $E_u E_u A_{1g}$ does contain A_{1g}, and the transition is allowed.

13 Spectroscopy 1: rotational and vibrational spectroscopy

Answers to discussion questions

D13.2 The gross selection rules tell us which are the allowed spectroscopic transitions. For both microwave and infrared spectroscopy, the allowed transitions depend on the existence of an oscillating dipole moment which can stir the electromagnetic field into oscillation (and *vice versa* for absorption). For microwave rotational spectroscopy, this implies that the molecule must have a permanent dipole moment, which is equivalent to an oscillating dipole when the molecule is rotating. See Figure 13.17 of the text. In the case of infrared vibrational spectroscopy, the physical basis of the gross selection rule is that the molecule have a structure that allows for the existence of an oscillating dipole moment when the molecule vibrates. Polar molecules necessarily satisfy this requirement, but non-polar molecules may also have a fluctuating dipole moment upon vibration. See Figure 13.28.

D13.4 The answer to this question depends precisely on what is meant by equilibrium bond length. See the solution to Problem 13.22 where it is demonstrated that the centrifugally distorted bond length r_c is given by the relation

$$r_c = \frac{r_e}{1 - m_{\text{eff}}\omega^2/k}.$$

The angular velocity depends upon the quantum number J through the relation

$$\omega^2 = J(J+1)\hbar^2/m_{\text{eff}}^2 r_e^4;$$

thus, the distortion is greater for higher rotational energy levels. But the equilibrium bond length r_e remains constant, if by that term one means the value of r corresponding to a vibrating non-rotating molecule with $J = 0$. However, if one describes the vibration of the molecule in a higher rotational state as having a new "equilibrium" distance r_c, the potential energy of vibration will also be different. It is lowered by the amount shown in eqn 13.33, that is, $-D_J J^2(J+1)^2$. A detailed analysis of the combined effects of rotation and vibration is quite complicated. The treatment in Section 13.12 ignores the effects of centrifugal distortion and anharmonicity. See the references under *Further Reading* for a more thorough discussion.

Solutions to exercises

E13.1(b) The ratio of coefficients A/B is

(a) $$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} = \frac{8\pi(6.626 \times 10^{-34}\,\text{J s}) \times (500 \times 10^6\,\text{s}^{-1})^3}{(2.998 \times 10^8\,\text{m s}^{-1})^3} = \boxed{7.73 \times 10^{-32}\,\text{J m}^{-3}\,\text{s}}$$

(b) The frequency is

$$\nu = \frac{c}{\lambda} \text{ so } \frac{A}{B} = \frac{8\pi h}{\lambda^3} = \frac{8\pi(6.626 \times 10^{-34}\,\text{J s})}{(3.0 \times 10^{-2}\,\text{m})^3} = \boxed{6.2 \times 10^{-28}\,\text{J m}^{-3}\,\text{s}}$$

E13.2(b) A source approaching an observer appears to be emitting light of frequency

$$\nu_{\text{approaching}} = \frac{\nu}{1 - \frac{s}{c}} \text{ [13.15, Section 13.3]}$$

Since $\nu \propto \frac{1}{\lambda}$, $\lambda_{\text{obs}} = (1 - s/c)\,\lambda$

For the light to appear green the speed would have to be

$$s = \left(1 - \frac{\lambda_{\text{obs}}}{\lambda}\right) c = (2.998 \times 10^8\,\text{m s}^{-1}) \times \left(1 - \frac{520\,\text{nm}}{660\,\text{nm}}\right) = \boxed{6.36 \times 10^7\,\text{m s}^{-1}}$$

or about 1.4×10^8 m.p.h.

(Since $s \approx c$, the relativistic expression

$$\nu_{\text{obs}} = \left(\frac{1 + (s/c)}{1 - (s/c)}\right)^{1/2} \nu$$

should really be used. It gives $s = 7.02 \times 10^7\,\text{m s}^{-1}$.)

E13.3(b) The linewidth is related to the lifetime τ by

$$\delta\tilde{\nu} = \frac{5.31\,\text{cm}^{-1}}{\tau/\text{ps}} \text{ [13.19] so } \tau = \frac{5.31\,\text{cm}^{-1}}{\delta\tilde{\nu}}\,\text{ps}$$

(a) We are given a frequency rather than a wavenumber

$$\tilde{\nu} = \nu/c \text{ so } \tau = \frac{(5.31\,\text{cm}^{-1}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}{100 \times 10^6\,\text{s}^{-1}}\text{ps} = 1.59 \times 10^3\,\text{ps}$$

or $\boxed{1.59\,\text{ns}}$

(b) $\tau = \dfrac{5.31\,\text{cm}^{-1}}{2.14\,\text{cm}^{-1}}\text{ps} = \boxed{2.48\,\text{ps}}$

E13.4(b) The linewidth is related to the lifetime τ by

$$\delta\tilde{\nu} = \frac{5.31\,\text{cm}^{-1}}{\tau/\text{ps}} \text{ so } \delta\nu = \frac{(5.31\,\text{cm}^{-1})c}{\tau/\text{ps}}$$

(a) If every collision is effective, then the lifetime is $1/(1.0 \times 10^9\,\text{s}^{-1}) = 1.0 \times 10^{-9}\,\text{s} = 1.0 \times 10^3\,\text{ps}$

$$\delta\tilde{\nu} = \frac{(5.31\,\text{cm}^{-1}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}{1.0 \times 10^3} = 1.6 \times 10^8\,\text{s}^{-1} = \boxed{160\,\text{MHz}}$$

(b) If only one collision in 10 is effective, then the lifetime is a factor of 10 greater, 1.0×10^4 ps

$$\delta\tilde{\nu} = \frac{(5.31\ \text{cm}^{-1}) \times (2.998 \times 10^{10}\ \text{cm s}^{-1})}{1.0 \times 10^4} = 1.6 \times 10^7\ \text{s}^{-1} = \boxed{16\ \text{MHz}}$$

E13.5(b) The frequency of the transition is related to the rotational constant by

$$h\nu = \Delta E = hc\Delta F = hcB[J(J+1) - (J-1)J] = 2hcBJ$$

where J refers to the upper state ($J = 3$). The rotational constant is related to molecular structure by

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c m_{\text{eff}} R^2}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length. Putting these expressions together yields

$$\nu = 2cBJ = \frac{\hbar J}{2\pi m_{\text{eff}} R^2}$$

The reciprocal of the effective mass is

$$m_{\text{eff}}^{-1} = m_{\text{C}}^{-1} + m_{\text{O}}^{-1} = \frac{(12\,\text{u})^{-1} + (15.9949\,\text{u})^{-1}}{1.660\,54 \times 10^{-27}\ \text{kg u}^{-1}} = 8.783\,48 \times 10^{25}\ \text{kg}^{-1}$$

$$\text{So } \nu = \frac{(8.783\,48 \times 10^{25}\ \text{kg}^{-1}) \times (1.0546 \times 10^{-34}\ \text{J s}) \times (3)}{2\pi(112.81 \times 10^{-12}\text{m})^2} = \boxed{3.4754 \times 10^{11}\ \text{s}^{-1}}$$

E13.6(b) **(a)** The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta F = hcB[J(J+1) - (J-1)J] = 2hcBJ$$

where J refers to the upper state ($J = 1$). The rotational constant is related to molecular structure by

$$B = \frac{\hbar}{4\pi cI}$$

where I is moment of inertia. Putting these expressions together yields

$$\tilde{\nu} = 2BJ = \frac{\hbar J}{2\pi cI} \text{ so } I = \frac{\hbar J}{c\tilde{\nu}} = \frac{(1.0546 \times 10^{-34}\ \text{J s}) \times (1)}{2\pi(2.998 \times 10^{10}\ \text{cm s}^{-1}) \times (16.93\ \text{cm}^{-1})}$$

$$I = \boxed{3.307 \times 10^{-47}\ \text{kg m}^2}$$

(b) The moment of inertia is related to the bond length by

$$I = m_{\text{eff}} R^2 \text{ so } R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{H}}^{-1} + m_{\text{Br}}^{-1} = \frac{(1.0078\,\text{u})^{-1} + (80.9163\,\text{u})^{-1}}{1.660\,54 \times 10^{-27}\ \text{kg u}^{-1}} = 6.0494 \times 10^{26}\ \text{kg}^{-1}$$

$$\text{and } R = \{(6.0494 \times 10^{26}\ \text{kg}^{-1}) \times (3.307 \times 10^{-47}\ \text{kg m}^2)\}^{1/2}$$

$$= 1.414 \times 10^{-10}\text{m} = \boxed{141.4\ \text{pm}}$$

E13.7(b) The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta F = hcB[J(J+1) - (J-1)J] = 2hcBJ$$

where J refers to the upper state. So wavenumbers of adjacent transitions (transitions whose upper states differ by 1) differ by

$$\Delta\tilde{\nu} = 2B = \frac{\hbar}{2\pi cI} \text{ so } I = \frac{\hbar}{2\pi c\Delta\tilde{\nu}}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length.

$$\text{So } I = \frac{(1.0546 \times 10^{-34}\ \text{J s})}{2\pi(2.9979 \times 10^{10}\ \text{cm s}^{-1}) \times (1.033\ \text{cm}^{-1})} = \boxed{5.420 \times 10^{-46}\ \text{kg m}^2}$$

The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2 \text{ so } R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{F}}^{-1} + m_{\text{Cl}}^{-1} = \frac{(18.9984\ \text{u})^{-1} + (34.9688\ \text{u})^{-1}}{1.660\,54 \times 10^{-27}\ \text{kg u}^{-1}} = 4.891\,96 \times 10^{25}\ \text{kg}^{-1}$$

$$\text{and } R = \{(4.891\,96 \times 10^{25}\ \text{kg}^{-1}) \times (5.420 \times 10^{-46}\ \text{kg m}^2)\}^{1/2}$$

$$= 1.628 \times 10^{-10}\,\text{m} = \boxed{162.8\ \text{pm}}$$

E13.8(b) The rotational constant is

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c(2m_{\text{O}}R^2)} \text{ so } R = \left(\frac{\hbar}{8\pi cm_{\text{O}}B}\right)^{1/2}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length.

$$R = \left(\frac{(1.0546 \times 10^{-34}\ \text{J s})}{8\pi(2.9979 \times 10^{10}\ \text{cm s}^{-1}) \times (15.9949\ \text{u}) \times (1.660\,54 \times 10^{-27}\ \text{kg u}^{-1})(0.390\,21)}\right)^{1/2}$$

$$= 1.1621 \times 10^{-10}\,\text{m} = \boxed{116.21\ \text{pm}}$$

E13.9(b) This exercise is analogous to Exercise 13.9(a), but here our solution will employ a slightly different algebraic technique. Let $R = R_{\text{OC}}$, $R' = R_{\text{CS}}$, O $= {}^{16}$O, C $= {}^{12}$C.

$$I = \frac{\hbar}{4\pi B} \text{ [}\textit{Comment}\text{ 13.4]}$$

$$I(\text{OC}^{32}\text{S}) = \frac{1.054\,57 \times 10^{-34}\ \text{J s}}{(4\pi) \times (6.0815 \times 10^{9}\ \text{s}^{-1})} = 1.3799 \times 10^{-45}\ \text{kg m}^2 = 8.3101 \times 10^{-19}\ \text{u m}^2$$

$$I(\text{OC}^{34}\text{S}) = \frac{1.054\,57 \times 10^{-34}\ \text{J s}}{(4\pi) \times (5.9328 \times 10^{9}\ \text{s}^{-1})} = 1.4145 \times 10^{-45}\ \text{kg m}^2 = 8.5184 \times 10^{-19}\ \text{u m}^2$$

The expression for the moment of inertia given in Table 13.1 may be rearranged as follows.

$$\begin{aligned} Im &= m_A m R^2 + m_C m R'^2 - (m_A R - m_C R')^2 \\ &= m_A m R^2 + m_C m R'^2 - m_A^2 R^2 + 2 m_A m_C R R' - m_C^2 R'^2 \\ &= m_A (m_B + m_C) R^2 + m_C (m_A + m_B) R'^2 + 2 m_A m_C R R' \end{aligned}$$

Let $m_C = m_{32_S}$ and $m'_C = m_{34_S}$

$$\frac{Im}{m_C} = \frac{m_A}{m_C}(m_B + m_C)R^2 + (m_A + m_B)R'^2 + 2m_A RR' \qquad \text{(a)}$$

$$\frac{I'm'}{m'_C} = \frac{m_A}{m'_C}(m_B + m'_C)R^2 + (m_A + m_B)R'^2 + 2m_A RR' \qquad \text{(b)}$$

Subtracting

$$\frac{Im}{m_C} - \frac{I'm'}{m'_C} = \left[\left(\frac{m_A}{m_C}\right)(m_B + m_C) - \left(\frac{m_A}{m'_C}\right)(m_B + m'_C)\right] R^2$$

Solving for R^2

$$R^2 = \frac{\left(\frac{Im}{m_C} - \frac{I'm'}{m'_C}\right)}{\left[\left(\frac{m_A}{m_C}\right)(m_B + m_C) - \left(\frac{m_A}{m'_C}\right)(m_B + m'_C)\right]} = \frac{m'_C Im - m_C I'm'}{m_B m_A (m'_C - m_C)}$$

Substituting the masses, with $m_A = m_O$, $m_B = m_C$, $m_C = m_{32_S}$, and $m'_C = m_{34_S}$

$$m = (15.9949 + 12.0000 + 31.9721)\ \text{u} = 59.9670\ \text{u}$$

$$m' = (15.9949 + 12.0000 + 33.9679)\ \text{u} = 61.9628\ \text{u}$$

$$\begin{aligned} R^2 &= \frac{(33.9679\ \text{u}) \times (8.3101 \times 10^{-19}\ \text{u m}^2) \times (59.9670\ \text{u})}{(12.0000\ \text{u}) \times (15.9949\ \text{u}) \times (33.9679\ \text{u} - 31.9721\ \text{u})} \\ &\quad - \frac{(33.9721\ \text{u}) \times (8.5184 \times 10^{-19}\ \text{u m}^2) \times (61.9628\ \text{u})}{(12.0000\ \text{u}) \times (15.9949\ \text{u}) \times (33.9679\ \text{u} - 31.9721\ \text{u})} \\ &= \frac{51.6446 \times 10^{-19}\ \text{m}^2)}{383.071} = 1.3482 \times 10^{-20}\ \text{m}^2 \end{aligned}$$

$$R = 1.161\overline{1} \times 10^{-10}\ \text{m} = \boxed{116.1\ \text{pm}} = R_{OC}$$

Because the numerator of the expression for R^2 involves the difference between two rather large numbers of nearly the same magnitude, the number of significant figures in the answer for R is certainly no greater than 4. Having solved for R, either equation (a) or (b) above can be solved for R'. The result is

$$R' = 1.559 \times 10^{-10}\ \text{m} = \boxed{155.9\ \text{pm}} = R_{CS}$$

E13.10(b) The wavenumber of a Stokes line in rotational Raman is

$$\tilde{\nu}_{\text{Stokes}} = \tilde{\nu}_i - 2B(2J + 3)\ [13.42a]$$

where J is the initial (lower) rotational state. So

$$\tilde{\nu}_{\text{Stokes}} = 20\,623\ \text{cm}^{-1} - 2(1.4457\ \text{cm}^{-1}) \times [2(2) + 3] = \boxed{20\,603\ \text{cm}^{-1}}$$

E13.11(b) The separation of lines is $4B$, so $B = \frac{1}{4} \times (3.5312\ \text{cm}^{-1}) = 0.882\,80\ \text{cm}^{-1}$

Then we use $R = \left(\dfrac{\hbar}{4\pi m_{\text{eff}} cB}\right)^{1/2}$ [Exercise 13.8(a)]

with $m_{\text{eff}} = \frac{1}{2}m(^{19}\text{F}) = \frac{1}{2} \times (18.9984\ \text{u}) \times (1.6605 \times 10^{-27}\ \text{kg u}^{-1}) = 1.577\,34\tilde{2} \times 10^{-26}\ \text{kg}$

$$R = \left(\frac{1.0546 \times 10^{-34}\ \text{J s}}{4\pi(1.577\,342 \times 10^{-26}\ \text{kg}) \times (2.998 \times 10^{10}\ \text{cm s}^{-1}) \times (0.882\,80\ \text{cm}^{-1})}\right)^{1/2}$$

$$= 1.417\,8\tilde{5} \times 10^{-10}\ \text{m} = \boxed{141.78\ \text{pm}}$$

E13.12(b) Polar molecules show a pure rotational absorption spectrum. Therefore, select the polar molecules based on their well-known structures. Alternatively, determine the point groups of the molecules and use the rule that only molecules belonging to C_n, C_{nv}, and C_s may be polar, and in the case of C_n and C_{nv}, that dipole must lie along the rotation axis. Hence all are polar molecules.

Their point group symmetries are

(a) H_2O, C_{2v}, **(b)** H_2O_2, C_2, **(c)** NH_3, C_{3v}, **(d)** N_2O, $C_{\infty v}$

$\boxed{\text{All}}$ show a pure rotational spectrum.

E13.13(b) A molecule must be anisotropically polarizable to show a rotational Raman spectrum; all molecules except spherical rotors have this property. So $\boxed{CH_2Cl_2}$, $\boxed{CH_3CH_3}$, and $\boxed{N_2O}$ can display rotational Raman spectra; SF_6 cannot.

E13.14(b) The angular frequency is

$$\omega = \left(\frac{k}{m}\right)^{1/2} = 2\pi\nu \quad \text{so} \quad k = (2\pi\nu)^2 m = (2\pi)^2 \times (3.0\ \text{s}^{-1})^2 \times (2.0 \times 10^{-3}\ \text{kg})$$

$$k = \boxed{0.71\ \text{N m}^{-1}}$$

E13.15(b) $\omega = \left(\dfrac{k}{m_{\text{eff}}}\right)^{1/2} \quad \omega' = \left(\dfrac{k}{m'_{\text{eff}}}\right)^{1/2}$ [prime = $^2\text{H}^{37}\text{Cl}$]

The force constant, k, is assumed to be the same for both molecules. The fractional difference is

$$\frac{\omega' - \omega}{\omega} = \frac{\left(\dfrac{k}{m'_{\text{eff}}}\right)^{1/2} - \left(\dfrac{k}{m_{\text{eff}}}\right)^{1/2}}{\left(\dfrac{k}{m_{\text{eff}}}\right)^{1/2}} = \frac{\left(\dfrac{1}{m'_{\text{eff}}}\right)^{1/2} - \left(\dfrac{1}{m_{\text{eff}}}\right)^{1/2}}{\left(\dfrac{1}{m_{\text{eff}}}\right)^{1/2}} = \left(\frac{m_{\text{eff}}}{m'_{\text{eff}}}\right)^{1/2} - 1$$

$$\frac{\omega' - \omega}{\omega} = \left(\frac{m_{\text{eff}}}{m'_{\text{eff}}}\right)^{1/2} - 1 = \left\{\frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} \times \frac{(m_{^2\text{H}} + m_{^{37}\text{Cl}})}{(m_{^2\text{H}} \times m_{^{37}\text{Cl}})}\right\}^{1/2} - 1$$

$$= \left\{\frac{(1.0078\ \text{u}) \times (34.9688\ \text{u})}{(1.0078\ \text{u}) + (34.9688\ \text{u})} \times \frac{(2.0140\ \text{u}) + (36.9651\ \text{u})}{(2.0140\ \text{u}) \times (36.9651\ \text{u})}\right\}^{1/2} - 1$$

$$= -0.284$$

Thus the difference is $\boxed{28.4\ \text{percent}}$

E13.16(b) The fundamental vibrational frequency is

$$\omega = \left(\frac{k}{m_{\text{eff}}}\right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad k = (2\pi c\tilde{\nu})^2 m_{\text{eff}}$$

We need the effective mass

$$m_{\text{eff}}^{-1} = m_1^{-1} + m_2^{-1} = (78.9183\ \text{u})^{-1} + (80.9163\ \text{u})^{-1} = 0.025\,029\,8\ \text{u}^{-1}$$

$$k = \frac{[2\pi(2.998 \times 10^{10}\ \text{cm s}^{-1}) \times (323.2\ \text{cm}^{-1})]^2 \times (1.66054 \times 10^{-27}\ \text{kg u}^{-1})}{0.025\,029\,8\ \text{u}^{-1}}$$

$$= \boxed{245.9\ \text{N m}^{-1}}$$

E13.17(b) The ratio of the population of the ground state (N_0) to the first excited state (N_1) is

$$\frac{N_0}{N_1} = \exp\left(\frac{-h\nu}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right)$$

(a) $$\frac{N_0}{N_1} = \exp\left(\frac{-(6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^{10}\ \text{cm s}^{-1}) \times (321\ \text{cm}^{-1})}{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (298\ \text{K})}\right) = \boxed{0.212}$$

(b) $$\frac{N_0}{N_1} = \exp\left(\frac{-(6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^{10}\ \text{cm s}^{-1}) \times (321\ \text{cm}^{-1})}{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (800\ \text{K})}\right) = \boxed{0.561}$$

E13.18(b) The relation between vibrational frequency and wavenumber is

$$\omega = \left(\frac{k}{m_{\text{eff}}}\right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{m_{\text{eff}}}\right)^{1/2} = \frac{(km_{\text{eff}}^{-1})^{1/2}}{2\pi c}$$

The reduced masses of the hydrogen halides are very similar, but not identical

$$m_{\text{eff}}^{-1} = m_{\text{D}}^{-1} + m_{\text{X}}^{-1}$$

We assume that the force constants as calculated in Exercise 13.18(a) are identical for the deuterium halide and the hydrogen halide.

For DF

$$m_{\text{eff}}^{-1} = \frac{(2.0140\ \text{u})^{-1} + (18.9984\ \text{u})^{-1}}{1.66054 \times 10^{-27}\ \text{kg u}^{-1}} = 3.3071 \times 10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.3071 \times 10^{26}\ \text{kg}^{-1}) \times (967.04\ \text{kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10}\ \text{cm s}^{-1})} = \boxed{3002.3\ \text{cm}^{-1}}$$

For DCl

$$m_{\text{eff}}^{-1} = \frac{(2.0140\ \text{u})^{-1} + (34.9688\ \text{u})^{-1}}{1.66054 \times 10^{-27}\ \text{kg u}^{-1}} = 3.1624 \times 10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.1624 \times 10^{26}\ \text{kg}^{-1}) \times (515.59\ \text{kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10}\ \text{cm s}^{-1})} = \boxed{2143.7\ \text{cm}^{-1}}$$

For DBr

$$m_{\text{eff}}^{-1} = \frac{(2.0140\text{ u})^{-1} + (80.9163\text{ u})^{-1}}{1.66054 \times 10^{-27}\text{ kg u}^{-1}} = 3.0646 \times 10^{26}\text{ kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.0646 \times 10^{26}\text{ kg}^{-1}) \times (411.75\text{ kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10}\text{ cm s}^{-1})} = \boxed{1885.8\text{ cm}^{-1}}$$

For DI

$$m_{\text{eff}}^{-1} = \frac{(2.0140\text{ u})^{-1} + (126.9045\text{ u})^{-1}}{1.66054 \times 10^{-27}\text{ kg u}^{-1}} = 3.0376 \times 10^{26}\text{ kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.0376 \times 10^{26}\text{ kg}^{-1}) \times (314.21\text{ kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10}\text{ cm s}^{-1})} = \boxed{1640.1\text{ cm}^{-1}}$$

E13.19(b) Data on three transitions are provided. Only two are necessary to obtain the value of $\tilde{\nu}$ and x_e. The third datum can then be used to check the accuracy of the calculated values.

$$\Delta G(v = 1 \leftarrow 0) = \tilde{\nu} - 2\tilde{\nu}x_e = 2345.15\text{ cm}^{-1}\ [13.57]$$

$$\Delta G(v = 2 \leftarrow 0) = 2\tilde{\nu} - 6\tilde{\nu}x_e = 4661.40\text{ cm}^{-1}\ [13.58]$$

Multiply the first equation by 3, then subtract the second.

$$\tilde{\nu} = (3) \times (2345.15\text{ cm}^{-1}) - (4661.40\text{ cm}^{-1}) = \boxed{2374.05\text{ cm}^{-1}}$$

Then from the first equation

$$x_e = \frac{\tilde{\nu} - 2345.15\text{ cm}^{-1}}{2\tilde{\nu}} = \frac{(2374.05 - 2345.15)\text{cm}^{-1}}{(2) \times (2374.05\text{ cm}^{-1})} = \boxed{6.087 \times 10^{-3}}$$

x_e data are usually reported as $x_e\tilde{\nu}$ which is

$$x_e\tilde{\nu} = 14.45\text{ cm}^{-1}$$

$$\Delta G(v = 3 \leftarrow 0) = 3\tilde{\nu} - 12\nu x_e = (3) \times (2374.05\text{ cm}^{-1}) - (12) \times (14.45\text{ cm}^{-1})$$
$$= 6948.74\text{ cm}^{-1}$$

which is close to the experimental value.

E13.20(b) $\Delta G_{v+1/2} = \tilde{\nu} - 2(v + 1)x_e\tilde{\nu}$ [13.57] where $\Delta G_{v+1/2} = G(v + 1) - G(v)$

Therefore, since

$$\Delta G_{v+1/2} = (1 - 2x_e)\tilde{\nu} - 2vx_e\tilde{\nu}$$

a plot of $\Delta G_{v+1/2}$ against v should give a straight line which gives $(1 - 2x_e)\tilde{\nu}$ from the intercept at $v = 0$ and $-2x_e\tilde{\nu}$ from the slope. We draw up the following table

v	0	1	2	3	4
$G(v)/\text{cm}^{-1}$	1144.83	3374.90	5525.51	7596.66	9588.35
$\Delta G_{v+1/2}/\text{cm}^{-1}$	2230.07	2150.61	2071.15	1991.69	

The points are plotted in Figure 13.1.

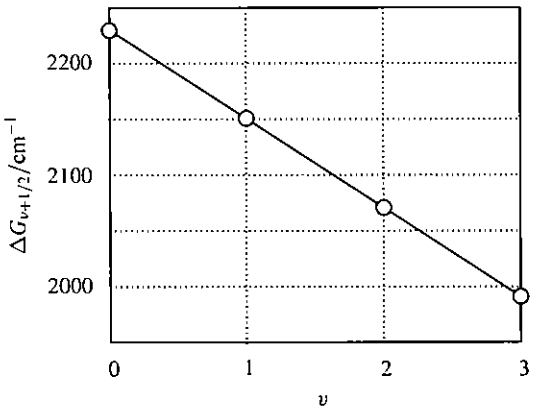


Figure 13.1

The intercept lies at 2230.51 and the slope $= -76.65\ \text{cm}^{-1}$; hence $x_e\tilde{\nu} = 39.83\ \text{cm}^{-1}$.

Since $\tilde{\nu} - 2x_e\tilde{\nu} = 2230.51\ \text{cm}^{-1}$ it follows that $\tilde{\nu} = 2310.16\ \text{cm}^{-1}$

The dissociation energy may be obtained by assuming that a Morse potential describes the molecule and that the constant D_e in the expression for the potential is an adequate first approximation for it. Then

$$D_e = \frac{\tilde{\nu}}{4x_e}\ [13.55] = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} = \frac{(2310.16\ \text{cm}^{-1})^2}{(4) \times (39.83\ \text{cm}^{-1})} = 33.50 \times 10^3\ \text{cm}^{-1} = 4.15\ \text{eV}$$

However, the depth of the potential well D_e differs from D_0, the dissociation energy of the bond, by the zero-point energy; hence

$$D_0 = D_e - \frac{1}{2}\tilde{\nu} = (33.50 \times 10^3\ \text{cm}^{-1}) - \left(\tfrac{1}{2}\right) \times (2310.16\ \text{cm}^{-1})$$
$$= \boxed{3.235 \times 10^4\ \text{cm}^{-1}} = \boxed{4.01\ \text{eV}}$$

E13.21(b) The wavenumber of an R-branch IR transition is

$$\tilde{\nu}_R = \tilde{\nu} + 2B(J + 1)\ [13.62c]$$

where J is the initial (lower) rotational state. So

$$\tilde{\nu}_R = 2308.09\ \text{cm}^{-1} + 2(6.511\ \text{cm}^{-1}) \times (2 + 1) = \boxed{2347.16\ \text{cm}^{-1}}$$

E13.22(b) See Section 13.10. Select those molecules in which a vibration gives rise to a change in dipole moment. It is helpful to write down the structural formulas of the compounds. The infrared active compounds are

(a) CH_3CH_3; **(b)** CH_4; **(c)** CH_3Cl

COMMENT. A more powerful method for determining infrared activity based on symmetry considerations is described in Section 13.15.

E13.23(b) A nonlinear molecule has $3N - 6$ normal modes of vibration, where N is the number of atoms in the molecule; a linear molecule has $3N - 5$.

(a) C_6H_6 has $3(12) - 6 = \boxed{30}$ normal modes.

(b) $C_6H_6CH_3$ has $3(16) - 6 = \boxed{42}$ normal modes.

(c) $HC{\equiv}C{-}C{\equiv}CH$ is linear; it has $3(6) - 5 = \boxed{13}$ normal modes.

E13.24(b) **(a)** A planar AB_3 molecule belongs to the D_{3h} group. Its four atoms have a total of 12 displacements, of which 6 are vibrations. We determine the symmetry species of the vibrations by first determining the characters of the reducible representation of the molecule formed from all 12 displacements and then subtracting from these characters the characters corresponding to translation and rotation. This latter information is directly available in the character table for the group D_{3h}. The resulting set of characters are the characters of the reducible representation of the vibrations. This representation can be reduced to the symmetry species of the vibrations by inspection or by use of the little orthogonality theorem.

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
χ (translation)	3	1	0	−2	−1	1
Unmoved atoms	4	4	1	1	2	2
χ (total, product)	12	4	0	−2	−2	2
χ (rotation)	3	−1	0	2	−1	−1
χ (vibration)	6	4	0	−2	0	2

χ (vibration) corresponds to $A_1' + A_2'' + 2E'$.

Again referring to the character table of D_{3h}, we see that E′ corresponds to x and y, A_2'' to z; hence $\boxed{A_2'' \text{ and } E' \text{ are IR active}}$. We also see from the character table that E' and A_1' correspond to the quadratic terms; hence $\boxed{A_1' \text{ and E}' \text{ are Raman active}}$.

(b) A trigonal pyramidal AB_3 molecule belongs to the group C_{3v}. In a manner similar to the analysis in part (a) we obtain

C_{3v}	E	$2C_3$	$3\sigma_v$
χ (total)	12	0	2
χ (vibration)	6	−2	2

χ (vibration) corresponds to $2A_1 + 2E$. We see from the character table that $\boxed{A_1 \text{ and E}}$ are IR active and that $\boxed{A_1 + E}$ are also Raman active. Thus all modes are observable in both the IR and the Raman spectra.

E13.25(b) **(b)** The boat-like bending of a benzene ring clearly changes the dipole moment of the ring, for the moving of the C—H bonds out of the plane will give rise to a non-cancelling component of their dipole moments. So the vibration is IR active.

(a) Since benzene has a centre of inversion, the exclusion rule applies: a mode which is IR active (such as this one) must be Raman inactive.

E13.26(b) The displacements span $A_{1g} + A_{1u} + A_{2g} + 2E_{1u} + E_{1g}$. The rotations R_x and R_y span E_{1g}, and the translations span $E_{1u} + A_{1u}$. So the vibrations span $A_{1g} + A_{2g} + E_{1u}$

Solutions to problems

Solutions to numerical problems

P13.2

$$\frac{\delta\lambda}{\lambda} = \frac{2}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2} \quad [13.17]$$

$$= \left(\frac{2}{2.998 \times 10^8\ \text{m s}^{-1}}\right) \times \left(\frac{(2) \times (1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (298\ \text{K}) \times (\ln 2)}{(m/\text{u}) \times (1.6605 \times 10^{-27}\ \text{kg})}\right)^{1/2}$$

$$= \frac{1.237 \times 10^{-5}}{(m/\text{u})^{1/2}}$$

(a) For $^1H^{35}Cl$, $m \approx 36$ u, so $\frac{\delta\lambda}{\lambda} \approx \boxed{2.1 \times 10^{-6}}$

(b) For $^{127}I^{35}Cl$, $m \approx 162$ u, so $\frac{\delta\lambda}{\lambda} \approx \boxed{9.7 \times 10^{-7}}$

For the second part of the problem, we also need

$$\frac{\delta\tilde{\nu}}{\tilde{\nu}} = \frac{\delta\nu}{\nu} = \frac{2}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2} [13.17] = \frac{\delta\lambda}{\lambda} \quad \left[\frac{\delta\lambda}{\lambda} \ll 1\right]$$

(a) For HCl, ν(rotation) $\approx 2Bc \approx (2) \times (10.6\ \text{cm}^{-1}) \times (2.998 \times 10^{10}\ \text{cm s}^{-1})$

$$\approx 6.4 \times 10^{11}\ \text{s}^{-1} \text{ or } 6.4 \times 10^{11}\ \text{Hz}$$

Therefore, $\delta\nu$(rotation) $\approx (2.1 \times 10^{-6}) \times (6.4 \times 10^{11}\ \text{Hz}) = \boxed{1.3\ \text{MHz}}$

$\tilde{\nu}$(vibration) $\approx 2991\ \text{cm}^{-1}$ [Table 13.2]; therefore

$\delta\tilde{\nu}$(vibration) $\approx (2.1 \times 10^{-6}) \times (2991\ \text{cm}^{-1}) = \boxed{0.0063\ \text{cm}^{-1}}$

(b) For ICl, ν(rotation) $\approx (2) \times (0.1142\ \text{cm}^{-1}) \times (2.998 \times 10^{10}\ \text{cm s}^{-1}) \approx 6.8 \times 10^9\ \text{Hz}$

$\delta\nu$(rotation) $\approx (9.7 \times 10^{-7}) \times (6.8 \times 10^9\ \text{Hz}) = \boxed{6.6\ \text{kHz}}$

$\tilde{\nu}$(vibration) $\approx 384\ \text{cm}^{-1}$

$\delta\tilde{\nu}$(vibration) $\approx (9.7 \times 10^{-7}) \times (384\ \text{cm}^{-1}) \approx \boxed{0.0004\ \text{cm}^{-1}}$

COMMENT. ICl is a solid which melts at 27.2 °C and has a significant vapor pressure at 25 °C.

P13.4 Rotational line separations are $2B$ (in wavenumber units), $2Bc$ (in frequency units), and $(2B)^{-1}$ in wavelength units. Hence the transitions are separated by $\boxed{596\text{ GHZ}}$, $\boxed{19.9\text{ cm}^{-1}}$, and $\boxed{0.503\text{ mm}}$.

Ammonia is a symmetric rotor (section 13.4) and we know that

$$B = \frac{\hbar}{4\pi c I_\perp} \quad [13.30]$$

and from Table 13.1,

$$I_\perp = m_A R^2(1 - \cos\theta) + \left(\frac{m_A m_B}{m}\right) R^2(1 + 2\cos\theta)$$

$m_A = 1.6735 \times 10^{-27}$ kg, $m_B = 2.3252 \times 10^{-26}$ kg, and $m = 2.8273 \times 10^{-26}$ kg with $R = 101.4$ pm and $\theta = 106°47'$, which gives

$$\begin{aligned} I_\perp &= (1.6735 \times 10^{-27}\text{ kg}) \times (101.4 \times 10^{-12}\text{ m})^2 \times (1 - \cos 106°47') \\ &\quad + \left(\frac{(1.6735 \times 10^{-27}) \times (2.3252 \times 10^{-26}\text{ kg}^2)}{2.8273 \times 10^{-26}\text{ kg}}\right) \\ &\quad \times (101.4 \times 10^{-12}\text{ m})^2 \times (1 + 2\cos 106°47') \\ &= 2.815\bar{8} \times 10^{-47}\text{ kg m}^2 \end{aligned}$$

Therefore,

$$B = \frac{1.05457 \times 10^{-34}\text{ J s}}{(4\pi) \times (2.9979 \times 10^8\text{ m s}^{-1}) \times (2.815\bar{8} \times 10^{-47}\text{ kg m}^2)} = 994.1\text{ m}^{-1} = \boxed{9.941\text{ cm}^{-1}}$$

which is in accord with the data.

P13.6 Rotation about any axis perpendicular to the C_6 axis may be represented in its essentials by rotation of the pseudolinear molecule in Figure 13.2(a) about the x-axis in the figure.

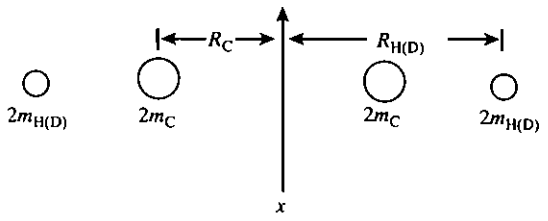


Figure 13.2(a)

The data allow for a determination of R_C and $R_{H(D)}$ which may be decomposed into R_{CC} and $R_{CH(D)}$.

$$I_H = 4m_H R_H^2 + 4m_C R_C^2 = 147.59 \times 10^{-47}\text{ kg m}^2$$

$$I_D = 4m_D R_D^2 + 4m_C R_C^2 = 178.45 \times 10^{-47}\text{ kg m}^2$$

Subtracting I_H from I_D (assume $R_H = R_D$) yields

$$4(m_D - m_H)R_H^2 = 30.86 \times 10^{-47}\ \text{kg m}^2$$

$$4(2.01417\ \text{u} - 1.0078\ \text{u}) \times (1.660\,54 \times 10^{-27}\ \text{kg u}^{-1}) \times (R_H^2) = 30.86 \times 10^{-47}\ \text{kg m}^2$$

$$R_H^2 = 4.616\bar{9} \times 10^{-20}\ \text{m}^2 \quad R_H = 2.149 \times 10^{-10}\ \text{m}$$

$$R_C^2 = \frac{(147.59 \times 10^{-47}\ \text{kg m}^2) - (4m_H R_H^2)}{4m_C}$$

$$= \frac{(147.59 \times 10^{-47}\ \text{kg m}^2) - (4) \times (1.0078\ \text{u}) \times (1.660\,54 \times 10^{-27}\ \text{kg u}^{-1}) \times (4.616\bar{9} \times 10^{-20}\ \text{m}^2)}{(4) \times (12.011\ \text{u}) \times (1.660\,54 \times 10^{-27}\ \text{kg u}^{-1})}$$

$$= 1.4626 \times 10^{-20}\ \text{m}^2$$

$$R_C = 1.209 \times 10^{-10}\ \text{m}$$

Figure 13.2(b) shows the relation between R_H, R_C, R_{CC}, and R_{CH}.

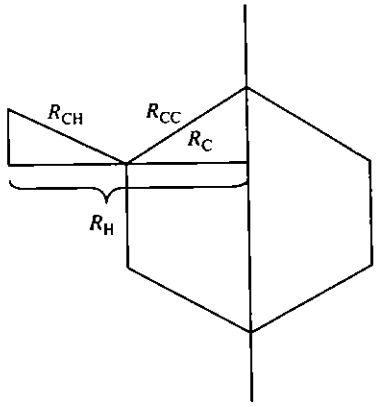


Figure 13.2(b)

$$R_{CC} = \frac{R_C}{\cos 30°} = \frac{1.209 \times 10^{-10}\text{m}}{0.8660} = 1.396 \times 10^{-10}\ \text{m} = \boxed{139.6\ \text{pm}}$$

$$R_{CH} = \frac{R_H - R_C}{\cos 30°} = \frac{0.940 \times 10^{-10}}{0.8660} = 1.08\bar{5} \times 10^{-10} = \boxed{108.\bar{5}\ \text{pm}}$$

$$R_{CD} = R_{CH}$$

COMMENT. These values are very close to the interatomic distances quoted by Herzberg in *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, p. 666 (*Further reading*, Chapter 14), which are 139.7 and 108.4 pm respectively.

P13.8 $\tilde{\nu} = 2B(J + 1)$ [13.37] $= 2B$

Hence, $B(^1\text{HCl}) = 10.4392\ \text{cm}^{-1}$, $B(^2\text{HCl}) = 5.3920\ \text{cm}^{-1}$

$$B = \frac{\hbar}{4\pi cI} \text{ [13.24]} \quad I = m_{\text{eff}}R^2 \text{ [Table 13.1]}$$

$$R^2 = \frac{\hbar}{4\pi c m_{\text{eff}} B} \quad \frac{\hbar}{4\pi c} = 2.799\,27 \times 10^{-44}\,\text{kg m}$$

$$m_{\text{eff}}(\text{HCl}) = \left(\frac{(1.007\,825\,\text{u}) \times (34.968\,85\,\text{u})}{(1.007\,825\,\text{u}) + (34.968\,85\,\text{u})}\right) \times (1.660\,54 \times 10^{-27}\,\text{kg u}^{-1})$$

$$= 1.626\,65 \times 10^{-27}\,\text{kg}$$

$$m_{\text{eff}}(\text{DCl}) = \left(\frac{(2.0140\,\text{u}) \times (34.968\,85\,\text{u})}{(2.0140\,\text{u}) + (34.968\,85\,\text{u})}\right) \times (1.660\,54 \times 10^{-27}\,\text{kg u}^{-1})$$

$$= 3.1622 \times 10^{-27}\,\text{kg}$$

$$R^2(\text{HCl}) = \frac{2.799\,27 \times 10^{-44}\,\text{kg m}}{(1.626\,65 \times 10^{-27}\,\text{kg}) \times (1.043\,92 \times 10^{3}\,\text{m}^{-1})} = 1.648\,48 \times 10^{-20}\,\text{m}^2$$

$$R(\text{HCl}) = 1.283\,93 \times 10^{-10}\,\text{m} = \boxed{128.393\ \text{pm}}$$

$$R^2(^2\text{HCl}) = \frac{2.799\,27 \times 10^{-44}\,\text{kg m}}{(3.1622 \times 10^{-27}\,\text{kg}) \times (5.3920 \times 10^{2}\,\text{m}^{-1})} = 1.6417 \times 10^{-20}\,\text{m}^2$$

$$R(^2\text{HCl}) = 1.2813 \times 10^{-10}\,\text{m} = \boxed{128.13\ \text{pm}}$$

COMMENT. Since the effects of centrifugal distortion have not been taken into account, the number of significant figures in the calculated values of R above should be no greater than 4, despite the fact that the data are precise to 6 figures.

P13.10 From the equation for a linear rotor in Table 13.1 it is possible to show that $I_{\text{m}} = m_{\text{a}}m_{\text{c}}(R + R')^2 + m_{\text{a}}m_{\text{b}}R^2 + m_{\text{b}}m_{\text{c}}R'^2$.

$$\text{Thus, } I(^{16}\text{O}^{12}\text{C}^{32}\text{S}) = \left(\frac{m(^{16}\text{O})m(^{32}\text{S})}{m(^{16}\text{O}^{12}\text{C}^{32}\text{S})}\right) \times (R + R')^2 + \left(\frac{m(^{12}\text{C})\{m(^{16}\text{O})R^2 + m(^{32}\text{S})R'^2\}}{m(^{16}\text{O}^{12}\text{C}^{32}\text{S})}\right)$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S}) = \left(\frac{m(^{16}\text{O})m(^{34}\text{S})}{m(^{16}\text{O}^{12}\text{C}^{34}\text{S})}\right) \times (R + R')^2 + \left(\frac{m(^{12}\text{C})\{m(^{16}\text{O})R^2 + m(^{34}\text{S})R'^2\}}{m(^{16}\text{O}^{12}\text{C}^{34}\text{S})}\right)$$

$m(^{16}\text{O}) = 15.9949\,\text{u}$, $m(^{12}\text{C}) = 12.0000\,\text{u}$, $m(^{32}\text{S}) = 31.9721\,\text{u}$, and $m(^{34}\text{S}) = 33.9679\,\text{u}$. Hence,

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S})/\text{u} = (8.5279) \times (R + R')^2 + (0.20011) \times (15.9949R^2 + 31.9721R'^2)$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S})/\text{u} = (8.7684) \times (R + R')^2 + (0.19366) \times (15.9949R^2 + 33.9679R'^2)$$

The spectral data provides the experimental values of the moments of inertia based on the relation $\tilde{\nu} = 2cB(J + 1)$ [13.37] with $B = \hbar/4\pi cI$ [13.24]. These values are set equal to the above equations which are then solved for R and R'. The mean values of I obtained from the data are

$$I(^{16}O^{12}C^{32}S) = 1.37998 \times 10^{-45}\,\text{kg m}^2$$

$$I(^{16}O^{12}C^{34}S) = 1.41460 \times 10^{-45}\,\text{kg m}^2$$

Therefore, after conversion of the atomic mass units to kg, the equations we must solve are

$$1.37998 \times 10^{-45}\,\text{m}^2 = (1.4161 \times 10^{-26}) \times (R + R')^2 + (5.3150 \times 10^{-27}R^2) + (1.0624 \times 10^{-26}R'^2)$$

$$1.41460 \times 10^{-45}\,\text{m}^2 = (1.4560 \times 10^{-26}) \times (R + R')^2 + (5.1437 \times 10^{-27}R^2) + (1.0923 \times 10^{-26}R'^2)$$

These two equations may be solved for R and R'. They are tedious to solve by hand, but straightforward. Exercise 13.9(b) illustrates the details of the solution. Readily available mathematical software can be used to quickly give the result. The outcome is $R = \boxed{116.28\ \text{pm}}$ and $R' = \boxed{155.97\ \text{pm}}$. These values may be checked by direct substitution into the equations.

COMMENT. The starting point of this problem is the actual experimental data on spectral line positions. Exercise 13.9(b) is similar to this problem; its starting point is, however, given values of the rotational constants B, which were themselves obtained from the spectral line positions. So the results for R and R' are expected to be essentially identical and they are.

Question. What are the rotational constants calculated from the data on the positions of the absorption lines?

P13.12 The wavenumbers of the transitions with $\Delta v = +1$ are

$$\Delta G_{v+1/2} = \tilde{\nu} - 2(v + 1)x_e\tilde{\nu}\ [13.57] \quad \text{and} \quad D_e = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}}\ [13.55]$$

A plot of $\Delta G_{v+1/2}$ against $v + 1$ should give a straight line with intercept $\tilde{\nu}$ at $v + 1 = 0$ and slope $-2x_e\tilde{\nu}$.

Draw up the following table

$v + 1$	1	2	3
$\Delta G_{v+1/2}/\text{cm}^{-1}$	284.50	283.00	281.502

The points are plotted in Figure 13.3.

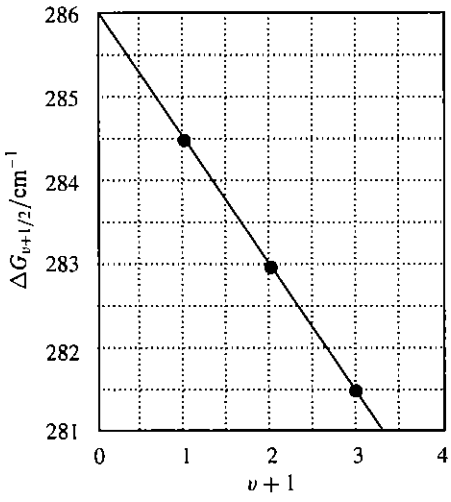


Figure 13.3

The intercept is at 286.0, so $\tilde{\nu} = 286\,\text{cm}^{-1}$. The slope is -1.50, so $x_e\tilde{\nu} = 0.750\,\text{cm}^{-1}$. It follows that

$$D_e = \frac{(286\,\text{cm}^{-1})^2}{(4) \times (0.750\,\text{cm}^{-1})} = 27\,300\,\text{cm}^{-1}, \quad \text{or} \quad 3.38\,\text{eV}$$

The zero-point level lies at $\boxed{142.81\ \text{cm}^{-1}}$ and so $D_0 = \boxed{3.36\ \text{eV}}$. Since

$$m_{\text{eff}} = \frac{(22.99) \times (126.90)}{(22.99) + (126.90)}\,\text{u} = 19.46\overline{4}\,\text{u}$$

the force constant of the molecule is

$$\begin{aligned} k &= 4\pi^2 m_{\text{eff}} c^2 \tilde{\nu}^2 \text{ [Exercise 13.16(a)]} \\ &= (4\pi^2) \times (19.46\overline{4}) \times (1.6605 \times 10^{-27}\,\text{kg}) \times [(2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (286\,\text{cm}^{-1})]^2 \\ &= \boxed{93.8\ \text{N m}^{-1}} \end{aligned}$$

P13.14 The set of peaks to the left of center are the P branch, those to the right are the R branch. Within the rigid rotor approximation the two sets are separated by $4B$. The effects of the interactions between vibration and rotation and of centrifugal distortion are least important for transitions with small J values hence the separation between the peaks immediately to the left and right of center will give good approximate values of B and bond length.

(a) $\tilde{\nu}_Q(J) = \tilde{\nu}$ [13.62b] $= 2143.26\,\text{cm}^{-1}$

(b) The zero-point energy is $\frac{1}{2}\tilde{\nu} = 1071.63\,\text{cm}^{-1}$. The molar zero-point energy in J mol^{-1} is

$$\begin{aligned} N_A hc \times (1071.63\,\text{cm}^{-1}) &= N_A hc \times (1.07163 \times 10^5\,\text{m}^{-1}) \\ &= 1.28195 \times 10^4\,\text{J mol}^{-1} = \boxed{12.8195\ \text{kJ mol}^{-1}} \end{aligned}$$

(c) $k = 4\pi^2\mu c^2\tilde{\nu}^2$

$$\mu(^{12}C^{16}O) = \frac{m_C m_O}{m_C + m_O} = \left(\frac{(12.0000\,\text{u}) \times (15.9949\,\text{u})}{(12.0000\,\text{u}) + (15.9949\,\text{u})}\right) \times (1.660\,54 \times 10^{-27}\,\text{kg u}^{-1})$$
$$= 1.138\,52 \times 10^{-26}\,\text{kg}$$

$$k = 4\pi^2 c^2 \times (1.138\,52 \times 10^{-26}\,\text{kg}) \times (2.143\,26 \times 10^5\,\text{m}^{-1})^2 = \boxed{1.855\,63 \times 10^3\,\text{N m}^{-1}}$$

(d) $4B \approx 7.655\,\text{cm}^{-1}$

$B \approx \boxed{1.91\,\text{cm}^{-1}}$ [4 significant figures not justified]

(e) $B = \dfrac{\hbar}{4\pi cI}$ [13.24] $= \dfrac{\hbar}{4\pi c\mu R^2}$ [Table 13.1]

$$R^2 = \frac{\hbar}{4\pi c\mu B} = \frac{\hbar}{(4\pi c) \times (1.138\,52 \times 10^{-26}\,\text{kg}) \times (191\,\text{m}^{-1})} = 1.28\bar{7} \times 10^{-20}\,\text{m}^2$$

$$R = 1.13 \times 10^{-10}\,\text{m} = \boxed{113\,\text{pm}}$$

P13.16 $V(R) = hcD_e\left\{1 - e^{-a(R-R_e)}\right\}^2$ [13.54]

$$\tilde{\nu} = \frac{\omega}{2\pi c} = 936.8\,\text{cm}^{-1} \quad x_e\tilde{\nu} = 14.15\,\text{cm}^{-1}$$

$$a = \left(\frac{m_{\text{eff}}}{2hcD_e}\right)^{1/2}\omega \quad x_e = \frac{\hbar a^2}{2m_{\text{eff}}\omega} \quad D_e = \frac{\tilde{\nu}}{4x_e}$$

$$m_{\text{eff}}(\text{RbH}) \approx \frac{(1.008) \times (85.47)}{(1.008) + (85.47)}\,\text{u} = 1.654 \times 10^{-27}\,\text{kg}$$

$$D_e = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} = \frac{(936.8\,\text{cm}^{-1})^2}{(4) \times (14.15\,\text{cm}^{-1})} = 1550\bar{5}\,\text{cm}^{-1}\ (1.92\,\text{eV})$$

$$a = 2\pi\nu\left(\frac{m_{\text{eff}}}{2hcD_e}\right)^{1/2}\ [13.54] = 2\pi c\tilde{\nu}\left(\frac{m_{\text{eff}}}{2hcD_e}\right)^{1/2}$$
$$= (2\pi) \times (2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (936.8\,\text{cm}^{-1})$$
$$\times \left(\frac{1.654 \times 10^{-27}\text{kg}}{(2) \times (15\,505\,\text{cm}^{-1}) \times (6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}\right)^{1/2}$$
$$= 9.144 \times 10^9\,\text{m}^{-1} = 9.44\,\text{nm}^{-1} = \frac{1}{0.1094\,\text{nm}}$$

Therefore, $\dfrac{V(R)}{hcD_e} = \left\{1 - e^{-(R-R_e)/(0.1094\,\text{nm})}\right\}^2$

with $R_e = 236.7$ pm. We draw up the following table

R/pm	50	100	200	300	400	500	600	700	800
$V/(hcD_e)$	20.4	6.20	0.159	0.193	0.601	0.828	0.929	0.971	0.988

These points are plotted in Figure 13.4 as the line labeled $J = 0$

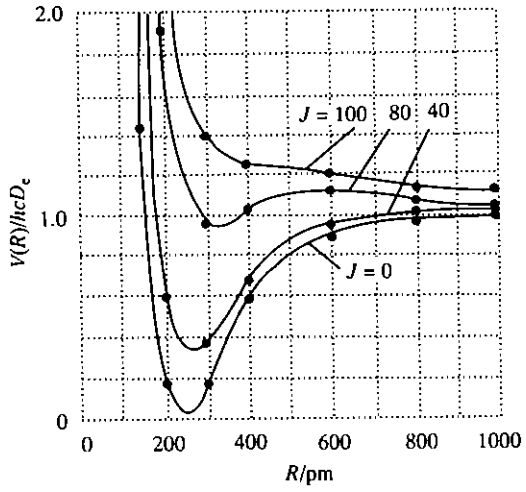


Figure 13.4

For the second part, we note that $B \propto \dfrac{1}{R^2}$ and write

$$V_J^* = V + hcB_eJ(J+1) \times \left(\frac{R_e^2}{R^2}\right)$$

with B_e the equilibrium rotational constant, $B_e = 3.020\ \text{cm}^{-1}$.

We then draw up the following table using the values of V calculated above

R/pm	50	100	200	300	400	600	800	1000
$\dfrac{R_e}{R}$	4.73	2.37	1.18	0.79	0.59	0.39	0.30	0.24
$\dfrac{V}{hcD_e}$	20.4	6.20	0.159	0.193	0.601	0.929	0.988	1.000
$\dfrac{V_{40}^*}{hcD_e}$	27.5	7.99	0.606	0.392	0.713	0.979	1.016	1.016
$\dfrac{V_{80}^*}{hcD_e}$	48.7	13.3	1.93	0.979	1.043	1.13	1.099	1.069
$\dfrac{V_{100}^*}{hcD_e}$	64.5	17.2	2.91	1.42	1.29	1.24	1.16	1.11

These points are also plotted in Figure 13.4

P13.18 (a) Vibrational wavenumbers ($\tilde{\nu}/\text{cm}^{-1}$) computed by PC Spartan Pro™ at several levels of theory are tabulated below, along with experimental values:

	A_1	A_1	B_2
Semi-empirical PM3	412	801	896
SCF 6-316G**	592	1359	1569
Density functional	502	1152	1359
Experimental	525	1151	1336

The vibrational modes are shown graphically in Figure 13.5.

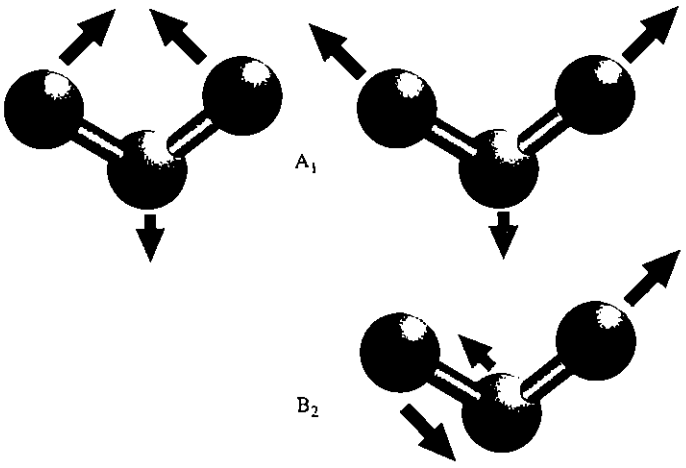


Figure 13.5

(b) The wavenumbers computed by density functional theory agree quite well with experiment. Agreement of the semi-empirical and SCF values with experiment is not so good. In this molecule, experimental wavenumbers can be correlated rather easily to computed vibrational modes even where the experimental and computed wavenumbers disagree substantially. Often, as in this case, computational methods that do a poor job of computing absolute transition wavenumbers still put transitions in proper order by wavenumber. That is, the modeling software systematically overestimates (as in this SCF computation) or underestimates (as in this semi-empirical computation) the wavenumbers, thus keeping them in the correct order. Group theory is another aid in the assignment of transitions: it can classify modes as forbidden, allowed only in particular polarizations, etc. Also, visual examination of the modes of motion can help to classify many modes as predominantly bond-stretching, bond-bending, or internal rotation; these different modes of vibration can be correlated to quite different ranges of wavenumbers (stretches highest, especially stretches involving hydrogen atoms, and internal rotations lowest.).

P13.20 Summarize the six observed vibrations according to their wavenumbers ($\tilde{\nu}/\text{cm}^{-1}$) :

IR	870	1370	2869	3417
Raman	877	1408	1435	3407

(a) If H_2O_2 were linear, it would have $3N - 5 = \boxed{7}$ vibrational modes.

(b) Follow the flow chart in Figure 12.7. Structure **2** is not linear, there is only one C_n axis (a C_2), and there is a σ_h; the point group is $\boxed{C_{2h}}$. Structure **3** is not linear, there is only one C_n axis (a C_2), no σ_h, but two σ_v; the point group is $\boxed{C_{2v}}$. Structure **4** is not linear, there is only one C_n axis (a C_2), no σ_h, no σ_v; the point group is $\boxed{C_2}$.

(c) The exclusion rule applies to structure **2** because it has a center of inversion: no vibrational modes can be both IR and Raman active. So structure **2** is inconsistent with observation. The vibrational modes of structure **3** span $3A_1 + A_2 + 2B_2$. (The full basis of 12 cartesian coordinates spans $4A_1 + 2A_2 + 2B_1 + 4B_2$; remove translations and rotations.) The C_{2v} character table says that five of these modes are IR active ($3A_1 + 2B_2$) and all are Raman active. All of the modes of structure **4** are both IR and Raman active. (A look at the character table shows that both symmetry species are IR and Raman active, so determining the symmetry species of the normal modes does not help here.) Both structures **3** and **4** have more active modes than were observed. This is consistent with the observations. After all, group theory can only tell us whether the transition moment *must* be zero by symmetry; it does not tell us whether the transition moment is sufficiently strong to be observed under experimental conditions.

Solutions to theoretical problems

P13.22 Because the centrifugal force and the restoring force balance,

$$k(r_c - r_e) = \mu\omega^2 r_c,$$

we can solve for the distorted bond length as a function of the equilibrium bond length:

$$r_c = \frac{r_e}{1 - \mu\omega^2/k}$$

Classically, then, the energy would be the rotational energy plus the energy of the stretched bond:

$$E = \frac{J^2}{2I} + \frac{k(r_c - r_e)^2}{2} = \frac{J^2}{2I} + \frac{k^2(r_c - r_e)^2}{2k} = \frac{J^2}{2I} + \frac{(\mu\omega^2 r_c)^2}{2k}$$

How is the energy different form the rigid-rotor energy? Besides the energy of stretching of the bond, the larger moment of inertia alters the strictly rotational piece of the energy. Substitute μr_e^2 for I and substitute for r_c in terms of r_e throughout:

$$\text{So } E = \frac{J^2(1 - \mu\omega^2/k)^2}{2\mu r_e^2} + \frac{\mu^2\omega^4 r_e^2}{2k(1 - \mu\omega^2/k)^2}.$$

Assuming that $\mu\omega^2/k$ is small (a reasonable assumption for most molecules), we can expand the expression and discard squares or higher powers of $\mu\omega^2/k$:

$$E \approx \frac{J^2(1 - 2\mu\omega^2/k)}{2\mu r_e^2} + \frac{\mu^2\omega^4 r_e^2}{2k}.$$

(Note that the entire second term has a factor of $\mu\omega^2/k$ even before squaring and expanding the denominator, so we discard all terms of that expansion after the first.) Begin to clean up the expression by using

classical definitions of angular momentum:

$$J = I\omega = \mu r^2 \omega \quad \text{so} \quad \omega = J/\mu r_e^2$$

which allows us to substitute expressions involving J for all ω s:

$$E \approx \frac{J^2}{2\mu r_e^2} - \frac{J^4}{\mu^2 r_e^6 k} + \frac{J^4}{2\mu^2 r_e^6 k}$$

(At the same time, we have expanded the first term, part of which we can now combine with the last term.) Continue to clean up the expression by substituting I/μ for r^2, and then carry the expression over to its quantum mechanical equivalent by substituting $J(J+1)\hbar^2$ for J^2:

$$E \approx \frac{J^2}{2I} - \frac{J^4\mu}{2I^3 k} \Rightarrow E \approx \frac{J(J+1)\hbar^2}{2I} - \frac{J^2(J+1)^2\hbar^4\mu}{2I^3 k}$$

Dividing by hc gives the rotational term, $F(J)$:

$$F(J) \approx \frac{J(J+1)\hbar^2}{2hcI} - \frac{J^2(J+1)^2\hbar^4\mu}{2hcI^3 k} = \frac{J(J+1)}{4\pi cI} - \frac{J^2(J+1)^2\hbar^3\mu}{4\pi cI^3 k}$$

where we have used $\hbar = h/2\pi$ to eliminate a common divisor of h. Now use the definition of the rotational constant,

$$B = \frac{\hbar}{4\pi cI} \Rightarrow F(J) \approx J(J+1)B - J^2(J+1)^2 B^3 \frac{16\pi^2 c^2 \mu}{k}$$

Finally, use the relationship between the force constant and vibrational wavenumber:

$$\left(\frac{k}{\mu}\right)^{1/2} = \omega_{\text{vib}} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \frac{\mu}{k} = \frac{1}{4\pi^2 c^2 \tilde{\nu}^2}$$

leaving $F(J) \approx BJ(J+1) - \dfrac{4B^3}{\tilde{\nu}^2} J^2(J+1)^2 = BJ(J+1) - DJ^2(J+1)^2$ where $\boxed{D = \dfrac{4B^3}{\tilde{\nu}^2}}$.

P13.24 $N \propto ge^{-E/kT}$ [Boltzmann distribution, Chapters 2 and 16]

$N_J \propto g_J e^{-E_J/kT} \propto (2J+1)\mathrm{e}^{-hcBJ(J+1)/kT}$ [$g_J = 2J+1$ for a diatomic rotor]

The maximum population occurs when

$$\frac{\mathrm{d}}{\mathrm{d}J} N_J \propto \left\{2 - (2J+1)^2 \times \left(\frac{hcB}{kT}\right)\right\} \mathrm{e}^{-hcBJ(J+1)/kT} = 0$$

and, since the exponential can never be zero at a finite temperature, when

$$(2J+1)^2 \times \left(\frac{hcB}{kT}\right) = 2$$

or when $J_{\max} = \boxed{\left(\dfrac{kT}{2hcB}\right)^{1/2} - \dfrac{1}{2}}$

For ICl, with $\frac{kT}{hc} = 207.22\ \text{cm}^{-1}$ (inside front cover)

$$J_{\max} = \left(\frac{207.22\ \text{cm}^{-1}}{0.2284\ \text{cm}^{-1}}\right)^{1/2} - \frac{1}{2} = \boxed{30}$$

For a spherical rotor, $N_J \propto (2J+1)^2 \mathrm{e}^{-hcBJ(J+1)/kT}$ $[g_J = (2J+1)^2]$

and the greatest population occurs when

$$\frac{\mathrm{d}N_J}{\mathrm{d}J} \propto \left(8J + 4 - \frac{hcB(2J+1)^3}{kT}\right)\mathrm{e}^{-hcBJ(J+1)/kT} = 0$$

which occurs when

$$4(2J+1) = \frac{hcB(2J+1)^3}{kT}$$

or at $J_{\max} = \boxed{\left(\frac{kT}{hcB}\right)^{1/2} - \frac{1}{2}}$

For CH_4, $J_{\max} = \left(\frac{207.22\ \text{cm}^{-1}}{5.24\ \text{cm}^{-1}}\right)^{1/2} - \frac{1}{2} = \boxed{6}$

P13.26 The energy levels of a Morse oscillator, expressed as wavenumbers, are given by:

$$G(v) = \left(v + \tfrac{1}{2}\right)\tilde{\nu} - \left(v + \frac{1}{2}\right)^2 x_{\mathrm{e}}\tilde{\nu} = \left(v + \frac{1}{2}\right)\tilde{\nu} - \left(v + \frac{1}{2}\right)^2 \tilde{\nu}^2/4D_{\mathrm{e}}.$$

States are bound only if the energy is less than the well depth, D_{e}, also expressed as a wavenumber:

$$G(v) < D_{\mathrm{e}} \quad \text{or} \quad \left(v + \tfrac{1}{2}\right)\tilde{\nu} - \left(v + \tfrac{1}{2}\right)^2 \tilde{\nu}^2/4D_{\mathrm{e}} < D_{\mathrm{e}}.$$

Solve for the maximum value of v by making the inequality into an equality:

$$\left(v + \tfrac{1}{2}\right)^2 \tilde{\nu}^2/4D_{\mathrm{e}} - \left(v + \frac{1}{2}\right)\tilde{\nu} + D_{\mathrm{e}} = 0.$$

Multiplying through by $4D_{\mathrm{e}}$ results in an expression that can be factored by inspection into:

$$\left[\left(v + \tfrac{1}{2}\right)\tilde{\nu} - 2D_{\mathrm{e}}\right]^2 = 0 \quad \text{so} \quad v + \frac{1}{2} = 2D_{\mathrm{e}}/\tilde{\nu} \quad \text{and} \quad v = \boxed{2D_{\mathrm{e}}/\tilde{\nu} - \tfrac{1}{2}}.$$

Of course, v is an integer, so its maximum value is really the greatest integer less than this quantity.

Solutions to applications

P13.28 **(a)** The molar absorption coefficient $\varepsilon(\tilde{\nu})$ is given by

$$\varepsilon(\tilde{\nu}) = \frac{\mathrm{A}(\tilde{\nu})}{l[\mathrm{CO_2}]} = \frac{RTA(\tilde{\nu})}{lx_{\mathrm{CO_2}}p} \quad [13.4,\ 1.8,\ \text{and}\ 1.15]$$

where $T = 298\,\text{K}$, $l = 10\,\text{cm}$, $p = 1\,\text{bar}$, and $x_{CO_2} = 0.021$.

The absorption band originates with the 001 ← 000 transition of the antisymmetric stretch vibrational mode at $2349\,\text{cm}^{-1}$ (Figure 13.40). The band is very broad because of accompanying rotational transitions and lifetime broadening of each individual absorption (also called collisional broadening or pressure broadening, Section 13.3). The spectra reveals that the Q branch is missing so we conclude that the transition $\boxed{\Delta J = 0 \text{ is forbidden}}$ (Section 13.12) for the $D_{\infty h}$ point group of CO_2. The P-branch ($\Delta J = -1$) is evident at lower energies and the R-branch ($\Delta J = +1$) is evident at higher energies. See Figures 13.16(a), (b).

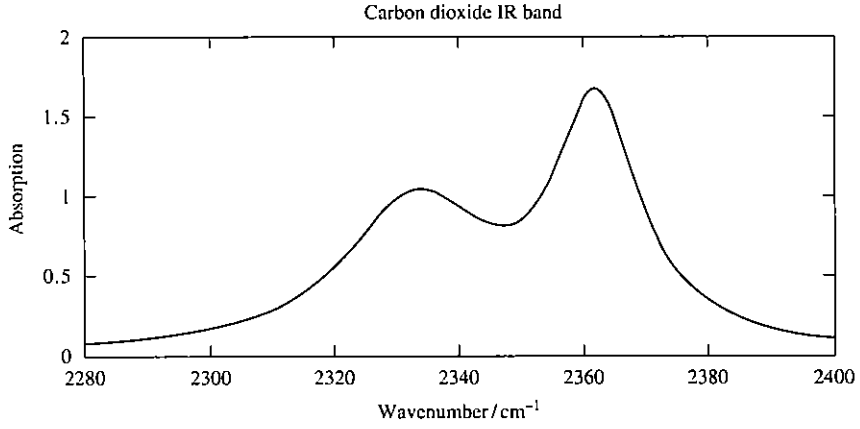


Figure 13.6(a)

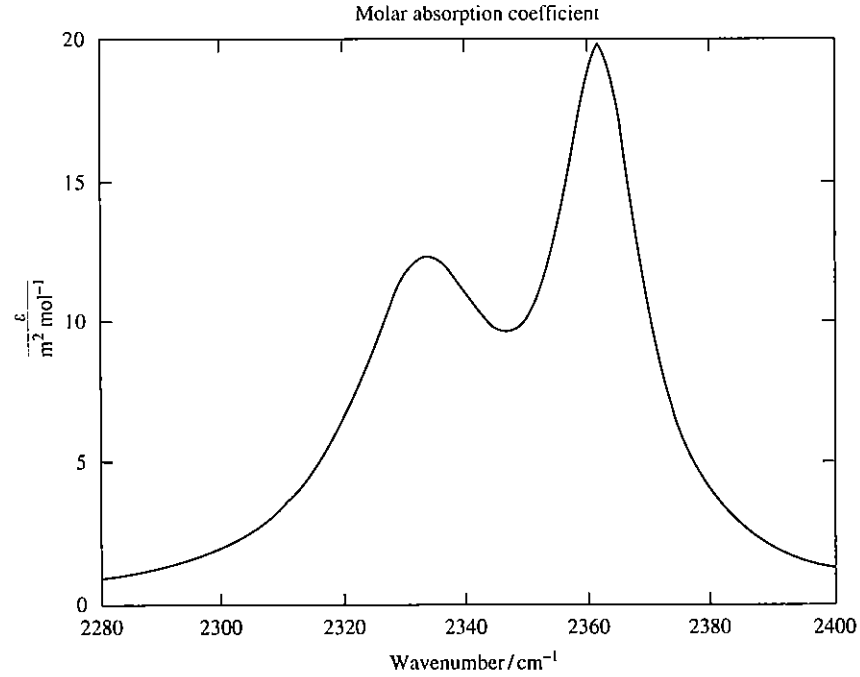


Figure 13.6(b)

(b) $^{16}O—^{12}C—^{16}O$ has two identical nuclei of zero spin so the CO_2 wavefunction must be symmetric w/r/t nuclear interchange and it must obey Bose–Einstein nuclear statistics (Section 13.8). Consequently, J takes on even values only for the $v = 0$ vibrational state and odd values only for the $v = 1$ state. The (v, J) states for this absorption band are $(1, J + 1) \leftarrow (0, J)$ for $J = 0, 2, 4, \ldots$ According to eqn 13.61, the energy of the $(0, J)$ state is

$$S(0, J) = \tfrac{1}{2}\tilde{\nu} + BJ(J + 1),$$

where $\tilde{\nu} = 2349\ \text{cm}^{-1}$

$$I = \frac{2M_O R^2}{N_A} = \frac{2(0.016\,00\ \text{kg mol}^{-1})(116.2 \times 10^{-12}\ \text{m})^2}{6.022 \times 10^{23}\ \text{mol}^{-1}}$$

$$= 7.175 \times 10^{-46}\ \text{kg m}^2 \quad \text{(Table 13.1)}$$

$$B = \frac{h}{8\pi^2 cI} \quad [13.24]$$

$$= \frac{6.626 \times 10^{-34}\ \text{J s}}{8\pi^2(2.998 \times 10^8\ \text{m s}^{-1})(7.175 \times 10^{-46}\ \text{kg m}^2)}$$

$$= 39.02\ \text{m}^{-1} = 0.3902\ \text{cm}^{-1}$$

The transitions of the P and R branches occur at

$$\tilde{\nu}_P = \tilde{\nu} - 2BJ \quad [13.62b]$$

and

$$\tilde{\nu}_R = \tilde{\nu} + 2B(J + 1) \quad [13.62c]$$

where $J = 0, 2, 4, 6 \ldots$

The highest energy transition of the P branch is at $\tilde{\nu} - 4B$; the lowest energy transition of the R branch is at $\tilde{\nu} + 2B$. Transitions are separated by $4B$ ($1.5608\ \text{cm}^{-1}$) within each branch. The probability of each transition is proportional to the lower state population, which we assume to be given by the Boltzman distribution with a degeneracy of $2J + 1$. The transition probability is also proportional to both a nuclear degeneracy factor (eqn 13.43) and a transition dipole moment, which is approximately independent of J. The former factors are absorbed into the constant of proportionality.

$$\text{transition probability} \propto (2J + 1)e^{-S(0,J)hc/kT}$$

A plot of the right-hand-side of this equation against J at 298 K indicates a maximum transition probability at $J_{max} = 16$. We "normalize" the maximum in the predicted structure, and eliminate the constant of proportionality by examining the transition probability ratio:

$$\frac{\text{transition probability for } J\text{th state}}{\text{transition probability for } J_{max} \text{ state}} = \frac{(2J + 1)e^{-S(0,J)hc/kT}}{33e^{-S(0.16)hc/RT}}$$

$$= \left(\frac{2J + 1}{33}\right) e^{-(J^2+J-272)Bhc/kT}$$

A plot, Figure 13.6(c), of the above ratio against predicted wavenumbers can be compared to the ratio $A(\tilde{\nu})/A_{max}$ where A_{max} is the observed spectrum maximum (1.677). It shows a fair degree of agreement between the experimental and simple theoretical band shapes.

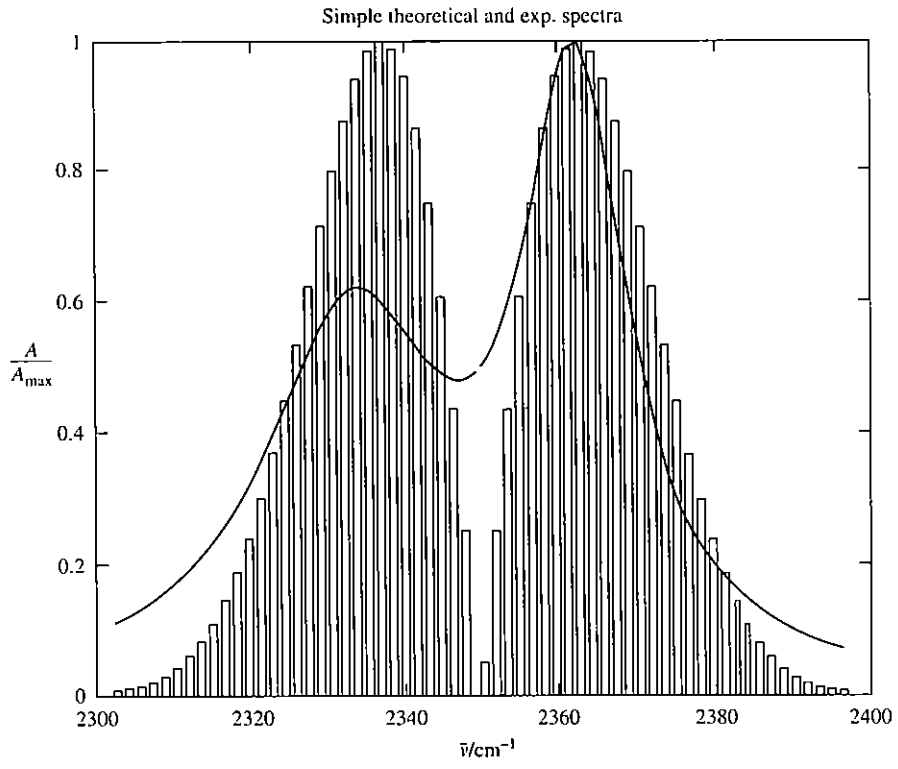


Figure 13.6(c)

(c) Using the equations of justification 13.1, we may write the relationship

$$A = \varepsilon(\tilde{\nu}) \int_0^h [CO_2]dh$$

The strong absorption of the band suggests that h should not be a very great length and that $[CO_2]$ should be constant between the Earth's surface and h. Consequently, the integration gives

$$A = \varepsilon(\tilde{\nu})[CO_2]h$$

$$= \varepsilon(\tilde{\nu})h \left\{ \frac{x_{CO_2}p}{RT} \right\} \quad \text{Dalton's law of partial pressures}$$

p and T are not expected to change much for modest values of h so we estimate that $p = 1$ bar and $T = 288$ K.

$$A = \varepsilon(\tilde{\nu})h \left\{ \frac{(3.3 \times 10^{-4}(1 \times 10^5 \text{ Pa})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(288 \text{ K})} \right\}$$

$$= (0.0138 \text{ m}^{-3} \text{ mol})\varepsilon(\tilde{\nu})h$$

$$\text{Transmittance} = 10^{-A} = 10^{-(0.0138 \text{ m}^{-3} \text{ mol})\varepsilon(\tilde{\nu})h} \quad [13.3]$$

The transmittance surface plot, Figure 13.6(d), clearly shows that before a height of about 30 m has been reached all of the Earth's IR radiation in the 2320–2380 cm^{-1} range has been absorbed by atmospheric carbon dioxide.

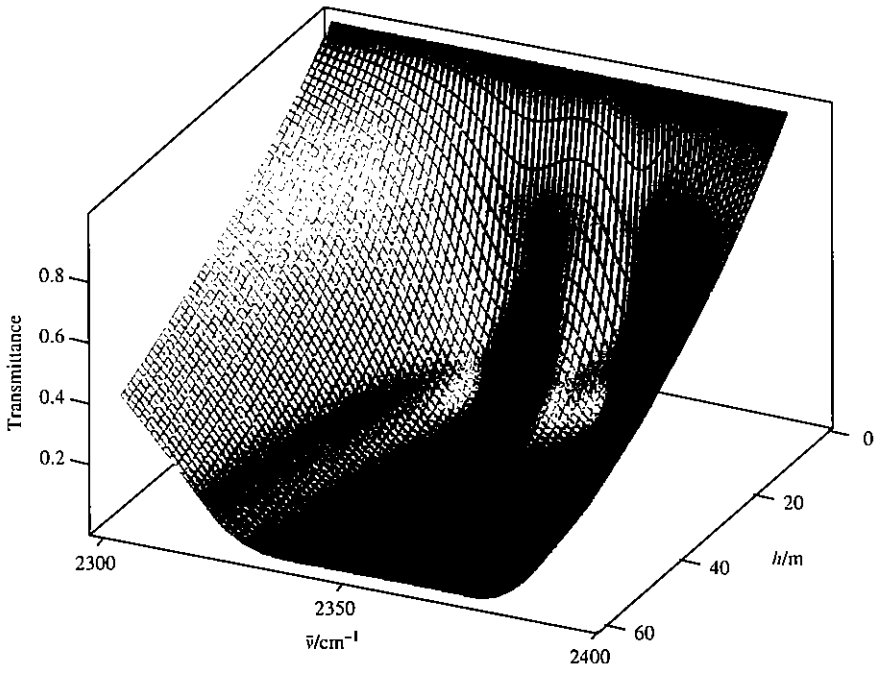


Figure 13.6(d)

See C.A. Meserole, F.M. Mulcahy, J. Lutz, and H.A. Yousif, *J. Chem. Ed.*, *74*, 316 (1997).

P13.30 The question of whether to use CN or CH within the interstellar cloud of constellation Ophiuchus for the determination of the temperature of the cosmic background radiation depends upon which one has a rotational spectrum that best spans blackbody radiation of 2.726 K. Given $B_0(\text{CH}) = 14.90\ \text{cm}^{-1}$, the rotational constant that is needed for the comparative analysis may be calculated from the 226.9 GHz spectral line of the Orion Nebula. Assuming that the line is for the $^{12}C^{14}N$ isotopic species and $J + 1 \leftarrow J = 1$, which gives a reasonable estimate of the CN bond length (117.4 pm), the CN rotational constant is calculated as follows.

$$B_0 = \nu/c = \frac{\nu}{2c(J+1)} = \frac{\nu}{4c} \tag{1}$$

$$= 1.892\ \text{cm}^{-1} \tag{2}$$

Blackbody radiation at 2.726 K may be plotted against radiation wavenumber with suitable transformation of eqn 11.5.

$$\rho(\tilde{\nu}) = \frac{8\pi hc\tilde{\nu}^3}{e^{hc\tilde{\nu}/kT} - 1}$$

Spectral absorption lines of $^{12}C^{14}N$ and $^{12}C^{1}H$ are calculated with eqn 16.44.

$$\tilde{\nu}(J+1 \leftarrow J) = 2B(J+1) \quad J = 0, 1, 2, 3, \ldots$$

The cosmic background radiation and molecular absorption lines are shown in the graph, Figure 13.7. It is evident that only CN spans the background radiation.

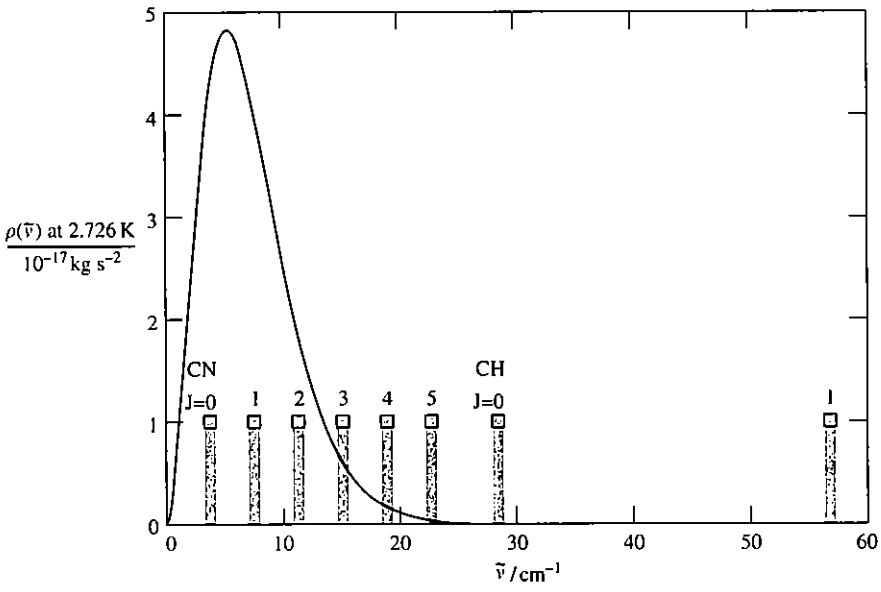


Figure 13.7

P13.32 (a) The H_3^+ molecule is held together by a two-electron, three-center bond, and hence its structure is expected to be an equilateral triangle. Looking at Figure 13.8 and using the law of cosines

$$R^2 = 2R_C^2 - 2R_C^2\cos(180° - 2\theta)$$
$$= 2R_C^2(1 - \cos(120°)) = 3R_C^2$$

Therefore

$$R_C = R/\sqrt{3}$$
$$I_C = 3mR_C^2 = 3m(R/\sqrt{3})^2 = mR^2$$
$$I_B = 2mR_B = 2m(R/2)^2 = mR^2/2$$

Therefore

$$I_C = 2I_B$$

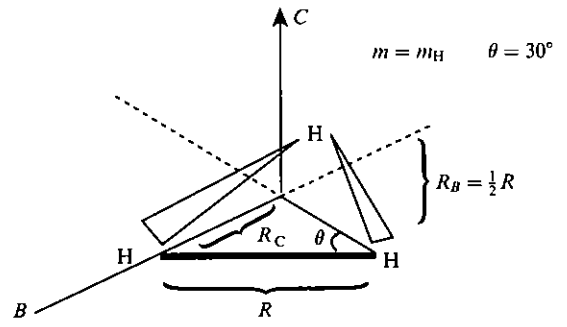


Figure 13.8

(b)

$$B = \frac{\hbar}{4\pi c I_B} = \frac{2\hbar}{4\pi c m R^2} = \frac{\hbar}{2\pi c m R^2} \text{ [13.30]}$$

$$R = \left(\frac{\hbar}{2\pi c m B}\right)^{1/2} = \left(\frac{\hbar N_A}{2\pi c M_H B}\right)^{1/2}$$

$$= \left(\frac{(1.0546 \times 10^{-34}\,\text{J s}) \times (6.0221 \times 10^{23}\,\text{mol}^{-1}) \times \left(\frac{10^{-2}\,\text{m}}{\text{cm}}\right)}{2\pi (2.998 \times 10^{8}\,\text{m s}^{-1}) \times (0.001\,008\,\text{kg mol}^{-1}) \times (43.55\,\text{cm}^{-1})} \right)^{1/2}$$

$$= 8.764 \times 10^{-11}\,\text{m} = \boxed{87.64\,\text{pm}}$$

Alternatively the rotational constant C can be used to calculate R.

$$C = \frac{\hbar}{4\pi c I_C} = \frac{\hbar}{4\pi c m R^2} \text{ [13.30]}$$

$$R = \left(\frac{\hbar}{4\pi c m C}\right)^{1/2} = \left(\frac{\hbar N_A}{4\pi c M_H C}\right)^{1/2}$$

$$= \left(\frac{(1.0546 \times 10^{-34}\,\text{J s}) \times (6.0221 \times 10^{23}\,\text{mol}^{-1}) \times \left(\frac{10^{-2}\,\text{m}}{\text{cm}}\right)}{4\pi (2.998 \times 10^{8}\,\text{m s}^{-1}) \times (0.001\,008\,\text{kg mol}^{-1}) \times (20.71\,\text{cm}^{-1})} \right)$$

$$= 8.986 \times 10^{-11}\,\text{m} = \boxed{89.86\,\text{pm}}$$

The values of R calculated with either the rotational constant C or the rotational constant B differ slightly. We approximate the bond length as the average of these two.

$$(R) \approx \frac{(87.64 + 89.86)\,\text{pm}}{2} = \boxed{88.7\,\text{pm}}$$

$$B = \frac{\hbar}{2\pi c m R^2} = \frac{(1.0546 \times 10^{-34}\,\text{J}\,s) \times (6.0221 \times 10^{23}\,\text{mol}^{-1}) \times \left(\frac{10^{-2}\,\text{m}}{\text{cm}}\right)}{2\pi (2.998 \times 10^{8}\,\text{m s}^{-1}) \times (0.001\,008\,\text{kg mol}^{-1}) \times (87.32 \times 10^{-12}\,\text{m})^2}$$

$$= \boxed{43.87\,\text{cm}^{-1}}$$

$$C = \tfrac{1}{2}B = \boxed{21.93\,\text{cm}^{-1}}$$

$$\frac{1}{m_{\text{eff}}} = \frac{3}{m} \quad \text{or} \quad m_{\text{eff}} = \tfrac{1}{3}m$$

Since $m_D = 2m_H$, $m_{\text{eff,D}} = 2m_H/3$

$$\tilde{\nu}_2(D_3^+) = \left(\frac{m_{\text{eff}}(H_3)}{m_{\text{eff}}(D_3)}\right)^{1/2} \tilde{\nu}_2(H_3)\ [13.51] = \left(\frac{m_H/3}{2m_H/3}\right)^{1/2} \tilde{\nu}_2(H_3) = \frac{\tilde{\nu}_2(H_2)}{2^{1/2}}$$

$$= \frac{2521.6\,\text{cm}^{-1}}{2^{1/2}} = \boxed{1783.0\,\text{cm}^{-1}}$$

Since B and $C \propto \frac{1}{m}$, where m = mass of H or D

$$B(D_3^+) = B(H_3^+) \times \frac{M_H}{M_D} = 43.55\,\text{cm}^{-1} \times \left(\frac{1.008}{2.014}\right) = \boxed{21.80\,\text{cm}^{-1}}$$

$$C(D_3^+) = C(H_3^+) \times \frac{M_H}{M_D} = 20.71\,\text{cm}^{-1} \times \left(\frac{1.008}{2.014}\right) = \boxed{10.37\,\text{cm}^{-1}}$$

14 Spectroscopy 2: electronic transitions

Answers to discussion questions

D14.2 The Franck–Condon principle states that because electrons are so much lighter than nuclei, an electronic transition occurs so rapidly compared to vibrational motions that the internuclear distance is relatively unchanged as a result of the transition. This implies that the most probable transitions $\nu_f \leftarrow \nu_i$ are vertical. This vertical line will, however, intersect any number of vibrational levels ν_f in the upper electronic state. Hence transitions to many vibrational states of the excited state will occur with transition probabilities proportional to the Frank–Condon factors which are in turn proportional to the overlap integral of the wavefunctions of the initial and final vibrational states. A vibrational progression is observed, the shape of which is determined by the relative horizontal positions of the two electronic potential energy curves. The most probable transitions are those to excited vibrational states with wavefunctions having a large amplitude at the internuclear position R_e.

Question. You might check the validity of the assumption that electronic transitions are so much faster than vibrational transitions by calculating the time scale of the two kinds of transitions. How much faster is the electronic transition, and is the assumption behind the Franck–Condon principle justified?

D14.4 Color can arise by emission, absorption, or scattering of electromagnetic radiation by an object. Many molecules have electronic transitions that have wavelengths in the visible portion of the electromagnetic spectrum. When a substance emits radiation the perceived color of the object will be that of the emitted radiation and it may be an additive color resulting from the emission of more than one wavelength of radiation. When a substance absorbs radiation its color is determined by the subtraction of those wavelengths from white light. For example, absorption of red light results in the object being perceived as green. Scattering, including the diffraction that occurs when light falls on a material with a grid of variation in texture or refractive index having dimensions comparable to the wavelength of light, for example, a bird's plumage, may also form color.

D14.6 The characteristics of fluorescence which are consistent with the accepted mechanism are: (1) it ceases as soon as the source of illumination is removed; (2) the time scale of fluorescence, $\approx 10^{-9}$ s, is typical of a process in which the rate determining step is a spontaneous radiative transition between states of the same multiplicity; slower than a stimulated transition, but faster than phosphorescence; (3) it occurs at longer wavelength (higher frequency) than the inducing radiation; (4) its vibrational structure is characteristic of that of a transition from the ground vibrational level of the excited electronic state to the vibrational levels of the ground electronic state; and (5), the observed shifting and in some instances quenching of the fluorescence spectrum by interactions with the solvent.

D14.8 See Table 14.4 for a summary of the characteristics of laser radiation that result in its many advantages for chemical and biochemical investigations. Two important applications of lasers in chemistry have been to Raman spectroscopy and to the development of time resolved spectroscopy. Prior to the invention of lasers the source of intense monochromatic radiation required for Raman spectroscopy was a large spiral discharge tube with liquid mercury electrodes. The intense heat generated by the large current required to produce the radiation had to be dissipated by clumsy water-cooled jackets and exposures of several weeks were sometimes necessary to observe the weaker Raman lines. These problems have been eliminated with the introduction of lasers as the source of the required monochromatic radiation. As a consequence, Raman spectroscopy has been revitalized and is now almost as routine as infrared spectroscopy. See Section 14.6(b). Time resolved laser spectroscopy can be used to study the dynamics of chemical reactions. Laser pulses are used to obtain the absorption, emission, and Raman spectrum of reactants, intermediates, products, and even transition states of reactions. When we want to study the rates at which energy is transferred from one mode to another in a molecule, we need femtosecond and picosecond pulses. These time scales are available from mode-locked lasers and their development has opened up the possibility of examining the details of chemical reactions at a level that would have been unimaginable before.

Solutions to exercises

E14.1(b) According to Hund's rule, we expect one $1\pi_u$ electron and one $2\pi_g$ electron to be unpaired. Hence $S = 1$ and the multiplicity of the spectroscopic term is $\boxed{3}$. The overall parity is $u \times g = \boxed{u}$ since (apart from the complete core), one electron occupies a u orbital another occupies a g orbital.

E14.2(b) Use the Beer–Lambert law

$$\log \frac{I}{I_0} = -\varepsilon[J]l = (-327\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}) \times (2.22 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}) \times (0.15\,\mathrm{cm})$$

$$= -0.10889$$

$$\frac{I}{I_1} = 10^{-0.10889} = 0.778$$

The reduction in intensity is $\boxed{22.2\ \text{percent}}$

E14.3(b) $\varepsilon = -\dfrac{1}{[J]l} \log \dfrac{I}{I_0}$ [13.2, 13.3]

$$= \frac{-1}{(6.67 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}) \times (0.35\,\mathrm{cm})} \log 0.655 = 787\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$$

$$= 787 \times 10^3\,\mathrm{cm^3\,mol^{-1}\,cm^{-1}} \quad [1\,\mathrm{dm} = 10\,\mathrm{cm}]$$

$$= \boxed{7.9 \times 10^5\ \mathrm{cm^2\,mol^{-1}}}$$

E14.4(b) The Beer–Lambert law is

$$\log \frac{I}{I_0} = -\varepsilon[J]l \quad \text{so} \quad [J] = \frac{-1}{\varepsilon l} \log \frac{I}{I_0}$$

$$[J] = \frac{-1}{(323\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}} \times (0.750\,\mathrm{cm})} \log(1 - 0.523) = \boxed{1.33 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}}$$

E14.5(b) Note: a parabolic lineshape is symmetrical, extending an equal distance on either side of its peak. The given data are not consistent with a parabolic lineshape when plotted as a function of either wavelength or wavenumber, for the peak does not fall at the center of either the wavelength or the wavenumber range. The exercise will be solved with the given data assuming a triangular lineshape as a function of wavenumber.

The integrated absorption coefficient is the area under an absorption peak

$$A = \int \varepsilon \, \mathrm{d}\tilde{\nu}$$

If the peak is triangular, this area is

$$\begin{aligned} A &= \tfrac{1}{2}(\text{base}) \times (\text{height}) \\ &= \tfrac{1}{2}[(199 \times 10^{-9}\,\text{m})^{-1} - (275 \times 10^{-9}\,\text{m})^{-1}] \times (2.25 \times 10^{4}\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}) \\ &= 1.5\overline{6} \times 10^{10}\,\text{dm}^3\,\text{m}^{-1}\,\text{mol}^{-1}\,\text{cm}^{-1} = \frac{(1.5\overline{6} \times 10^{9}\,\text{dm}^3\,\text{m}^{-1}\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (100\,\text{cm}\,\text{m}^{-1})}{10^{3}\,\text{dm}^3\,\text{m}^{-3}} \\ &= 1.5\overline{6} \times 10^{9}\,\text{m}\,\text{mol}^{-1} = \boxed{1.5\overline{6} \times 10^{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-2}} \end{aligned}$$

E14.6(b) Modeling the π electrons of 1,3,5-hexatriene as free electrons in a linear box yields non-degenerate energy levels of

$$E_n = \frac{n^2h^2}{8m_eL^2}$$

The molecule has six π electrons, so the lowest-energy transition is from $n = 3$ to $n = 4$. The length of the box is 5 times the C—C bond distance R. So

$$\Delta E_{\text{linear}} = \frac{(4^2 - 3^3)h^2}{8m_e(5R)^2}$$

Modelling the π electrons of benzene as free electrons on a ring of radius R yields energy levels of

$$E_{m_l} = \frac{m_l^2\hbar^2}{2I}$$

where I is the moment of inertia: $I = m_eR^2$. These energy levels are doubly degenerate, except for the non-degenerate $m_l = 0$. The six π electrons fill the $m_l = 0$ and 1 levels, so the lowest-energy transition is from $m_l = 1$ to $m_l = 2$

$$\Delta E_{\text{ring}} = \frac{(2^2 - 1^2)\hbar^2}{2m_eR^2} = \frac{(2^2 - 1^2)h^2}{8\pi^2m_eR^2}$$

Comparing the two shows

$$\Delta E_{\text{linear}} = \frac{7}{25}\left(\frac{h^2}{8m_eR^2}\right) < \Delta E_{\text{ring}} = \frac{3}{\pi^2}\left(\frac{h^2}{8m_eR^2}\right)$$

Therefore, the lowest-energy absorption will $\boxed{\text{rise}}$ in energy.

E14.7(b) The Beer–Lambert law is

$$\log \frac{I}{I_0} = -\varepsilon[J]l = \log T$$

so a plot (Figure 14.1) of $\log T$ versus [J] should give a straight line through the origin with a slope m of $-\varepsilon l$. So $\varepsilon = -m/l$.

The data follow

[dye]/(mol dm^{-3})	T	$\log T$
0.0010	0.73	−0.1367
0.0050	0.21	−0.6778
0.0100	0.042	−1.3768
0.0500	1.33×10^{-7}	−6.8761

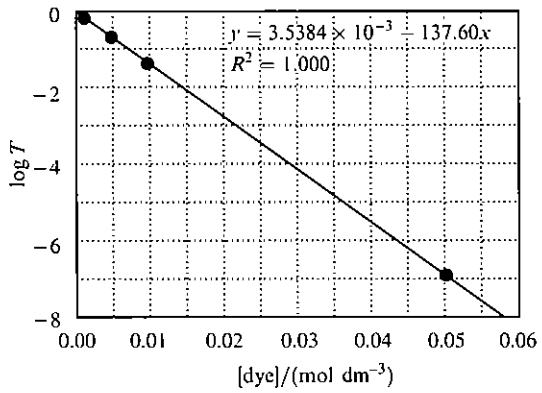


Figure 14.1

The molar absorptivity is

$$\varepsilon = -\frac{-138\,\text{dm}^3\,\text{mol}^{-1}}{0.250\,\text{cm}} = \boxed{522\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}}$$

E14.8(b) The Beer–Lambert law is

$$\log T = -\varepsilon[J]l \quad \text{so} \quad \varepsilon = \frac{-1}{[J]l}\log T$$

$$\varepsilon = \frac{-1}{(0.0155\,\text{mol dm}^{-3}) \times (0.250\,\text{cm})}\log 0.32 = \boxed{128\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}}$$

Now that we have ε, we can compute T of this solution with any size of cell

$$T = 10^{-\varepsilon[J]l} = 10^{-\{(128\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (0.0155\,\text{mol dm}^{-3}) \times (0.450\,\text{cm})\}} = \boxed{0.13}$$

E14.9(b) The Beer–Lambert law is

$$\log \frac{I}{I_0} = -\varepsilon[J]l \quad \text{so} \quad l = -\frac{1}{\varepsilon[J]} \log \frac{I}{I_0}$$

(a) $$l = -\frac{1}{(30\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (1.0\,\text{mol}\,\text{dm}^{-3})} \times \log \frac{1}{2} = \boxed{0.010\,\text{cm}}$$

(b) $$l = -\frac{1}{(30\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (1.0\,\text{mol}\,\text{dm}^{-3})} \times \log 0.10 = \boxed{0.033\,\text{cm}}$$

E14.10(b) The integrated absorption coefficient is the area under an absorption peak

$$A = \int \varepsilon \, \mathrm{d}\tilde{\nu}$$

We are told that ε is a Gaussian function, i.e. a function of the form

$$\varepsilon = \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right)$$

where $x = \tilde{\nu} - \tilde{\nu}_{\max}$ and a is a parameter related to the width of the peak. The integrated absorption coefficient, then, is

$$A = \int_{-\infty}^{\infty} \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right) \mathrm{d}x = \varepsilon_{\max} a \sqrt{\pi}$$

We must relate a to the half-width at half-height, $x_{1/2}$

$$\tfrac{1}{2}\varepsilon_{\max} = \varepsilon_{\max} \exp\left(\frac{-x_{1/2}^2}{a^2}\right) \quad \text{so} \quad \ln \tfrac{1}{2} = \frac{-x_{1/2}^2}{a^2} \quad \text{and} \quad a = \frac{x_{1/2}}{\sqrt{\ln 2}}$$

So $$A = \varepsilon_{\max} x_{1/2} \left(\frac{\pi}{\ln 2}\right)^{1/2} = (1.54 \times 10^4\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (4233\,\text{cm}^{-1}) \times \left(\frac{\pi}{\ln 2}\right)^{1/2}$$

$$= \boxed{1.39 \times 10^8\ \text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-2}}$$

In SI base units

$$A = \frac{(1.39 \times 10^8\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-2}) \times (1000\,\text{cm}^3\,\text{dm}^{-3})}{100\,\text{cm}\,\text{m}^{-1}}$$

$$= \boxed{1.39 \times 10^9\ \text{m}\,\text{mol}^{-1}}$$

E14.11(b) F_2^+ is formed when F_2 loses an antibonding electron, so we would expect F_2^+ to have a shorter bond than F_2. The difference in equilibrium bond length between the ground state (F_2) and excited state ($F_2^+ + e^-$) of the photoionization experiment leads us to expect some vibrational excitation in the upper state. The vertical transition of the photoionization will leave the molecular ion with a stretched bond relative to its equilibrium bond length. A stretched bond means a vibrationally excited molecular ion, hence a **stronger** transition to a vibrationally excited state than to the vibrational ground state of the cation.

Solutions to problems

Solutions to numerical problems

P14.2 The energy of the dissociation products of the B state, $O(^3P)$ and $O(^1D)$ above the $v = 0$ state of the ground state is 7760 cm^{-1} + 49 363 cm^{-1} = 57 123 cm^{-1}. One of these products, $O(^1D)$, has energy 15 870 cm^{-1} above the energy of the ground-state atom, $O(^3P)$. Hence, the energy of two ground-state atoms, $2O(^3P)$ above the $v = 0$ state of the ground electronic state is $57\,123\,cm^{-1} - 15\,870\,cm^{-1} = 41\,253\,cm^{-1} = \boxed{5.1147\ eV}$. These energy relations are indicated (not to scale) in Figure 14.2 of the *Instructor's Solutions Manual*.

P14.4 We write $\varepsilon = \varepsilon_{max}e^{-x^2} = \varepsilon_{max}e^{-\tilde{\nu}^2/2\Gamma}$ the variable being $\tilde{\nu}$ and Γ being a constant. $\tilde{\nu}$ is measured from the band center, at which $\tilde{\nu} = 0, \varepsilon = \frac{1}{2}\varepsilon_{max}$ when $\tilde{\nu}^2 = 2\Gamma \ln 2$. Therefore, the width at half height is

$$\Delta\tilde{\nu}_{1/2} = 2 \times (2\Gamma \ln 2)^{1/2}, \text{ implying that } \Gamma = \frac{\Delta\tilde{\nu}_{1/2}^2}{8 \ln 2}$$

Now we carry out the integration

$$A = \int \varepsilon d\tilde{\nu} = \varepsilon_{max} \int_{-\infty}^{\infty} e^{-\tilde{\nu}/2\Gamma} d\tilde{\nu} = \varepsilon_{max}(2\Gamma\pi)^{1/2} \quad \left[\int_{-\infty}^{\infty} e^{-x^2}\,dx = \pi^{1/2}\right]$$

$$= \varepsilon_{max}\left(\frac{2\pi\Delta\tilde{\nu}_{1/2}^2}{8 \ln 2}\right)^{1/2} = \left(\frac{\pi}{4 \ln 2}\right)^{1/2} \varepsilon_{max}\Delta\tilde{\nu}_{1/2} = 1.0645\varepsilon_{max}\Delta\tilde{\nu}_{1/2}$$

From Figure 14.50 of the text we estimate $\varepsilon_{max} \approx 9.5\ dm^3\ mol^{-1}\ cm^{-1}$ and $\Delta\tilde{\nu}_{1/2} \approx 4760\ cm^{-1}$. Then

$$A = 1.0645 \times (9.5\,dm^3\,mol^{-1}\,cm^{-1}) \times (4760\,cm^{-1}) = \boxed{4.8 \times 10^4\,dm^3\,mol^{-1}\,cm^{-2}}$$

The area under the curve on the printed page is about 1288 mm^2, each mm^2 corresponds to about 190.5 $cm^{-1} \times 0.189\ dm^3\ mol^{-1}\ cm^{-1}$, and so $\int \varepsilon d\tilde{\nu} \approx 4.64 \times 10^4\ dm^3\ mol^{-1}\ cm^{-2}$. The agreement with the calculated value above is good.

P14.6 For a photon to induce a spectroscopic transition, the transition moment $\langle\mu\rangle$ must be nonzero. The Laporte selection rule forbids transitions that involve no change in parity. So transitions to the Π_u states are forbidden. (Note, these states may not even be reached by a vibronic transition, for these molecules have only one vibrational mode and it is centrosymmetric.)

We will judge transitions to the other states with the assistance of the $D_{\infty h}$ character table. The transition moment is the integral $\int \psi_f^* \boldsymbol{\mu} \psi_i\, d\tau$, where the dipole moment operator has components proportional to the Cartesian coordinates. The integral vanishes unless the integrand, or at least some part of it, belongs to the totally symmetric representation of the molecule's point group. To find the character of the integrand, we multiply together the characters of its factors. Note that the μ_z has the same symmetry species as the ground state, namely A_{1u}, and the product of the ground state and μ_z has the A_{1g} symmetry species; since the symmetry species are mutually orthogonal, only a state with A_{1g} symmetry can be reached

from the ground state with z-polarized light. The $^2\Sigma_g^+$ state is such a state, so $\boxed{^2\Sigma_g^+ \leftarrow {}^2\Sigma_u^+ \text{ is allowed.}}$ That leaves x- or y-polarized transitions to the $^2\Pi_g$ states to consider.

	E	$\infty C_2'$	$2C_\phi$	i	$\infty\sigma_v$	$2S_\phi$
$\Sigma_u^+(A_{1u})$	1	−1	1	−1	1	−1
μ_x or $_y(E_{1u})$	2	0	$2\cos\phi$	−2	0	$2\cos\phi$
$\Pi_g(E_{1g})$	2	0	$2\cos\phi$	2	0	$-2\cos\phi$
Integrand	4	0	$4\cos^2\phi$	4	0	$4\cos^2\phi$

The little orthogonality theorem (see the solution to Problem 12.18) gives the coefficient of A_{1g} in the integrand as

$$c_{A_{1g}} = (1/h)\Sigma_c g(C)\chi(C) = [4 + 0 + 2(4\cos^2\phi) + 4 + 0 + 2(4\cos^2\phi)]/\infty = 0.$$

So the integrand does not contain A_{1g}, and the $\boxed{\text{transition to } ^2\Pi_g \text{ would be forbidden.}}$

P14.8 The weak absorption at 30 000 cm^{-1} is typical of a carbonyl group. The strong C=C absorption, which typically occurs at about 180 nm, has been shifted to longer wavelength (213 nm) because of the double bond and the CO group.

P14.10 The ratio of the transition probabilities of spontaneous emission to stimulated emission at a frequency ν is given by

$$A = \left(\frac{8\pi h\nu^3}{c^3}\right) B \text{ [13.11]} = \frac{k}{\lambda^3}B, \text{ where } k \text{ is a constant and we have } \nu = \frac{c}{\lambda}.$$

Thus at 400 nm

$$A(400) = \frac{k}{(400)^3}B(400), \quad \text{and at 500 nm} \quad A(500) = \frac{k}{(500)^3}B(500)$$

$$\text{Then, } \frac{A(500)}{A(400)} = \left(\frac{(400)^3}{(500)^3}\right) \times \left(\frac{B(500)}{B(400)}\right) = \left(\frac{64}{125}\right) \times 10^{-5} = 5 \times 10^{-6}$$

Lifetimes and half-lives are inversely proportional to transition probabilities (rate constants) and hence

$$t_{1/2}(T \rightarrow S) = \frac{1}{5 \times 10^{-6}} t_{1/2}(S^* \rightarrow S) = (2 \times 10^5) \times (1.0 \times 10^{-9}\text{ s}) = \boxed{2 \times 10^{-4}\text{ s}}$$

P14.12 The laser is delivering photons of energy

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\text{ J s}) \times (2.998 \times 10^8\text{ m s}^{-1})}{488 \times 10^{-9}\text{ m}} = 4.07 \times 10^{-19}\text{ J}$$

Since the laser is putting out 1.0 mJ of these photons every second, the rate of photon emisssion is:

$$r = \frac{1.0 \times 10^{-3}\text{ J s}^{-1}}{4.07 \times 10^{-19}\text{ J}} = 2.5 \times 10^{15}\text{ s}^{-1}$$

The time it takes the laser to deliver 10^6 photons (and therefore the time the dye remains fluorescent) is

$$t = \frac{10^6}{2.5 \times 10^{15}\,\mathrm{s}^{-1}} = \boxed{4 \times 10^{-10}\ \mathrm{s\ or\ 0.4\ ns}}!$$

Solutions to theoretical problems

P14.14 **(a)** Ethene (ethylene) belongs to D_{2h}. In this group the x, y, and z components of the dipole moment transform as B_{3u}, B_{2u}, and B_{1u} respectively. (See a more extensive set of character tables than in the text.) The π orbital is B_{1u} (like z, the axis perpendicular to the plane) and π^* is B_{3g}. Since $B_{3g} \times B_{1u} = B_{2u}$ and $B_{2u} \times B_{2u} = A_{1g}$, the transition is $\boxed{\text{allowed}}$ (and is y-polarized).

(b) Regard the CO group with its attached groups as locally C_{2v}. The dipole moment has components that transform as $A_1(z)$, $B_1(x)$, and $B_2(y)$, with the z-axis along the C=O direction and x perpendicular to the R_2CO plane. The n orbital is p_y (in the R_2CO plane), and hence transforms as B_2. The π^* orbital is p_x (perpendicular to the R_2CO plane), and hence transforms as B_1. Since $\Gamma_f \times \Gamma_i = B_1 \times B_2 = A_2$, but no component of the dipole moment transforms as A_2, the transition is $\boxed{\text{forbidden}}$.

P14.16 $$\mu = -e \int \psi_{v'} x \psi_v \, dx$$

From Problem 9.15, $\mu_{10} = -e \int \psi_1 x \psi_0 \, dx = -e \left[\dfrac{\hbar}{2(m_e k)^{1/2}} \right]^{1/2}$

Hence, $f = \dfrac{8\pi^2 m_e \nu}{3he^2} \times \dfrac{e^2\hbar}{2(m_e k)^{1/2}} = \boxed{\dfrac{1}{3}} \left[2\pi\nu = \left(\dfrac{k}{m_e} \right)^{1/2} \right]$

P14.18 **(a)** Vibrational energy spacings of the $\boxed{\text{lower}}$ state are determined by the spacing of the peaks of A. From the spectrum, $\tilde{\nu} \approx 1800\ \mathrm{cm}^{-1}$.

(b) Nothing can be said about the spacing of the upper state levels (without a detailed analysis of the intensities of the lines). For the second part of the question, we note that after some vibrational decay the benzophenone (which does absorb near 360 nm) can transfer its energy to naphthalene. The latter then emits the energy radiatively.

P14.20 **(a)** The Beer–Lambert Law is:

$$A = \log \frac{I_0}{I} = \varepsilon[\mathrm{J}]l.$$

The absorbed intensity is:

$$I_{abs} = I_0 - I \quad \text{so} \quad I = I_0 - I_{abs}.$$

Substitute this expression into the Beer–Lambert law and solve for I_{abs}:

$$\log \frac{I_0}{I_0 - I_{abs}} = \varepsilon[\mathrm{J}]l \quad \text{so} \quad I_0 - I_{abs} = I_0 \times 10^{-\varepsilon[\mathrm{J}]l},$$

and $I_{abs} = \boxed{I_0 \times (1 - 10^{-\varepsilon[\mathrm{J}]l})}$.

(b) The problem states that $I_f(\tilde{\nu}_f)$ is proportional to ϕ_f and to $I_{abs}(\tilde{\nu})$, so:

$$I_f(\tilde{\nu}_f) \propto \phi_f I_0(\tilde{\nu}) \times (1 - 10^{\varepsilon[J]l}).$$

If the exponent is small, we can expand $1 - 10^{-\varepsilon[J]l}$ in a power series:

$$10^{-\varepsilon[J]l} = (e^{\ln 10})^{-\varepsilon[J]l} \approx 1 - \varepsilon[J]l \ln 10 + \cdots,$$

and $$I_f(\tilde{\nu}_f) \propto \boxed{\phi_f I_0(\tilde{\nu}) \varepsilon[J]l \ln 10}$$

Solutions to applications

P14.22 There are three isosbestic wavelengths (wavenumbers). The presence of two or more isosbestic points is good evidence that only two solutes in equilibrium with each other are present. The solutes here being $Her(CNS)_8$ and $Her(OH)_8$.

P14.24 The following table summarizes AM1 calculations (an extended Hückel method) of the LUMO–HOMO separation in the 11-*cis* and 11-*trans* molecule (7) model of retinal. The −46.0° torsional angle between the first two alternate double bonds indicates that they are not coplanar. In contrast, the C11C12C13C14 torsion angle shows that the C11C12 double bond is close to coplanar with neighboring double bonds. The aromatic character of the alternating π-bond system is evidenced by contrasting the computed bond lengths at a single bond away from the π-system (C1—C2), a double bond (C11—C12), and a single bond between doubles (C12—C13) within the Lewis structure. We see a typical single bond length, a slightly elongated double bond length, and a bond length that is intermediate between a single and a double, respectively. The latter lengths are characteristic of aromaticity.

Conformation	11-*trans* (5)	11-*cis* (5)
$\Delta_f H^{\ominus}$/kJ mol^{-1}	725.07	738.1
E_{LUMO}/eV	−5.142	−5.138
E_{HOMO}/eV	−10.770	−10.888
ΔE/eV	(a) 5.628	(b) 5.750
λ/nm	(a) 220.3	(b) 215.6
C5C6C7C8 torsion angle/°	−44.5	−46.0
C11C12C13C14 torsion angle/°	179.7	−165.5
C1—C2/pm	153.2	153.2
C11—C12/pm	137.3	136.7
C12—C13/pm	1.420	1.421

(c) The lowest $\pi^* \leftarrow \pi$ transition occurs in the ultraviolet with the 11-*cis* transition at higher energy (higher frequency, lower wavelength). It is apparent that important interactions between retinal and a surrounding opsin molecule are responsible for reducing the transition energy to the observed strong absorption in the 400 to 600 nm visible range.

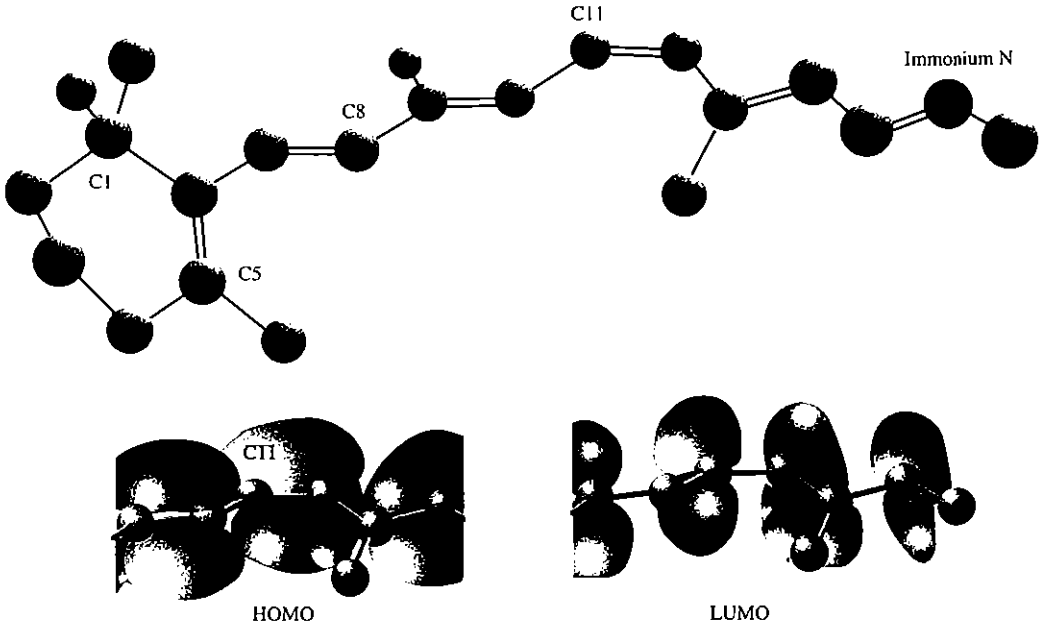


Figure 14.2

P14.26 The concentration of the hypothetical pure layer is

$$[O_3] = \frac{n}{V} = \frac{p}{RT} = \frac{1\text{ atm}}{(0.08206\,\text{dm}^3\,\text{atm}\,\text{mol}^{-1}\,\text{K}^{-1}) \times (273\,\text{K})} = 4.46 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$$

So for 300 DU

$$A = \varepsilon c l = (476\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (0.300\,\text{cm}) \times (4.46 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}) = \boxed{6.37}$$

and for 100 DU

$$A = \varepsilon c l = (476\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}) \times (0.100\,\text{cm}) \times (4.46 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}) = \boxed{2.12}$$

P14.28 The reaction enthalpy for process (2) is

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\text{Cl}) + \Delta_f H^\ominus(\text{OClO}^+) + \Delta_f H^\ominus(\text{e}^-) - \Delta_f H^\ominus(\text{Cl}_2\text{O}_2)$$

so $\Delta_f H^\ominus(\text{Cl}_2\text{O}_2) = \Delta_f H^\ominus(\text{Cl}) + \Delta_f H^\ominus(\text{OClO}^+) + \Delta_f H^\ominus(\text{e}^-) - \Delta_r H^\ominus$

$$\Delta_f H^\ominus(\text{Cl}_2\text{O}_2) = (121.68 + 1096 + 0)\,\text{kJ}\,\text{mol}^{-1} - (10.95\,\text{eV}) \times (96.485\,\text{kJ}\,\text{eV}^{-1})$$
$$= 161\,\text{kJ}\,\text{mol}^{-1}$$

We see that the Cl_2O_2 in process (2) is different from that in process (1), for its heat of formation is $\boxed{28\,\text{kJ}\,\text{mol}^{-1}}$ greater. This is consistent with the computations, which say that ClOOCl is likely to be the lowest-energy isomer. Experimentally we see that the Cl_2O_2 of process (2), which is not ClOOCl, is not very much greater in energy than the lowest-energy isomer.

15 Spectroscopy 3: magnetic resonance

Answers to discussion questions

D15.2 Before the application of a pulse the magnetization vector, $\boldsymbol{M}$, points along the direction of the static external magnetic field $\mathscr{B}_0$. There are more α spins than β spins. When we apply a rotating magnetic field $\mathscr{B}_1$ at right angles to the static field, the magnetization vector as seen in the rotating frame begins to precess about the $\mathscr{B}_1$ field with angular frequency $\omega_1 = \gamma\mathscr{B}_1$. The angle through which $\boldsymbol{M}$ rotates is $\theta = \gamma\mathscr{B}_1 t$, where t is the time for which the $\mathscr{B}_1$ pulse is applied. When $t = \pi/2\gamma\mathscr{B}_1, \theta = \pi/2 = 90°$, and $\boldsymbol{M}$ has rotated into the xy plane. Now there are equal numbers of α and β spins. A 180° pulse applied for a time $\pi/\gamma\mathscr{B}_1$, rotates $\boldsymbol{M}$ antiparallel to the static field. Now there are more β spins than α spins. A population inversion has occurred.

D15.4 The basic COSY experiment uses the simplest of all two-dimensional pulse sequences: a single 90° pulse to excite the spins at the end of the preparation period, and a mixing period containing just a second 90° pulse (see Figure 15.46 of the text).

The key to the COSY technique is the effect of the second 90° pulse, which can be illustrated by consideration of the four energy levels of an AX system (as shown in Figure 15.12). At thermal equilibrium, the population of the αA αX level is the greatest, and that of βA βX level is the smallest; the other two levels have the same energy and an intermediate population. After the first 90° pulse, the spins are no longer at thermal equilibrium. If a second 90° pulse is applied at a time t_1 that is short compared to the spin–lattice relaxation time T_1 the extra input of energy causes further changes in the populations of the four states. The changes in populations will depend on how far the individual magnetizations have precessed during the evolution period.

For simplicity, let us consider a COSY experiment in which the second 90° pulse is split into two selective pulses, one applied to X and one to A. Depending on the evolution time t_1, the 90° pulse that excites X may leave the population differences across each of the two X transitions unchanged, inverted, or somewhere in between. Consider the extreme case in which one population difference is inverted and the other unchanged (Figure 15.50). The 90° pulse that excites A will now generate an FID in which one of the two A transitions has increased in intensity, and the other has decreased. The overall effect is that precession of the X spins during the evolution period determines the amplitudes of the signals from the A spins obtained during the detection period. As the evolution time t_1 is increased, the intensities of the signals from A spins oscillate at rates determined by the frequencies of the two X transitions.

This transfer of information between spins is at the heart of two-dimensional NMR spectroscopy and leads to the correlation of different signals in a spectrum. In this case, information transfer tells us

that there is a scalar coupling between A and X. If we conduct a series of experiments in which t_1 is incremented, Fourier transformation of the FIDs on t_2 yields a set of spectra $I(\nu_1, \nu_2)$ in which the A signal amplitudes oscillate as a function of t_1. A second Fourier transformation, this time on t_1, converts these oscillations into a two-dimensional spectrum $I(\nu_1, \nu_2)$. The signals are spread out in ν_1 according to their precession frequencies during the detection period. Thus, if we apply the COSY pulse sequence to our AX spin system (Figure 15.46), the result is a two-dimensional spectrum that contains four groups of signals centered on the two chemical shifts in ν_1 and ν_2. Each group will show fine structure, consisting of a block of four signals separated by J_{AX}. The diagonal peaks are signals centered on $(\delta_A \delta_A)$ and $(\delta_X \delta_X)$ and lie along the diagonal $\nu_1 = \nu_2$. They arise from signals that did not change chemical shift between t_1 and t_2. The cross peaks (or *off-diagonal peaks*) are signals centered on $(\delta_A \delta_X)$ and $(\delta_X \delta_A)$ and owe their existence to the coupling between A and X. Consequently, cross peaks in COSY spectra allow us to map the couplings between spins and to trace out the bonding network in complex molecules. Figure 15.52 shows a simple example of a proton COSY spectrum of isoleucine.

D15.6 The ESR spectra of a spin probe, such as the di-*tert*-butyl nitroxide radical, broadens with restricted motion of the probe. This suggests that the width of spectral lines may correlate with the depth to which a probe may enter into a biopolymer crevice. Deep crevices are expected to severely restrict probe motion and broaden the spectral lines. Additionally, the splitting and center of ESR spectra of an oriented sample can provide information about the shape of the biopolymer-probe environment because the probe ESR signal is anisotropic and depends upon the orientation of the probe with the external magnetic field. Oriented biopolymers occur in lipid membranes and in muscle fibers.

Solutions to exercises

E15.1(b) For ^{19}F, $\dfrac{\mu}{\mu_N} = 2.62835, \quad g = 5.2567$

$$\nu = \nu_L = \frac{\gamma \mathscr{B}}{2\pi} \text{ with } \gamma = \frac{g_I \mu_N}{\hbar}$$

$$\text{Hence, } \nu = \frac{g_I \mu_N \mathscr{B}}{h} = \frac{(5.2567) \times (5.0508 \times 10^{-27}\,\text{J T}^{-1}) \times (16.2\,\text{T})}{(6.626 \times 10^{-34}\,\text{J s})}$$

$$= 6.49 \times 10^8\,\text{s}^{-1} = \boxed{649\,\text{MHz}}$$

E15.2(b) $E_{m_I} = -\gamma \hbar \mathscr{B} m_I = -g_I \mu_N \mathscr{B} m_I$

$m_I = 1, 0, -1$

$E_{m_I} = -(0.404) \times (5.0508 \times 10^{-27}\,\text{J T}^{-1}) \times (11.50\,\text{T}) m_I$

$= -\left(2.34\overline{66} \times 10^{-26}\,\text{J}\right) m_I$

$\boxed{-2.35 \times 10^{-26}\,\text{J},\ 0,\ +2.35 \times 10^{-26}\,\text{J}}$

E15.3(b) The energy separation between the two levels is

$$\Delta E = h\nu \text{ where } \nu = \frac{\gamma\mathscr{B}}{2\pi} = \frac{(1.93 \times 10^7\, T^{-1}\, s^{-1}) \times (15.4\, T)}{2\pi}$$
$$= 4.73 \times 10^7\, s^{-1} = \boxed{47.3\,\text{MHz}}$$

E15.4(b) A 600 MHz NMR spectrometer means 600 MHz is the resonance field for protons for which the magnetic field is 14.1 T as shown in Exercise 15.1(a). In high-field NMR it is the field not the frequency that is fixed.

(a) A ^{14}N nucleus has three energy states in a magnetic field corresponding to $m_I = +1, 0, -1$. But $\Delta E(+1 \rightarrow 0) = \Delta E(0 \rightarrow -1)$

$$\Delta E = E_{m_I'} - E_{m_I} = -\gamma\hbar\mathscr{B}m_I' - (-\gamma\hbar\mathscr{B}m_I)$$
$$= -\gamma\hbar\mathscr{B}(m_I' - m_I) = -\gamma\hbar\mathscr{B}\Delta_{m_I}$$

The allowed transitions correspond to $\Delta_{m_I} = \pm 1$; hence

$$\Delta E = h\nu = \gamma\hbar\mathscr{B} = g_I\mu_N\mathscr{B} = (0.4036) \times \left(5.051 \times 10^{-27}\text{JT}^{-1}\right) \times (14.1\text{T})$$
$$= \boxed{2.88 \times 10^{-26}\,\text{J}}$$

(b) We assume that the electron g-value in the radical is equal to the free electron g-value, $g_e = 20023$. Then

$$\Delta E = h\nu = g_e\mu_B\mathscr{B}\,[37] = (2.0023) \times (9.274 \times 10^{-24}\,\text{J T}^{-1}) \times (0.300\,\text{T})$$
$$= \boxed{5.57 \times 10^{-24}\,\text{J}}$$

COMMENT. The energy level separation for the electron in a free radical in an ESR spectrometer is far greater than that of nuclei in an NMR spectrometer, despite the fact that NMR spectrometers normally operate at much higher magnetic fields.

E15.5(b) $\Delta E = h\nu = \gamma\hbar\mathscr{B} = g_I\mu_N\mathscr{B}$ [Solution to Exercise 15.1(a)]

$$\text{Hence, } \mathscr{B} = \frac{h\nu}{g_I\mu_N} = \frac{(6.626 \times 10^{-34}\,\text{J Hz}^{-1}) \times (150.0 \times 10^6\,\text{Hz})}{(5.586) \times (5.051 \times 10^{-27}\,\text{J T}^{-1})} = \boxed{3.523\,\text{T}}$$

E15.6(b) In all cases the selection rule $\Delta m_I = \pm 1$ is applied; hence (Exercise 15.4(b)(a))

$$\text{B} = \frac{h\nu}{g_I\mu_N} = \frac{6.626 \times 10^{-34}\,\text{J Hz}^{-1}}{5.0508 \times 10^{-27}\,\text{JT}^{-1}} \times \frac{\nu}{g_I}$$
$$= \left(1.3119 \times 10^{-7}\right) \times \frac{\left(\frac{\nu}{\text{Hz}}\right)}{g_I}\text{T} = (0.13119) \times \frac{\left(\frac{\nu}{\text{MHz}}\right)}{g_I}\text{T}$$

We can draw up the following table

	$\mathscr{B}$/T	^{14}N	^{19}F	^{31}P
	g_I	0.40356	5.2567	2.2634
(a)	300 MHz	97.5	7.49	17.4
(b)	750 MHz	244	18.7	43.5

COMMENT. Magnetic fields above 20 T have not yet been obtained for use in NMR spectrometers. As discussed in the solution to Exercise 15.4(b), it is the field, not the frequency, that is fixed in high-field NMR spectrometers. Thus an NMR spectrometer that is called a 300 MHz spectrometer refers to the resonance frequency for protons and has a magnetic field fixed at 7.05 T.

E15.7(b) The relative population difference for spin $-\frac{1}{2}$ nuclei is given by

$$\frac{\delta N}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \approx \frac{\gamma h \mathscr{B}}{2kT} = \frac{g_I \mu_N \mathscr{B}}{2kT} \quad \textit{[Justification 15.1]}$$

$$= \frac{1.405\,(5.05 \times 10^{-27}\,\mathrm{J\,T^{-1}})\,\mathscr{B}}{2\,(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})} = 8.62 \times 10^{-7}\,(\mathscr{B}/\mathrm{T})$$

(a) For 0.50 T $\dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (0.50) = \boxed{4.3 \times 10^{-7}}$

(b) For 2.5 T $\dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (2.5) = \boxed{2.2 \times 10^{-6}}$

(c) For 15.5 T $\dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (15.5) = \boxed{1.34 \times 10^{-5}}$

E15.8(b) The ground state has

$$m_I = +\frac{1}{2} = \alpha \text{ spin}, \quad m_I = -\frac{1}{2} = \beta \text{ spin}$$

Hence, with

$$\delta N = N_\alpha - N_\beta$$

$$\frac{\delta N}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \frac{N_\alpha - N_\alpha e^{-\Delta E/kT}}{N_\alpha + N_\alpha e^{-\Delta E/kT}} \quad \textit{[Justification 15.1]}$$

$$= \frac{1 - e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}} \approx \frac{1 - (1 - \Delta E/kT)}{1 + 1} \approx \frac{\Delta E}{2kT} = \frac{g_I \mu_N \mathscr{B}}{2kT} \quad [\text{for } \Delta E \ll kT]$$

$$\delta N = \frac{N g_I \mu_N \mathscr{B}}{2kT} = \frac{Nh\nu}{2kT}$$

Thus, $\delta N \propto \nu$

$$\frac{\delta N(800\,\mathrm{MHz})}{\delta N(60\,\mathrm{MHz})} = \frac{(800\,\mathrm{MHz})}{(60\,\mathrm{MHz})} = \boxed{13}$$

This ratio is not dependent on the nuclide as long as the approximation $\Delta E \ll kT$ holds.

(a) $\delta = \dfrac{\nu - \nu^\circ}{\nu^\circ} \times 10^6$ [15.8]

Since both ν and ν° depend upon the magnetic field in the same manner, namely

$$\nu = \frac{g_I \mu_N \mathscr{B}}{h} \quad \text{and} \quad \nu^\circ = \frac{g_I \mu_N \mathscr{B}_0}{h} \text{ [Exercise 15.1(a)]}$$

δ is $\boxed{\text{independent}}$ of both $\mathscr{B}$ and ν.

(b) Rearranging [15.18], $\nu - \nu^\circ = \nu^\circ \delta \times 10^{-6}$ and we see that the relative chemical shift is

$$\frac{\nu - \nu^\circ(800\,\text{MHz})}{\nu - \nu^\circ(60\,\text{MHz})} = \frac{(800\,\text{MHz})}{(60\,\text{MHz})} = \boxed{13}$$

COMMENT. This direct proportionality between $\nu - \nu^\circ$ and ν° is one of the major reasons for operating an NMR spectrometer at the highest frequencies possible.

E15.9(b) $\mathscr{B}_{\text{loc}} = (1 - \sigma)\mathscr{B}$

$$|\Delta\mathscr{B}_{\text{loc}}| = |(\Delta\sigma)|\mathscr{B} \approx |[\delta(CH_3) - \delta(CH_2)]|\mathscr{B}$$
$$= |1.16 - 3.36| \times 10^{-6}\mathscr{B} = 2.20 \times 10^{-6}\mathscr{B}$$

(a) $\mathscr{B} = 1.9\,\text{T}, |\Delta\mathscr{B}_{\text{loc}}| = (2.20 \times 10^{-6}) \times (1.9\,\text{T}) = \boxed{4.2 \times 10^{-6}\,\text{T}}$

(b) $\mathscr{B} = 16.5\,\text{T}, |\Delta\mathscr{B}_{\text{loc}}| = (2.20 \times 10^{-6}) \times (16.5\,\text{T}) = \boxed{3.63 \times 10^{-5}\,\text{T}}$

E15.10(b) $\nu - \nu^\circ = \nu^\circ \delta \times 10^{-6}$

$$|\Delta\nu| \equiv (\nu - \nu^\circ)(CH_2) - (\nu - \nu^\circ)(CH_3) = \nu(CH_2) - \nu(CH_3)$$
$$= \nu^\circ[\delta(CH_2) - \delta(CH_3)] \times 10^{-6}$$
$$= (3.36 - 1.16) \times 10^{-6}\nu^\circ = 2.20 \times 10^{-6}\nu^\circ$$

(a) $\nu^\circ = 350\,\text{MHz} \quad |\Delta\nu| = (2.20 \times 10^{-6}) \times (350\,\text{MHz}) = 770\,\text{Hz}$ [Figure 15.1]

(b) $\nu^\circ = 650\,\text{MHz} \quad |\Delta\nu| = (2.20 \times 10^{-6}) \times (650\,\text{MHz}) = 1.43\,\text{kHz}$

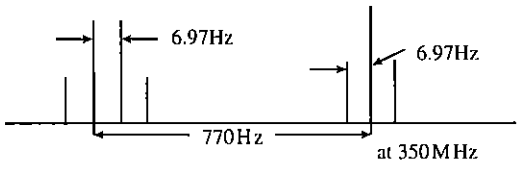


Figure 15.1

At 650 MHz, the spin–spin splitting remains the same at 6.97 Hz, but as $\Delta\nu$ has increased to 1.43 kHz, the splitting appears narrower on the δ scale.

E15.11(b) The difference in resonance frequencies is

$$\Delta\nu = \left(\nu^{\circ} \times 10^{-6}\right)\Delta\delta = \left(350\,\mathrm{s}^{-1}\right) \times (6.8 - 5.5) = 4.6 \times 10^{2}\,\mathrm{s}^{-1}$$

The signals will be resolvable as long as the conformations have lifetimes greater than

$$\tau = (2\pi\,\Delta\delta)^{-1}$$

The interconversion rate is the reciprocal of the lifetime, so a resolvable signal requires an interconversion rate less than

$$\text{rate} = (2\pi\,\Delta\delta) = 2\pi\left(4.6 \times 10^{2}\,\mathrm{s}^{-1}\right) = \boxed{2.9 \times 10^{3}\,\mathrm{s}^{-1}}$$

E15.12(b) $\nu = \dfrac{g_I \mu_N \mathscr{B}}{h}$ [Solution to exercise 15.1(*a*)]

Hence, $\dfrac{\nu(^{31}\mathrm{P})}{\nu(^{1}\mathrm{H})} = \dfrac{g(^{31}\mathrm{P})}{g(^{1}\mathrm{H})}$

or $\nu(^{31}\mathrm{P}) = \dfrac{2.2634}{5.5857} \times 500\,\mathrm{MHz} = \boxed{203\,\mathrm{MHz}}$

The proton resonance consists of 2 lines $\left(2 \times \frac{1}{2} + 1\right)$ and the ^{31}P resonance of 5 lines $\left[2 \times \left(4 \times \frac{1}{2}\right) + 1\right]$. The intensities are in the ratio 1:4:6:4:1 (Pascal's triangle for four equivalent spin $\frac{1}{2}$ nuclei, Section 15.6). The lines are spaced $\dfrac{5.5857}{2.2634} = 2.47$ times greater in the phosphorus region than the proton region. The spectrum is sketched in Figure 15.2.

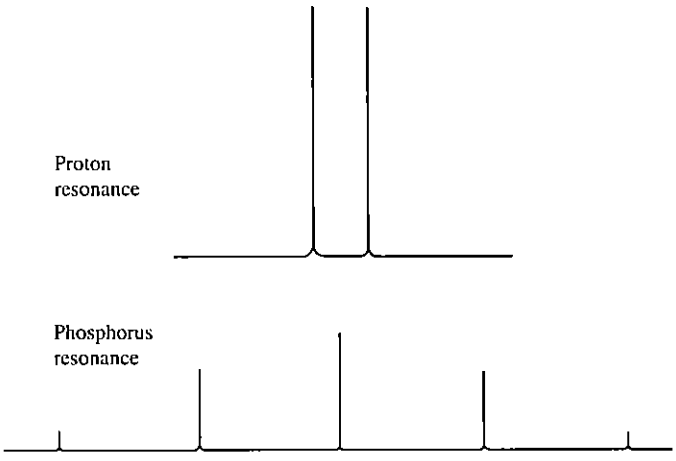


Figure 15.2

E15.13(b) Look first at A and M, since they have the largest splitting. The A resonance will be split into a widely spaced triplet (by the two M protons); each peak of that triplet will be split into a less widely spaced sextet (by the five X protons). The M resonance will be split into a widely spaced triplet (by the two A protons); each peak of that triplet will be split into a narrowly spaced sextet (by the five X protons).

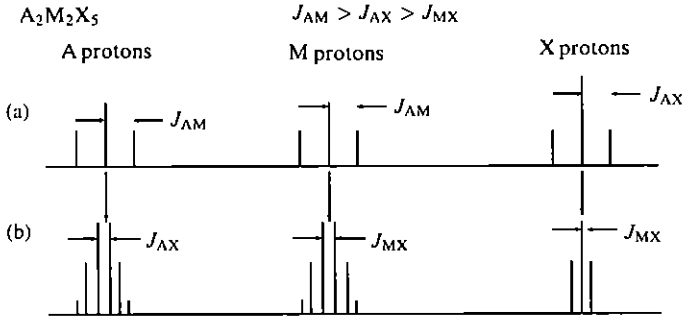


Figure 15.3

The X resonance will be split into a less widely spaced triplet (by the two A protons); each peak of that triplet will be split into a narrowly spaced triplet (by the two M protons). (See Figure 15.3.)

Only the splitting of the central peak of Figure 15.3(a) is shown in Figure 15.3(b).

E15.14(b) **(a)** Since all J_{HF} are equal in this molecule (the CH_2 group is perpendicular to the CF_2 group), the H and F nuclei are both chemically and magnetically equivalent.

(b) Rapid rotation of the PH_3 groups about the Mo–P axes makes the P and H nuclei chemically and magnetically equivalent in both the *cis*- and *trans*-forms.

E15.15(b) Precession in the rotating frame follows

$$\nu_L = \frac{\gamma \mathscr{B}_1}{2\pi} \quad \text{or} \quad \omega_1 = \gamma \mathscr{B}_1$$

Since ω is an angular frequency, the angle through which the magnetization vector rotates is

$$\theta = \gamma \mathscr{B}_1 t = \frac{g_I \mu_N}{\hbar} \mathscr{B}_1 t$$

$$\text{So } \mathscr{B}_1 = \frac{\theta \hbar}{g_I \mu_N t} = \frac{(\pi) \times (1.0546 \times 10^{-34}\,\text{J s})}{(5.586) \times (5.0508 \times 10^{-27}\,\text{J T}^{-1}) \times (12.5 \times 10^{-6}\,\text{s})} = \boxed{9.40 \times 10^{-4}\,\text{T}}$$

a 90° pulse requires $\frac{1}{2} \times 12.5\,\mu\text{s} = \boxed{6.25\,\mu\text{s}}$

E15.16(b) $$\mathscr{B} = \frac{h\nu}{g_e \mu_B} = \frac{hc}{g_e \mu_B \lambda}$$

$$= \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{(2) \times (9.274 \times 10^{-24}\,\text{J T}^{-1}) \times (8 \times 10^{-3}\,\text{m})} = \boxed{1.\bar{3}\,\text{T}}$$

E15.17(b) The g factor is given by

$$g = \frac{h\nu}{\mu_B \mathscr{B}}; \quad \frac{h}{\mu_B} = \frac{6.62608 \times 10^{-34}\,\text{J s}}{9.2740 \times 10^{-24}\,\text{J T}^{-1}} = 7.1448 \times 10^{-11}\,\text{T Hz}^{-1} = 71.448\,\text{mT GHz}^{-1}$$

$$g = \frac{71.448\,\text{mT GHz}^{-1} \times 9.2482\,\text{GHz}}{330.02\,\text{mT}} = \boxed{2.0022}$$

E15.18(b) The hyperfine coupling constant for each proton is $\boxed{2.2\ \text{mT}}$, the difference between adjacent lines in the spectrum. The g value is given by

$$g = \frac{h\nu}{\mu_B \mathscr{B}} = \frac{(71.448\,\text{mT GHz}^{-1}) \times (9.332\,\text{GHz})}{334.7\,\text{mT}} = \boxed{1.992}$$

E15.19(b) If the spectrometer has sufficient resolution, it will see a signal split into eight equal parts at $\pm\ 1.445 \pm 1.435 \pm 1.055$ mT from the center, namely

$$\boxed{328.865,\ 330.975,\ 331.735,\ 331.755,\ 333.845,\ 333.865,\ 334.625,\ \text{and}\ 336.735\ \text{mT}}$$

If the spectrometer can only resolve to the nearest 0.1 mT, then the spectrum will appear as a sextet with intensity ratios of 1:1:2:2:1:1. The four central peaks of the more highly resolved spectrum would be the two central peaks of the less resolved spectrum.

E15.20(b) **(a)** If the CH_2 protons have the larger splitting there will be a triplet (1:2:1) of quartets (1:3:3:1). Altogether there will be 12 lines with relative intensities 1(4 lines), 2(2 lines), 3(4 lines), and 6(2 lines). Their positions in the spectrum will be determined by the magnitudes of the two proton splittings which are not given.

(b) If the CD_2 deuterons have the larger splitting there will be a quintet (1:2:3:2:1) of septets (1:3:6:7:6:3:1). Altogether there will be 35 lines with relative intensities 1(4 lines), 2(4 lines), 3(6 lines), 6(8 lines), 7(2 lines), 9(2 lines), 12(4 lines), 14(2 lines), 18(2 lines),and 21(1 line). Their positions in the spectrum will determined by the magnitude of the two deuteron splittings which are not given.

E15.21(b) The hyperfine coupling constant for each proton is $\boxed{2.2\,\text{mT}}$, the difference between adjacent lines in the spectrum. The g value is given by

$$g = \frac{h\nu}{\mu_B \mathscr{B}} \text{ so } \mathscr{B} = \frac{h\nu}{\mu_B g}, \quad \frac{h}{\mu_B} = 71.448\,\text{mT GHz}^{-1}$$

(a) $$\mathscr{B} = \frac{(71.448\,\text{mT GHz}^{-1}) \times (9.312\,\text{GHz})}{2.0024} = \boxed{332.3\,\text{mT}}$$

(b) $$\mathscr{B} = \frac{(71.448\,\text{mT GHz}^{-1}) \times (33.88\,\text{GHz})}{2.0024} = \boxed{1209\,\text{mT}}$$

E15.22(b) Two nuclei of spin $\boxed{I = 1}$ give five lines in the intensity ratio 1:2:3:2:1 (Figure 15.4).

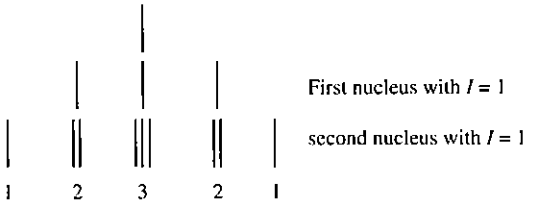


Figure 15.4

E15.23(b) The X nucleus produces four lines of equal intensity. Three H nuclei split each into a 1:3:3:1 quartet. The three D nuclei split each line into a septet with relative intensities 1:3:6:7:6:3:1 (see Exercise 15.20(a)). (See Figure 15.5.)

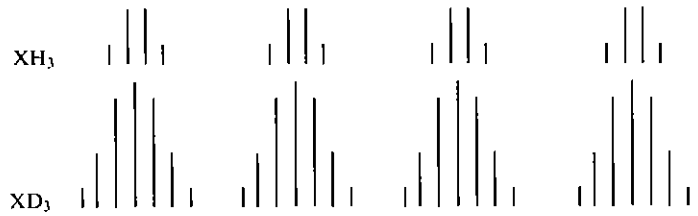


Figure 15.5

Solutions to problems

Solutions to numerical problems

P15.2

$$\tau_J \approx \frac{1}{2\pi\delta\nu} = \frac{1}{(2\pi) \times \left((5.2 - 4.0) \times 10^{-6}\right) \times \left(60 \times 10^6\,\text{Hz}\right)}$$

≈ 2.2 ms, corresponding to a jump rate of $450\,\text{s}^{-1}$.

When $\nu = 300$ MHz

$$\tau_J \approx \frac{1}{(2\pi) \times \left\{(5.2 - 4.0) \times 10^{-6}\right\} \times \left(300 \times 10^6\,\text{Hz}\right)} = 0.44\,\text{ms}$$

corresponding to a jump rate of $2.3 \times 10^3\,\text{s}^{-1}$. Assume an Arrhenius-like jumping process (Chapter 22)

$$\text{rate} \propto e^{-E_a/RT}$$

Then, $$\ln\left[\frac{\text{rate}(T')}{\text{rate}(T)}\right] = \frac{-E_a}{R}\left(\frac{1}{T'} - \frac{1}{T}\right)$$

and therefore $$E_a = \frac{R\ln(r'/r)}{\frac{1}{T} - \frac{1}{T'}} = \frac{8.314\,\text{J K}^{-1}\,\text{mol}^{-1} \times \ln\frac{2.3 \times 10^3}{450}}{\frac{1}{280\,\text{K}} - \frac{1}{300\,\text{K}}} = \boxed{57\,\text{kJ mol}^{-1}}$$

P15.4 The three rotational conformations of $F_2BrC{-}CBrCl_2$ are shown in Figure 15.6. In conformation I, the two F atoms are equivalent. However, in conformations II and III they are non-equivalent. At low temperature, the molecular residence time in conformation I is longer (because this conformation has the lowest repulsive energy of the large bromine atoms) than that of conformations II and III, which have equal residence times. With its longer residence time, we expect that the NMR signal intensity of conformation I should be stronger and we can conclude that it is the low-temperature singlet. It is a singlet because equivalent atoms do not have detectable spin–spin couplings.

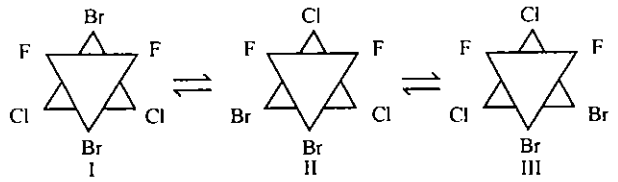


Figure 15.6

The fluorines of conformations II and III are non-equivalent, so their coupling is observed at low-temperature. Fluorine has a nuclear spin of 1/2, so we expect a doublet for each fluorine. These are observed with strong geminal coupling of 160 Hz. As temperature increases, the rate of rotation between II and III increases and the two fluorines become equivalent in these conformations, though remaining distinct from I. The doublets collapse to singlets. With a further temperature increase to −30 °C, and above, the rate of rotation about the C—C bond becomes so rapid that the residence times of the three conformations become equal. The very short residence times produce an average NMR signal that is a singlet and the fluorines appear totally equivalent.

The spectra shown in Figure 15.63 of the text for conformations II and III show both spin–spin coupling and differences in chemical shift. The spin–spin splitting is 160 Hz. The difference in chemical shift can be estimated from the separation between the doublet centers, Δ

$$\Delta = (J^2 + \delta\nu^2)^{1/2}$$

Δ is estimated from the figure to be 210 Hz. This yields for $\delta\nu$, the chemical shift,

$$\delta\nu = (\Delta^2 - J^2)^{1/2}$$
$$= (210^2 - 160^2)^{1/2}\,\text{Hz} \approx 140\,\text{Hz}$$

Collapse to a single line will occur when the rate of interconversion satisfies

$$k \approx \frac{1}{\tau} \approx \frac{\pi\Delta}{\sqrt{2}}\ [15.29]$$

$$k = \frac{\pi \times 200\,\text{s}^{-1}}{\sqrt{2}} \approx \boxed{4 \times 10^2\,\text{s}^{-1}}$$

The relative intensities, I, of the lines at −80 °C can be used to estimate the energy difference $(E_{II} - E_I)$ between conformation I and conformations II and III. We assume that the relative intensities of the lines are proportional to the populations of conformers and that these populations follow the Boltzmann distribution (Chapters 2 and 16). Then

$$\frac{I_I}{I_{II}} \simeq \frac{e^{-E_I/RT}}{e^{-E_{II}/RT}} = e^{(E_{II}-E_I)/RT}$$

$$E_{II} - E_I = RT \ln\left(\frac{I_I}{I_{II}}\right) = 8.314\,\text{J K}^{-1}\,\text{mol}^{-1} \times (273 - 80)\,\text{K} \ln(10)$$
$$= 3.7 \times 10^3\,\text{J mol}^{-1} = \boxed{3.7\,\text{kJ mol}^{-1}}$$

This energy difference is not, however, the rotational energy barrier between the rotational isomers. The latter can be estimated from the rate of interconversion between the isomers as a function of temperature. That rate of interconversion is roughly $4 \times 10^2\,\text{s}^{-1}$ at −30 °C. At −60 °C, as estimated from the line width at that temperature [13.19], it is roughly 1/3 of that value, or $\sim 1.3 \times 10^2\,\text{s}^{-1}$. Assuming that the rate of interconversion satisfies an Arrhenius type of behavior, $k \propto e^{-E_a/RT}$, where E_a is the rotational energy barrier,

$$\frac{k(-30\,^\circ\text{C})}{k(-60\,^\circ\text{C})} = 3 = e^{\left[-\frac{E_a}{R}\left(\frac{1}{243\,\text{K}} - \frac{1}{213\,\text{K}}\right)\right]}$$

$$E_a = \frac{R \ln 3}{\left(\frac{1}{213\,\text{K}} - \frac{1}{243\,\text{K}}\right)} = 1.6 \times 10^4\,\text{J mol}^{-1} = \boxed{16\,\text{kJ mol}^{-1}}$$

This value is typical of the rotational barriers observed in compounds of this kind.

P15.6 **(a)** The Karplus equation [15.27] for $^3J_{HH}$ is a linear equation in $\cos\phi$ and $\cos 2\phi$. The experimentally determined equation for $^3J_{SnSn}$ is a linear equation in $^3J_{HH}$. In general, if $F(f)$ is linear in f, and if $f(x)$ is linear in x, then $F(x)$ is linear. So we expect $^3J_{SnSn}$ to be linear in $\cos\phi$ and $\cos 2\phi$. This is demonstrated in (b).

(b) $^3J_{SnSn}/\text{Hz} = 78.86(^3J_{HH}/\text{Hz}) + 27.84$

Inserting the Karplus equation for $^3J_{HH}$ we obtain

$^3J_{SnSn}/\text{Hz} = 78.86\{A + B\cos\phi + C\cos 2\phi\} + 27.84$. Using $A = 7, B = -1$, and $C = 5$, we obtain

$$^3J_{SnSn}/\text{Hz} = \boxed{580 - 79\cos\phi + 395\cos 2\phi}$$

The plot of $^3J_{SnSn}$ is shown in Figure 15.7.

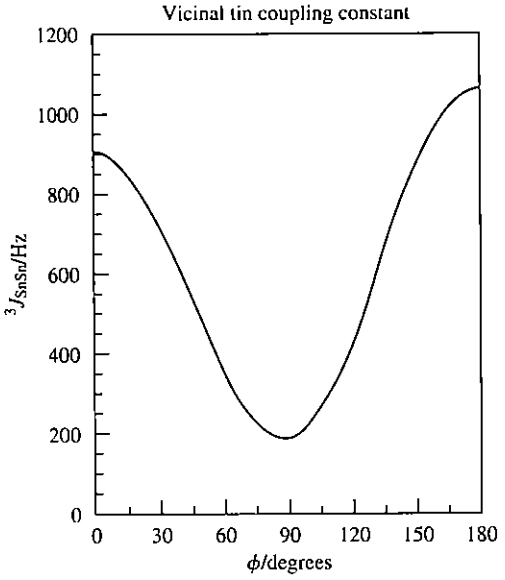


Figure 15.7

(c) A staggered configuration (Figure 15.8) with the $SnMe_3$ groups *trans* to each other is the preferred configuration. The $SnMe_3$ repulsions are then at a minimum.

P15.8

$$g = \frac{h\nu}{\mu_B \mathscr{B}_0}\ [15.40] = \frac{(7.144\,78 \times 10^{-11}\,\text{T}) \times (\nu/\text{Hz})}{\mathscr{B}_0}$$

$$= \frac{(7.144\,78 \times 10^{-11}\,\text{T}) \times (9.302 \times 10^9)}{\mathscr{B}_0} = \frac{0.664\,6\overline{1}}{\mathscr{B}_0/T}$$

$$g_\parallel = \frac{0.664\,6\overline{1}}{0.333\,64} = \boxed{1.992} \quad g_\perp = \frac{0.664\,6\overline{1}}{0.331\,94} = \boxed{2.002}$$

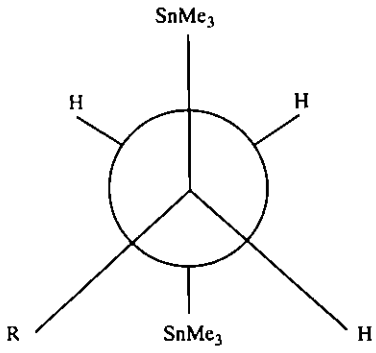


Figure 15.8

P15.10 Construct the spectrum by taking into account first the two equivalent ^{14}N splitting (producing a 1 : 2 : 3 : 2 : 1 quintet) and then the splitting of each of these lines into a 1 : 4 : 6 : 4 : 1 quintet by the four equivalent protons. The resulting 25-line spectrum is shown in Figure 15.9. Note that Pascal's triangle does not apply to the intensities of the quintet due to ^{14}N, but does apply to the quintet due to the protons.

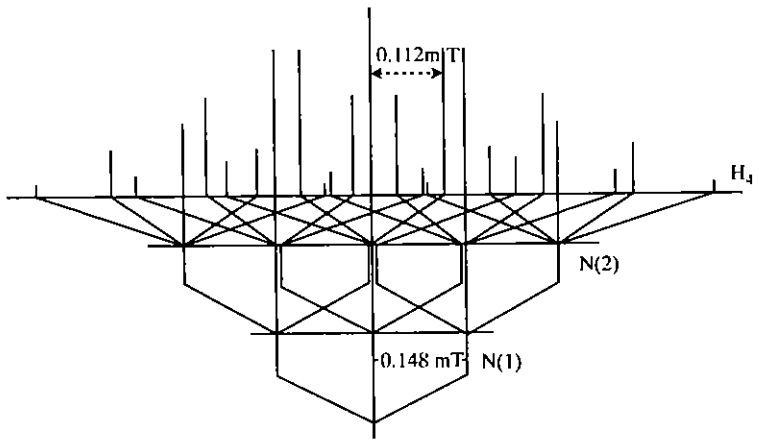
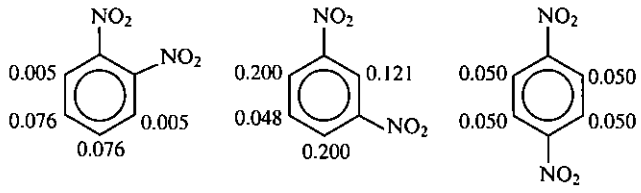


Figure 15.9

P15.12 For $C_6H_6^-$, $a = Q\rho$ with $Q = 2.25$ mT [15.43]. If we assume that the value of Q does not change from this value (a good assumption in view of the similarity of the anions), we may write

$$\rho = \frac{a}{Q} = \frac{a}{2.25\,\text{mT}}$$

Hence, we can construct the following maps



Solutions to theoretical problems

P15.14 (a) The table displays experimental ^{13}C chemical shifts and computed* atomic charges on the carbon atom *para* to a number of substituents in substituted benzenes. Two sets of charges are shown, one derived by fitting the electrostatic potential and the other by Mulliken population analysis.

Substituent	OH	CH_3	H	CF_3	CN	NO_2
δ	130.1	128.4	128.5	128.9	129.1	129.4
Electrostatic charge/e	−0.1305	−0.1273	−0.0757	−0.0227	−0.0152	−0.0541
Mulliken charge/e	−0.1175	−0.1089	−0.1021	−0.0665	−0.0805	−0.0392

*Semi-empirical, PM3 level, PC Spartan Pro™

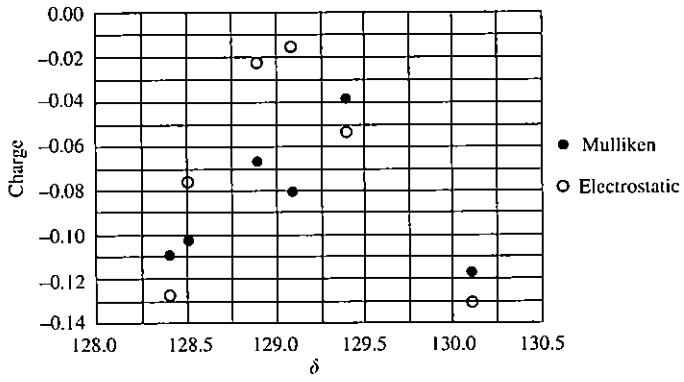


Figure 15.10

(b) Neither set of charges correlates well to the chemical shifts. If one removes phenol from the data set, a correlation would be apparent, particularly for the Mulliken charges.

(c) The diamagnetic local contribution to shielding is roughly proportional to the electron density on the atom. The extent to which the *para*-carbon atom is affected by electron-donating or withdrawing groups on the other side of the benzene ring is reflected in the net charge on the atom. If the diamagnetic local contribution dominated, then the more positive the atom, the greater the deshielding and the greater the chemical shift δ would be. That no such correlation is observed leads to several possible hypotheses: for example, the diamagnetic local contribution is not the dominant contribution in these molecules (or not in all of these molecules), or the computation is not sufficiently accurate to provide meaningful atomic charges.

P15.16 Equation 15.39 may be written

$$\mathscr{B} = k(1 - 3\cos^2\theta)$$

where k is a constant independent of angle. Thus

$$\begin{aligned}\langle\mathscr{B}\rangle &\propto \int_0^{\pi} (1 - 3\cos^2\theta)\sin\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \\ &\propto \int_1^{-1} (1 - 3x^2)\,\mathrm{d}x \times 2\pi \quad [x = \cos\theta, \mathrm{d}x = -\sin\theta\,\mathrm{d}\theta] \\ &\propto (x - x^3)\Big|_1^{-1} = 0\end{aligned}$$

P15.18 We have seen (Problem 15.17) that, if $G \propto \cos \omega_0 t$, then $I(\omega) \propto \dfrac{1}{\left[1 + (\omega_0 - \omega)^2 \tau^2\right]}$

which peaks at $\omega \approx \omega_0$. Therefore, if

$$G(t) \propto a \cos \omega_1 t + b \cos \omega_2 t$$

we can anticipate that

$$I(\omega) \propto \frac{a}{1 + (\omega_1 - \omega)^2 \tau^2} + \frac{b}{1 + (\omega_2 - \omega)^2 \tau^2}$$

and explicit calculation shows this to be so. Therefore. $I(\omega)$ consists of two absorption lines, one peaking at $\omega \approx \omega_1$ and the other at $\omega \approx \omega_2$.

Solutions to applications

P15.20 Methionine-105 is in the vicinity of both typtophan-28 and tyrosine-23 but the latter two residues are not in the vicinity of each other. The methionine residue may lay between them as represented in the figure.

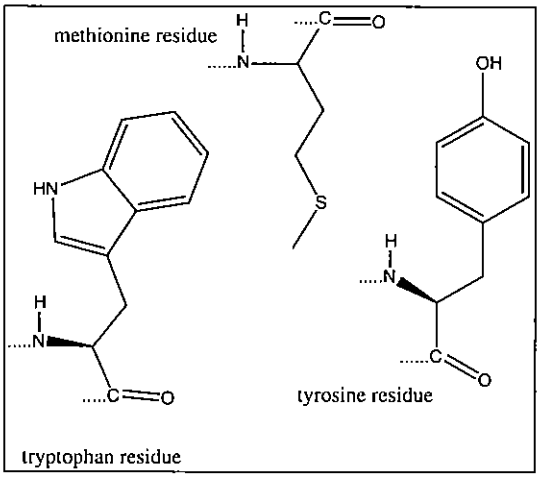
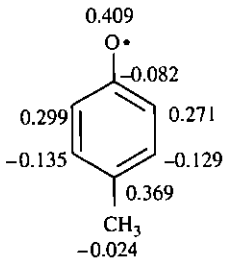


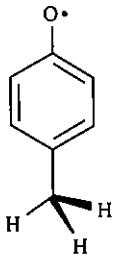
Figure 15.11

P15.22 At, say, room temperature, the tumbling rate of benzene, the small molecule, in a mobile solvent, may be close to the Larmor frequency, and hence its spin–lattice relaxation time will be short. As the temperature increases, the tumbling rate may increase well beyond the Larmor frequency, resulting in an increased spin–lattice relaxation time.

For the large oligopeptide at room temperature, the tumbling rate may be well below the Larmor frequency, but with increasing temperature it will approach the Larmor frequency due to the increased thermal motion of the molecule combined with the decreased viscosity of the solvent. Therefore, the spin–lattice relaxation time may decrease.

P15.24 (a) The first figure displays spin densities computed by molecular modeling software (*ab initio*, density functional theory, Gaussian 98™).





(b) First, note that the software assigned slightly different values to the two protons *ortho* to the oxygen and to the two protons *meta* to the oxygen. This is undoubtedly a computational artifact, a result of the minimum-energy structure having one methyl proton in the plane of the ring, which makes the right and left side of the ring slightly non-equivalent. (See second figure.) In fact, fast internal rotation makes the two halves of the ring equivalent. We will take the spin density at the *ortho* carbons to be 0.285 and those of the *meta* carbons to be −0.132. Predict the form of the spectrum by using the McConnell equation (15.43) for the splittings. The two *ortho* protons give rise to a 1:2:1 triplet with splitting $0.285 \times 2.25\,\text{mT} = 0.64\,\text{mT}$; these will in turn be split by the two *meta* protons into 1:2:1 triplets with splitting

$$0.132 \times 2.25\,\text{mT} = 0.297\,\text{mT} = 0.297\,\text{mT}.$$

And finally, these lines will be seen to be further split by the three methyl protons into 1:3:3:1 quartets with splittings 1.045 mT. Note that the McConnell relation cannot be applied to calculate these latter splittings, but the software generates them directly from calculated spin densities on the methyl hydrogens. The computed splittings agree well with experiment at the *ortho* positions (0.60 mT) and at the methyl hydrogens (1.19 mT), but less well at the *meta* positions (0.145 mT).

P15.26 We use $\nu = \dfrac{\gamma_N \mathscr{B}_{\text{loc}}}{2\pi} = \dfrac{\gamma_N}{2\pi}(1-\sigma)\mathscr{B}$ [15.17]

where $\mathscr{B}$ is the applied field.

Because shielding constants are quite small (a few parts per million) compared to 1, we may write for the purposes of this calculation

$$\nu = \frac{\gamma_N \mathscr{B}}{2\pi}$$

$$\nu_L - \nu_R = 100\,\text{Hz} = \frac{\gamma_N}{2\pi}(\mathscr{B}_L - \mathscr{B}_R)$$

$$\mathscr{B}_L - \mathscr{B}_R = \frac{2\pi \times 100\,\text{s}^{-1}}{\gamma_N}$$

$$= \frac{2\pi \times 100\,\text{s}^{-1}}{26.752 \times 10^7\,\text{T}^{-1}\text{s}^{-1}} - 2.35 \times 10^{-6}\,\text{T}$$

$$= 2.35\,\mu\text{T}$$

The field gradient required is then

$$\frac{2.35\,\mu\text{T}}{0.08\,\text{m}} = \boxed{29\,\mu\text{T m}^{-1}}$$

Note that knowledge of the spectrometer frequency, applied field, and the numerical value of the chemical shift (because constant) is not required.

16 Statistical thermodynamics 1: the concepts

Answers to discussion questions

D16.2 See Figure 16.11 and 16.13, *Illustration* 16.4, Self-test 16.6 in the text and the solution to Exercise 16.8(a)

D16.4 The simple zipper model for the conversion of a polypeptide helical (h) chain to a random coil (c) begins with nucleation whereby an h residue makes an independent transition to a c residue with a probability that depends upon σs where $\sigma < 1$ and s is the stability parameter. After the nucleation conversion, only residues adjacent to a c undergo the h to c transition and they do so non-cooperatively with a probability that depends upon the stability parameter. The Zimm–Brag model allows for multiple nucleation sites.

D16.6 Identical particles can be regarded as distinguishable when they are localized as in a crystal lattice where we can assign a set of coordinates to each particle. Strictly speaking, it is the lattice site that carries the set of coordinates, but as long as the particle is fixed to the site, it too can be considered distinguishable.

Solutions to exercises

E16.1(b) $$n_i = \frac{Ne^{-\beta\varepsilon_i}}{q} \quad \text{where } q = \sum_j e^{-\beta\varepsilon_j}$$

Thus

$$\frac{n_2}{n_1} = \frac{e^{-\beta\varepsilon_2}}{e^{-\beta\varepsilon_1}} = e^{-\beta(\varepsilon_2-\varepsilon_1)} = e^{-\beta\Delta\varepsilon} = e^{-\Delta\varepsilon/kT}$$

Given $\frac{n_2}{n_1} = \frac{1}{2}$, $\Delta\varepsilon = 300\,\text{cm}^{-1}$

$$k = (1.380\,66 \times 10^{-23}\,\text{J K}^{-1}) \times \left(\frac{1\,\text{cm}^{-1}}{1.9864 \times 10^{-23}\,\text{J}}\right) = 0.695\,06\,\text{cm}^{-1}\,\text{K}^{-1}$$

$$\frac{n_2}{n_1} = e^{-\Delta\varepsilon/kT}$$

$$\ln\left(\frac{n_2}{n_1}\right) = -\Delta\varepsilon/kT$$

$$T = \frac{-\Delta\varepsilon}{k\ln(n_2/n_1)} = \frac{\Delta\varepsilon}{k\ln(n_1/n_2)}$$

$$= \frac{300\,\text{cm}^{-1}}{(0.695\,06\,\text{cm}^{-1}\,\text{K}^{-1})\ln(2)} = 622.\bar{7}\,\text{K} \approx \boxed{623\,\text{K}}$$

E16.2(b) (a) $$\Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} [16.19] = h\left(\frac{1}{2\pi mkT}\right)^{1/2}$$

$$= (6.626 \times 10^{-34}\,\mathrm{J\,s}) \times \left(\frac{1}{(2\pi) \times (39.95) \times (1.6605 \times 10^{-27}\,\mathrm{kg}) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times T}\right)^{1/2}$$

$$\simeq \frac{276\,\mathrm{pm}}{(T/\mathrm{K})^{1/2}}$$

(b) $$q = \frac{V}{\Lambda^3}\,[16.19] = \frac{(1.00 \times 10^{-6}\,\mathrm{m^3}) \times (T/\mathrm{K})^{3/2}}{(2.76 \times 10^{-10}\,\mathrm{m})^3} = 4.76 \times 10^{22}(T/\mathrm{K})^{3/2}$$

(i) $T = 300\,\mathrm{K}$, $\Lambda = 1.59 \times 10^{-11}\,\mathrm{m} = \boxed{15.9\,\mathrm{pm}}$, $q = \boxed{2.47 \times 10^{26}}$,

(ii) $T = 3000\,\mathrm{K}$, $\Lambda = \boxed{5.04\,\mathrm{pm}}$, $q = \boxed{7.82 \times 10^{27}}$

Question. At what temperature does the thermal wavelength of an argon atom become comparable to its diameter?

E16.3(b) The translational partition function is

$$q_{\mathrm{tr}} = \frac{V}{h^3}(2kT\pi m)^{3/2}$$

so $$\frac{q_{\mathrm{Xe}}}{q_{\mathrm{He}}} = \left(\frac{m_{\mathrm{Xe}}}{m_{\mathrm{He}}}\right)^{3/2} = \left(\frac{131.3\,\mathrm{u}}{4.003\,\mathrm{u}}\right)^{3/2} = \boxed{187.9}$$

E16.4(b) $$q = \sum_{\text{levels}} g_j \mathrm{e}^{-\beta\varepsilon_j} = 2 + 3\mathrm{e}^{-\beta\varepsilon_1} + 2\mathrm{e}^{-\beta\varepsilon_2}$$

$$\beta\varepsilon = \frac{hc\tilde{\nu}}{kT} \simeq \frac{1.4388(\tilde{\nu}/\mathrm{cm^{-1}})}{T/K}$$

Thus $$q = 2 + 3\mathrm{e}^{-(1.4388\times 1250/2000)} + 2\mathrm{e}^{-(1.4388\times 1300/2000)}$$

$$= 2 + 1.2207 + 0.7850 = \boxed{4.006}$$

E16.5(b) $$E = U - U(0) = -\frac{N}{q}\frac{\mathrm{d}q}{\mathrm{d}\beta} = -\frac{N}{q}\frac{\mathrm{d}}{\mathrm{d}\beta}(2 + 3\mathrm{e}^{-\beta\varepsilon_1} + 2\mathrm{e}^{-\beta\varepsilon_2})$$

$$= -\frac{N}{q}\left(-3\varepsilon_1\mathrm{e}^{-\beta\varepsilon_1} - 2\varepsilon_2\mathrm{e}^{-\beta\varepsilon_2}\right) = \frac{Nhc}{q}\left(3\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}_1} + 2\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}_2}\right)$$

$$= \left(\frac{N_{\mathrm{A}}hc}{4.006}\right) \times \left\{3(1250\,\mathrm{cm^{-1}}) \times \left(\mathrm{e}^{-(1.4388\times 1250/2000)}\right) + 2(1300\,\mathrm{cm^{-1}}) \times \left(\mathrm{e}^{-(1.4388\times 1300/2000)}\right)\right\}$$

$$= \left(\frac{N_{\mathrm{A}}hc}{4.006}\right) \times (2546\,\mathrm{cm^{-1}})$$

$$= (6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}}) \times (2546\,\mathrm{cm^{-1}})/4.006$$

$$= \boxed{7.605\,\mathrm{kJ\,mol^{-1}}}$$

E16.6(b) In fact there are two upper states, but one upper level. And of course the answer is different if the question asks when 15 percent of the molecules are in the upper level, or if it asks when 15 percent of the molecules are in *each* upper state. The solution below assumes the former.

The relative population of states is given by the Boltzmann distribution

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right) \quad \text{so} \quad \ln\frac{n_2}{n_1} = \frac{-hc\tilde{\nu}}{kT}$$

Thus $T = \dfrac{-hc\tilde{\nu}}{k\ln(n_2/n_1)}$

Having 15 percent of the molecules in the upper level means

$$\frac{2n_2}{n_1} = \frac{0.15}{1-0.15} \quad \text{so} \quad \frac{n_2}{n_1} = 0.088$$

$$\text{and } T = \frac{-(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^{10}\,\text{cm s}^{-1})\times(360\,\text{cm}^{-1})}{(1.381\times10^{-23}\,\text{J K}^{-1})\times(\ln 0.088)}$$

$$= \boxed{213\,\text{K}}$$

E16.7(b) The energies of the states relative to the energy of the state with $m_I = 0$ are $-\gamma_N\hbar\mathscr{B}, 0, +\gamma_N\hbar\mathscr{B}$, where $\gamma_N\hbar = 2.04\times10^{-27}\,\text{J T}^{-1}$. With respect to the lowest level they are $0, \gamma_N\hbar, 2\gamma_N\hbar$.

The partition function is

$$q = \sum_{\text{states}} e^{-E_{\text{state}}/kT}$$

where the energies are measured with respect to the lowest energy. So in this case

$$q = 1 + \exp\left(\frac{-\gamma_N\hbar\mathscr{B}}{kT}\right) + \exp\left(\frac{-2\gamma_N\hbar\mathscr{B}}{kT}\right)$$

As $\mathscr{B}$ is increased at any given T, q decays from $q = 3$ toward $q = 1$ as shown in Figure 16.1(a).

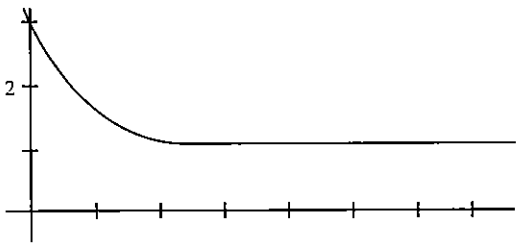


Figure 16.1(a)

The average energy (measured with respect to the lowest state) is

$$\langle E\rangle = \frac{\sum_{\text{states}} E_{\text{state}} e^{-E_{\text{state}}/kT}}{q} = \frac{1 + \gamma_N\hbar\mathscr{B}\exp(-\gamma_N\hbar\mathscr{B}/kT) + 2\gamma_N\hbar\mathscr{B}\exp(-2\gamma_N\hbar\mathscr{B}/kT)}{1 + \exp(-\gamma_N\hbar\mathscr{B}/kT) + \exp(-2\gamma_N\hbar\mathscr{B}/kT)}$$

The expression for the mean energy measured based on zero spin having zero energy becomes

$$E = \frac{\gamma_N \hbar \mathscr{B} - \gamma_N \hbar \mathscr{B} \exp(-2\gamma_N \hbar \mathscr{B}/kT)}{1 + \exp(-\gamma_N \hbar \mathscr{B}/kT) + \exp(-2\gamma_N \hbar \mathscr{B}/kT)} = \frac{\gamma_N \hbar \mathscr{B}\,(1 - \exp(-2\gamma_N \hbar \mathscr{B}/kT))}{1 + \exp(-\gamma_N \hbar \mathscr{B}/kT) + \exp(-2\gamma_N \hbar \mathscr{B}/kT)}$$

As $\mathscr{B}$ is increased at constant T, the mean energy varies as shown in Figure 16.1(b).

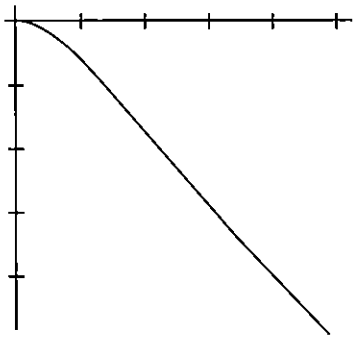


Figure 16.1(b)

The relative populations (with respect to that of the lowest state) are given by the Boltzmann factor

$$\exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-\gamma_N \hbar \mathscr{B}}{kT}\right) \quad \text{or} \quad \exp\left(\frac{-2\gamma_N \hbar \mathscr{B}}{kT}\right)$$

Note that $\dfrac{\gamma_N \hbar \mathscr{B}}{k} = \dfrac{(2.04 \times 10^{-27}\,\mathrm{J\,T^{-1}}) \times (20.0\,\mathrm{T})}{1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}} = 2.95 \times 10^{-3}\,\mathrm{K}$

so the populations are

(a) $\exp\left(\dfrac{-2.95 \times 10^{-3}\,\mathrm{K}}{1.0\,\mathrm{K}}\right) = \boxed{0.99\overline{7}}$ and $\exp\left(\dfrac{2(-2.95 \times 10^{-3}\,\mathrm{K})}{1.0\,\mathrm{K}}\right) = \boxed{0.99\overline{4}}$

(b) $\exp\left(\dfrac{-2.95 \times 10^{-3}\,\mathrm{K}}{298}\right) = \boxed{0.99999}$

and $\exp\left(\dfrac{2(-2.95 \times 10^{-3}\,\mathrm{K})}{298}\right) = \boxed{0.99998}$

E16.8(b) **(a)** The ratio of populations is given by the Boltzmann factor

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = \mathrm{e}^{-25.0\,\mathrm{K}/T} \quad \text{and} \quad \frac{n_3}{n_1} = \mathrm{e}^{-50.0\,\mathrm{K}/T}$$

(1) At 1.00 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\mathrm{K}}{1.00\,\mathrm{K}}\right) = \boxed{1.39 \times 10^{-11}}$$

$$\text{and } \frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\mathrm{K}}{1.00\,\mathrm{K}}\right) = \boxed{1.93 \times 10^{-22}}$$

(2) At 25.0 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\text{K}}{25.0\,\text{K}}\right) = \boxed{0.368} \quad \text{and} \quad \frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\text{K}}{25.0\,\text{K}}\right) = \boxed{0.135}$$

(3) At 100 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\text{K}}{100\,\text{K}}\right) = \boxed{0.779} \quad \text{and} \quad \frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\text{K}}{100\,\text{K}}\right) = \boxed{0.607}$$

(b) The molecular partition function is

$$q = \sum_{\text{states}} \text{e}^{-E_{\text{state}}/kT} = 1 + \text{e}^{-25.0\,\text{K}/T} + \text{e}^{-50.0\,\text{K}/T}$$

At 25.0 K, we note that $\text{e}^{-25.0\,\text{K}/T} = \text{e}^{-1}$ and $\text{e}^{-50.0\,\text{K}/T} = \text{e}^{-2}$

$$q = 1 + \text{e}^{-1} + \text{e}^{-2} = \boxed{1.503}$$

(c) The molar internal energy is

$$U_{\text{m}} = U_{\text{m}}(0) - \frac{N_{\text{A}}}{q}\left(\frac{\partial q}{\partial \beta}\right) \quad \text{where } \beta = (kT)^{-1}$$

So $U_{\text{m}} = U_{\text{m}}(0) - \dfrac{N_{\text{A}}}{q}(-25.0\,\text{K})k\left(\text{e}^{-25.0\,\text{K}/T} + 2\text{e}^{-50.0\,\text{K}/T}\right)$

At 25.0 K

$$U_{\text{m}} - U_{\text{m}}(0) = -\frac{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (-25.0\,\text{K}) \times (1.381 \times 10^{-23}\,\text{J K}^{-1})}{1.503} \times (\text{e}^{-1} + 2\text{e}^{-2})$$

$$= \boxed{88.3\,\text{J mol}^{-1}}$$

(d) The molar heat capacity is

$$C_{V,\text{m}} = \left(\frac{\partial U_{\text{m}}}{\partial T}\right)_V = N_{\text{A}}(25.0\,\text{K})k\frac{\partial}{\partial T}\frac{1}{q}\left(\text{e}^{-25.0\,\text{K}/T} + 2\text{e}^{-50.0\,\text{K}/T}\right)$$

$$= N_{\text{A}}(25.0\,\text{K})k \times \left(\frac{25.0\,\text{K}}{qT^2}\left(\text{e}^{-25.0\,\text{K}/T} + 4\text{e}^{-50.0\,\text{K}/T}\right)\right.$$

$$\left. -\frac{1}{q^2}\left(\text{e}^{-25.0\,\text{K}/T} + 2\text{e}^{-50.0\,\text{K}/T}\right)\frac{\partial q}{\partial T}\right)$$

where $\dfrac{\partial q}{\partial T} = \dfrac{25.0\,\text{K}}{T^2}\left(\text{e}^{-25.0\,\text{K}/T} + 2\text{e}^{-50.0\,\text{K}/T}\right)$

$$\text{so } C_{V,\mathrm{m}} = \frac{N_\mathrm{A}(25.0\,\mathrm{K})^2 k}{T^2 q}\left(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 4\mathrm{e}^{-50.0\,\mathrm{K}/T} - \frac{(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 2\mathrm{e}^{-50.0\,\mathrm{K}/T})^2}{q}\right)$$

At 25.0 K

$$C_{V,\mathrm{m}} = \frac{(6.022 \times 10^{23}\,\mathrm{mol}^{-1}) \times (25.0\,\mathrm{K})^2 \times (1.381 \times 10^{-23}\,\mathrm{J\,K}^{-1})}{(25.0\,\mathrm{K})^2 \times (1.503)} \times \left(\mathrm{e}^{-1} + 4\mathrm{e}^{-2} - \frac{(\mathrm{e}^{-1} + 2\mathrm{e}^{-2})^2}{1.503}\right)$$

$$= \boxed{3.53\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}}$$

(e) The molar entropy is

$$S_\mathrm{m} = \frac{U_\mathrm{m} - U_\mathrm{m}(0)}{T} + N_\mathrm{A} k \ln q$$

At 25.0 K

$$S_\mathrm{m} = \frac{88.3\,\mathrm{J\,mol}^{-1}}{25.0\,\mathrm{K}} + (6.022 \times 10^{23}\,\mathrm{mol}^{-1}) \times (1.381 \times 10^{-23}\,\mathrm{J\,K}^{-1}) \ln 1.503$$

$$= \boxed{6.92\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}}$$

E16.9(b)

$$\frac{n_1}{n_0} = \frac{g_1 \mathrm{e}^{-\varepsilon_1/kT}}{g_0 \mathrm{e}^{-\varepsilon_0/kT}} = g_1 \mathrm{e}^{-\Delta\varepsilon/kT} = 3\mathrm{e}^{-hcB/kT}$$

Set $\frac{n_1}{n_0} = \frac{1}{\mathrm{e}}$ and solve for T.

$$\ln\left(\frac{1}{\mathrm{e}}\right) = \ln 3 + \left(\frac{-hcB}{kT}\right)$$

$$T = \frac{hcB}{k(1 + \ln 3)}$$

$$= \frac{6.626 \times 10^{-34}\,\mathrm{J\,s} \times 2.998 \times 10^{10}\,\mathrm{cm\,s}^{-1} \times 10.593\,\mathrm{cm}^{-1}}{+1.381 \times 10^{-23}\,\mathrm{J\,K}^{-1} \times (1 + 1.0986)}$$

$$= \boxed{7.26\,\mathrm{K}}$$

E16.10(b) The Sackur–Tetrode equation gives the entropy of a monatomic gas as

$$S = nR \ln\left(\frac{\mathrm{e}^{5/2} kT}{p\Lambda^3}\right) \quad \text{where } \Lambda = \frac{h}{\sqrt{2kT\pi m}}$$

(a) At 100 K

$$\Lambda = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{\{2(1.381 \times 10^{-23}\,\mathrm{J\,K}^{-1}) \times (100\,\mathrm{K}) \times \pi(131.3\,\mathrm{u}) \times (1.66054 \times 10^{-27}\,\mathrm{kg\,u}^{-1})\}^{1/2}}$$

$$= 1.52 \times 10^{-11}\,\mathrm{m}$$

$$\text{and } S_m = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \ln\left(\frac{e^{5/2}(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (100\,\text{K})}{(1.013 \times 10^5\,\text{Pa}) \times (1.52 \times 10^{-11}\,\text{m})^3}\right)$$

$$= \boxed{147\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

(b) At 298.15 K

$$\Lambda = \frac{6.626 \times 10^{-34}\,\text{J s}}{\left\{2(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298.15\,\text{K}) \times \pi(131.3\,\text{u}) \times (1.660\,54 \times 10^{-27}\,\text{kg u}^{-1})\right\}^{1/2}}$$

$$= 8.822 \times 10^{-12}\,\text{m}$$

and

$$S_m = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \ln\left(\frac{e^{5/2}(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298.15\,\text{K})}{(1.013 \times 10^5\,\text{Pa}) \times (8.822 \times 10^{-12}\,\text{m})^3}\right)$$

$$= \boxed{169.6\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

E16.11(b) $$q = \frac{1}{1 - e^{-\beta\varepsilon}} = \frac{1}{1 - e^{-hc\beta\tilde{\nu}}}$$

$$hc\beta\tilde{\nu} = \frac{(1.4388\,\text{cm K}) \times (321\,\text{cm}^{-1})}{600\,\text{K}} = 0.769\overline{76}$$

Thus $$q = \frac{1}{1 - e^{-0.769\overline{76}}} = 1.86\overline{3}$$

The internal energy due to vibrational excitation is

$$U - U(0) = \frac{N\varepsilon e^{-\beta\varepsilon}}{1 - e^{-\beta\varepsilon}}$$

$$= \frac{Nhc\nu e^{-hc\tilde{\nu}\beta}}{1 - e^{-hc\tilde{\nu}\beta}} = \frac{Nhc\tilde{\nu}}{e^{hc\tilde{\nu}\beta} - 1} = (0.86\overline{3}) \times (Nhc) \times (321\,\text{cm}^{-1})$$

$$\text{and hence } \frac{S_m}{N_A k} = \frac{U - U(0)}{N_A kT} + \ln q = (0.863) \times \left(\frac{hc}{kT}\right) \times (321\,\text{cm}^{-1}) + \ln(1.86\overline{3})$$

$$= \frac{(0.86\overline{3}) \times (1.4388\,\text{K cm}) \times (321\,\text{cm}^{-1})}{600\,\text{K}} + \ln(1.86\overline{3})$$

$$= 0.66\overline{4} + 0.6219\overline{9} = 1.28\overline{6}$$

$$\text{and } S_m = 1.28\overline{6}R = \boxed{10.7\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

E16.12(b) Inclusion of a factor of $(N!)^{-1}$ is necessary when considering indistinguishable particles. Because of their translational freedom, gases are collections of indistinguishable particles. The factor, then, must be included in calculations on $\boxed{\text{(a) } CO_2 \text{ gas}}$.

Solutions to problems

Solutions to numerical problems

P16.2 Although He is a liquid at these temperatures ($T_b = 4.22\,K$), we will test it as if it were a perfect gas with no interaction potential

$$p_i = \frac{N_i}{N} = g_i e^{-\beta\varepsilon_i}/q \quad [16.6a]$$

$$\varepsilon_i = \frac{h^2}{8mX^2}\{n_x^2 + n_y^2 + n_z^2\} \quad [16.16]; \quad q = \frac{V}{\Lambda^3}; \quad \Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} \quad [16.19]$$

Ground state $n_x = n_y = n_z = 1$; $g = 1$

First excited state

$$\left.\begin{array}{ll} n_x = n_y = 1; & n_z = 2 \\ n_x = n_z = 1; & n_y = 2 \\ n_y = n_z = 1; & n_x = 2 \end{array}\right\} g = 3$$

$$q = \frac{V}{\Lambda^3} = \frac{V}{h^3}(2\pi mkT)^{3/2}$$

$$= \frac{(1\,cm^3) \times \left(\frac{1\,m^3}{10^6\,cm^3}\right) \times [2\pi\,(1.381 \times 10^{-23}\,J\,K^{-1})]^{+3/2} \times (mT)^{+3/2}}{(6.626 \times 10^{-34}\,J\,s)^3}$$

$$= 2.28 \times 10^{60}\,kg^{-3/2}\,K^{-3/2}\,(mT)^{3/2}$$

$$\beta\varepsilon_{1st\,excited} = \left(\frac{1}{kT}\right) \times \left(\frac{h^2}{8mX^2}\right)(6)$$

$$= \frac{6\,(6.626 \times 10^{-34}\,J\,s)^2}{8\,(1.381 \times 10^{-23}\,J\,K^{-1}) \times (0.01\,m)^2}\frac{1}{mT}$$

$$= \frac{2.38 \times 10^{-40}\,kg\,K}{mT}$$

$$p_{1st\,excited} = \frac{3e^{-\left(\frac{2.38 \times 10^{-40}\,kg\,K}{mT}\right)}}{(2.78 \times 10^{60}\,kg^{-3/2}\,K^{-3/2}) \times (mT)^{3/2}}$$

Isotope	m/kg	T/K	$p_{1st\,excited}$	Occupancy $= pN = 10^{22}\,p$
^4He	6.64×10^{-27}	0.0010	6.30×10^{-17}	6.30×10^5
		2.0	7.04×10^{-22}	7
		4.0	2.49×10^{-22}	2
^3He	5.01×10^{-27}	0.0010	9.63×10^{-17}	9.63×10^5
		2.0	1.08×10^{-21}	11
		4.0	3.81×10^{-22}	4

These results may at first seem to contradict the expected common sense result that the populations of excited states increase as the temperature increases, but the energy separations of these states is so small that even a slight increase in temperature promotes the particles to much higher quantum states.

P16.4 $S = k \ln W \quad \text{or} \quad W = e^{S/k}$ [16.34]

$$\left(\frac{\partial W}{\partial V}\right)_{T,N} = \frac{W}{k}\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

$$S = nR \ln \frac{e^{5/2} V}{N\Lambda^3} = nR\left[\ln V + \ln \frac{e^{5/2}}{N\Lambda^3}\right]$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = nR\left(\frac{\partial \ln V}{\partial V}\right)_{T,N} = \frac{nR}{V} = \frac{NR}{N_A V}$$

$$\left(\frac{\partial W}{\partial V}\right)_{T,N} = \frac{NRW}{N_A k V} = \frac{NW}{V}$$

$$\frac{\Delta W}{W} \approx N\frac{\Delta V}{V} = \frac{pV}{kT}\frac{\Delta V}{V}$$

$$\approx \frac{(1 \times 10^5\,\text{Pa}) \times (20\,\text{m}^3) \times (1 \times 10^{-5})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (300\,\text{K})}$$

$$\approx \boxed{4.8 \times 10^{21}}$$

Notice that the value of W is much larger than that of $\Delta W/W$. For example, at the conventional temperature the molar entropy of helium is $126\,\text{J K}^{-1}\,\text{mol}^{-1}$. Therefore,

$$S = nS_\text{m} = \left(\frac{pV}{RT}\right)S_\text{m} = \frac{(1 \times 10^5\,\text{Pa}) \times (20\,\text{m}^3) \times (126\,\text{J K}^{-1}\,\text{mol}^{-1})}{(8.315\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}$$

$$= 1.02 \times 10^5\,\text{J K}^{-1}$$

$$\frac{S}{k} = \frac{1.02 \times 10^5\,\text{J K}^{-1}}{1.381 \times 10^{-23}\,\text{J K}^{-1}} = 7.36 \times 10^{27}$$

$$W = e^{S/k} = e^{7.36 \times 10^{27}} = 10^{3.20 \times 10^{27}}$$

P16.6
$$\frac{n_1}{n_0} = \frac{g_1 e^{-\varepsilon_1/kT}}{g_0 e^{-\varepsilon_0/kT}} = \frac{4}{2} \times e^{-\Delta\varepsilon/kT} = \frac{4}{2} \times e^{-hc\tilde{\nu}/kT} = 2e^{-\{(1.4388 \times 450)/300\}} = 0.23$$

The observed ratio is $0.30/0.70 = 0.43$. Hence the populations are $\boxed{\text{not at equilibrium}}$.

P16.8 First we evaluate the partition function

$$q = \sum_j g_j e^{-\beta\varepsilon_j}\,[16.9] = \sum_j g_j e^{-hc\beta\tilde{\nu}_j}$$

At 3287 °C = 3560 K, $hc\beta = \dfrac{1.438\,77\ \text{cm K}}{3560\ \text{K}} = 4.041 \times 10^{-4}\ \text{cm}$

$$q = 5 + 7\mathrm{e}^{-\{(4.041\times10^{-4}\,\text{cm})\times(170\,\text{cm}^{-1})\}} + 9\mathrm{e}^{-\{(4.041\times10^{-4}\,\text{cm})\times(387\,\text{cm}^{-1})\}} + 3\mathrm{e}^{-\{(4.041\times10^{-4}\,\text{cm})\times(6557\,\text{cm}^{-1})\}}$$
$$= (5) + (7) \times (0.934) + (9) \times (0.855) + (3) \times (0.0707) = 19.445$$

The fractions of molecules in the various states are

$$p_j = \frac{g_j\mathrm{e}^{-\beta\varepsilon_j}}{q}\ [16.7] = \frac{g_j\mathrm{e}^{-hc\beta\tilde{\nu}_j}}{q}$$

$$p(^3\mathrm{F}_2) = \frac{5}{19.445} = \boxed{0.257} \qquad p(^3\mathrm{F}_3) = \frac{(7) \times (0.934)}{19.445} = \boxed{0.336}$$

$$p(^3\mathrm{F}_4) = \frac{(9) \times (0.855)}{19.445} = \boxed{0.396} \qquad p(^4\mathrm{F}_1) = \frac{(3) \times (0.0707)}{19.445} = \boxed{0.011}$$

COMMENT. $\sum_j p_j = 1$. Note that the most highly populated level is not the ground state.

P16.10 The partition function is the sum over states of the Boltzmann factor

$$q = \sum_{\text{states}} \exp\left(-\frac{E}{kT}\right) = \sum_{\text{states}} \exp\left(-\frac{hcG}{kT}\right) = \sum_{\text{levels}} g\exp\left(-\frac{hcG}{kT}\right)$$

where g is the degeneracy. So, at 298 K

$$q = 1 + 3\exp\left(-\frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (557.1\,\text{cm}^{-1})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})}\right) + \cdots$$
$$= \boxed{1.209}$$

At 1000 K

$$q = 1 + 3\exp\left(-\frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (557.1\,\text{cm}^{-1})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (1000\,\text{K})}\right) + \cdots$$
$$= \boxed{3.004}$$

P16.12 **(a)** Total entropy, $S = S_1 + S_2 = (5.69 + 11.63)\,\text{J K}^{-1} = 17.32\,\text{J K}^{-1}$

$$W = \mathrm{e}^{S/k} = \mathrm{e}^{17.32\,\text{J K}^{-1}/1.381\times10^{-23}}\ [16.34]$$
$$= \mathrm{e}^{1.254\times10^{24}} = 10^{5.44\times10^{23}}$$

(b) Total entropy, $S = 2\,\text{mol}\,(9.03\,\text{J K}^{-1}\,\text{mol}^{-1}) = 18.06\,\text{J K}^{-1}$

$$W = \mathrm{e}^{S/k} = \mathrm{e}^{18.06\,\text{J K}^{-1}/1.381\times10^{-23}\,\text{J K}^{-1}}$$
$$= \mathrm{e}^{1.31\times10^{24}} = 10^{5.69\times10^{23}}$$

The final temperature is not the average because the molar heat capacity of graphite increases with temperature. At 298 K. it is $8.54\,\mathrm{J\,K^{-1}\,mol^{-1}}$, whereas at 498 K it is $14.64\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

(c) At constant internal energy and volume the condition for spontaneity is $\boxed{\Delta S_{U,V} > 0}$. Since $\boxed{W_{(b)} > W_{(a)}}$, the process part (b) is $\boxed{\text{spontaneous}}$

Solutions to theoretical problems

P16.14 We draw up the following table

0	ε	2ε	3ε	4ε	5ε	6ε	7ε	8ε	9ε	W
8	0	0	0	0	0	0	0	0	1	9
7	1	0	0	0	0	0	0	1	0	72
7	0	1	0	0	0	0	1	0	0	72
7	0	0	1	0	0	1	0	0	0	72
7	0	0	0	1	1	0	0	0	0	72
6	2	0	0	0	0	0	1	0	0	252
6	0	2	0	0	1	0	0	0	0	252
6	0	0	3	0	0	0	0	0	0	84
6	1	0	0	2	0	0	0	0	0	252
6	1	1	0	0	0	1	0	0	0	504
6	1	0	1	0	1	0	0	0	0	504
6	0	1	1	1	0	0	0	0	0	504
5	3	0	0	0	0	1	0	0	0	504
5	0	3	1	0	0	0	0	0	0	504
5	2	1	0	0	1	0	0	0	0	1512
5	2	0	1	1	0	0	0	0	0	1512
5	1	2	0	1	0	0	0	0	0	1512
5	1	1	2	0	0	0	0	0	0	1512
4	4	0	0	0	1	0	0	0	0	630
4	3	1	0	1	0	0	0	0	0	2520
4	3	0	2	0	0	0	0	0	0	1260
4	2	2	1	0	0	0	0	0	0	3780
3	5	0	0	1	0	0	0	0	0	504
3	4	1	1	0	0	0	0	0	0	2520
2	6	0	1	0	0	0	0	0	0	252
2	5	2	0	0	0	0	0	0	0	756
1	7	1	0	0	0	0	0	0	0	72
0	9	0	0	0	0	0	0	0	0	1

The most probable configuration is the "almost exponential" $\boxed{\{4,2,2,1,0,0,0,0,0,0\}}$

P16.16 (a) $q = \sum_j g_j \mathrm{e}^{-\beta\varepsilon_j} = 1 + 3\mathrm{e}^{-\beta\varepsilon} = \boxed{1 + 3\mathrm{e}^{-\varepsilon/kT}}$

at $T = \dfrac{\varepsilon}{k}$, $q = 1 + 3\mathrm{e}^{-1} = 2.104$

(b) $U_m - U_m(0) = E = -\dfrac{N_A}{q}\dfrac{dq}{d\beta} = \dfrac{N_A}{q}(3\varepsilon e^{-\beta\varepsilon})$

$$= \frac{N_A}{q}(3RTe^{-1}) = \frac{3RT}{2.104\,e} = \boxed{0.5245\,RT}$$

A numerical value cannot be obtained for the energy without specific knowledge of the temperature, but that is not required for the heat capacity or the entropy.

$$C_V = \left(\frac{\partial U_m}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

Since $\dfrac{d}{dT} = \dfrac{d\beta}{dT} \times \dfrac{d}{d\beta} = -\dfrac{1}{kT^2}\dfrac{d}{d\beta} = -k\beta^2\dfrac{d}{d\beta}$

$$C_V = -k\beta^2\left(\frac{\partial E}{\partial \beta}\right)_V = -k\beta^2(3\varepsilon N_A)\frac{\partial}{\partial\beta}\left(\frac{e^{-\beta\varepsilon}}{q}\right)$$

$$= -k\beta^2(3\varepsilon N_A)\frac{\partial}{\partial\beta}\left(\frac{e^{-\beta\varepsilon}}{1+3e^{-\beta\varepsilon}}\right)$$

$$= -k\beta^2(3\varepsilon N_A)\left[\frac{(1+3e^{-\beta\varepsilon}) \times (-\varepsilon)e^{-\beta\varepsilon} - e^{-\beta\varepsilon}(-3\varepsilon e^{-\beta\varepsilon})}{(1+3e^{-\beta\varepsilon})^2}\right]$$

$$= -k\beta^2(3\varepsilon N_A)\left[\frac{-\varepsilon e^{-\beta\varepsilon} - 3\varepsilon e^{-2\beta\varepsilon} + 3\varepsilon e^{-2\beta\varepsilon}}{(1+3e^{-\beta\varepsilon})^2}\right]$$

$$= -k\beta^2(3\varepsilon N_A)\left[\frac{-\varepsilon e^{-\beta\varepsilon}}{(1+3e^{-\beta\varepsilon})^2}\right]$$

$$= \frac{3R\varepsilon^2 e^{-\beta\varepsilon}}{(kT)^2(1+3e^{-\beta\varepsilon})^2}$$

For $\varepsilon = kT$, $C_V = \dfrac{3Re^{-1}}{(1+3e^{-1})^2} = \dfrac{3R}{e\,(1+(3/e))^2} = \boxed{2.074\,J\,K^{-1}\,mol^{-1}}$

Note that taking the derivative of $0.5245\,RT$ with regard to T does not give the correct answer. That is because the temperature dependence of q is not taken into account by that process.

$$\frac{\partial}{\partial T}(0.5245RT) = 0.5245R = 4.361\,J\,K^{-1}\,mol^{-1}$$

and this is not the correct value.

The calculation of S does not require taking another derivative, so we can use $E = 0.5245\,RT$

$$S_m = \frac{E}{T} + R\ln q = 0.5245R + R\ln(2.104) = \boxed{10.55\,J\,K^{-1}\,mol^{-1}}.$$

P16.18 **(a)** The form of Stirling's approximation used in the text in the derivation of the Boltzmann distribution is

$$\ln x! = x\ln x - x\ [16.2] \quad \text{or} \quad \ln N! = N\ln N - N$$

and $\ln n_i! = n_i \ln n_i - n_i$ which then leads to [$N$is cancelled by $-\sum_i n_i$]

$$\ln W = N \ln N - \sum_i n_i \ln n_i \quad [16.3]$$

If $N! = N^N$, $\ln N! = N \ln N$, likewise $\ln n_i! = n_i \ln n_i$ and eqn 3 is again obtained.

(b) For $\ln x! = (x + \frac{1}{2}) \ln x - x + \frac{1}{2} \ln 2\pi$ [Comment 16.2],
Since the method of undetermined multipliers requires only (*Further Information* 16.1) dln W, only the terms dln $n_i!$ survive. The constant term, $\frac{1}{2} \ln 2\pi$, drops out, as do all terms d in N. The difference, then, is in terms arising from ln $n_i!$ We need to compare $n_i \ln n_i$ to $\frac{1}{2} \ln n_i$, as both these terms survive the differentiation. The derivatives are

$$\frac{\partial}{\partial n_i}(n_i \ln n_i) = 1 + \ln n_i \approx \ln n_i [\text{large } n_i]$$

$$\frac{\partial}{\partial n_i}\left(\frac{1}{2} \ln n_i\right) = \frac{1}{2n_i}$$

Whereas ln n_i increases as n_i increases, $1/2n_i$ decreases and in the limit becomes negligible. For $n_i = 1 \times 10^6$, $\ln n_i = 13.8$, $1/2n_i = 5 \times 10^{-7}$; the ratio is about 2×10^8 which could probably not be seen in experiments. However, for experiments on, say, 1000 molecules, such as molecular dynamics simulations, there could be a measurable difference.

Solutions to applications

P16.20

$$\frac{p(h)}{p(h_0)} = \frac{N(h)/V}{N(h_0)/V} = e^{-\{(\varepsilon(h) - \varepsilon(h_0))/kT\}} \quad [16.6a]$$

$$= e^{-mg(h-h_0)/kT}$$

For $p(0) \equiv p_0$,

$$\boxed{\frac{p(h)}{p_0} = e^{-mgh/kt}}$$

$$\frac{N(8.0\,\text{km})}{N(0)} = \frac{N(8.0\,\text{km})/V}{N(0)/V} = e^{\frac{-M(O_2)gh}{RT}}$$

$$\frac{N(8.0\,\text{km})}{N(0)}[O_2] = e^{-\left\{\frac{(0.032\,\text{kg mol}^{-1}) \times (9.81\,\text{m s}^{-2}) \times (8.0 \times 10^3\,\text{m})}{(8.315\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}\right\}}$$

$$= \boxed{0.36} \text{ for } O_2$$

$$\frac{N(8.0\,\text{km})}{N(0)}[H_2O] = e^{-\left\{\frac{(0.018\,\text{kg mol}^{-1}) \times (9.81\,\text{m s}^{-2}) \times (8.0 \times 10^3\,\text{m})}{(8.315\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}\right\}}$$

$$= \boxed{0.57} \text{ for } H_2O$$

P16.22 (a) The electronic partition function, q_E, of a perfect, atomic hydrogen gas consists of the electronic energies E_n that can be written in the form:

$$E_n = \left(1 - \frac{1}{n^2}\right) hcR_H, \quad n = 1, 2, 3, \ldots, \infty,$$

where we have used the state $n = 1$ as the zero of energy (in contrast to the usual zero being at infinite separation of the proton and electron, eqn 10.11). The degeneracy of each level is $g_n = 2n^2$ where the n^2 factor is the orbital degeneracy of each shell and the factor of 2 accounts for spin degeneracy.

$$q_E = \sum_{n=1}^{\infty} g_n \, e^{-E_n/kT} = 2\sum_{n=1}^{\infty} n^2 e^{-\left(1-\frac{1}{n^2}\right)C},$$

where $C = hcR_H/kT_{\text{photosphere}} = 27.301$. q_E, when written as an infinite sum, is infinitely large because $\lim_{n\to\infty}\{n^2 e^{-(1-(1/n^2))C}\} = \lim_{n\to\infty}\{n^2 e^{-C}\} = e^{-C}\lim_{n\to\infty}(n^2) = \infty$. The inclusion of partition function terms corresponding to large n values is clearly an error.

(b) States corresponding to large n values have very large average radii and most certainly interact with other atoms, thereby, blurring the distinct energy level of the state. Blurring interaction most likely occurs during the collision between an atom in state n and an atom in the ground state $n = 1$. Collisional lifetime broadening (eqn 13.18) is given by:

$$\delta E_n = \frac{h}{2\pi\tau} = \frac{z_n h}{2\pi},$$

where z_n = collisional frequency of nth state of atomic perfect gas

$$= \frac{\sqrt{2}\sigma_n \bar{c} p}{kT} = \frac{\sqrt{2}\sigma_n \bar{c} \rho N_A}{M_H} \quad [21.11(b)]$$

$\bar{c}$ = mean speed $= \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = 1.106 \times 10^4 \, \text{ms}^{-1}$ [21.7]

σ_n = collisional cross-section of *nth* state (Figure 21.9)

$$= \pi((r)_n + a_0)^2$$

$$= \pi a_0^2 \left(\frac{3n^2 + 2}{2}\right)^2 \text{ (Example 10.2)}$$

Any quantum state within δE of the continuum of an isolated atom will have its energy blurred by collisions so as to be indistinguishable from the continuum. Only states having energies in the range $0 \leq E < E_\infty - \delta E$ will be a distinct atomic quantum state.

The maximum term, $n_{\max}$, that should be retained in the partition function of a hydrogen atom is given by

$$E_{n_{\max}} = E_\infty - \delta E_{n_{\max}}$$

$$\left(1 - \frac{1}{n_{\max}^2}\right) hcR_H = hcR_H - \frac{\sqrt{2}\pi a_0^2 \left(\frac{3n_{\max}^2 + 2}{2}\right)^2 \bar{c}\rho^{N_A h}}{2\pi M_H}$$

with $\rho = 1.99 \times 10^{-4} \, \text{kg m}^{-3}$ and $M_H = 0.001 \, \text{kg mol}^{-1}$.

The root function of a calculator or mathematical software may be used to solve this equation for n_{max}:

$\boxed{n_{max} = 28}$ for atomic hydrogen of the photosphere

Furthermore, examination of the partition function terms $n = 2, 3, \ldots, n_{max}$ indicates that they are negligibly small and may be discarded. The point is that very large n values should not be included in q_E because they do not reflect reality.

$$\rho_n = \frac{2n^2 e^{-E_n/kT}}{q_E} \quad \text{where} \quad T = 5780\,\text{K [eqn 16.6]}$$

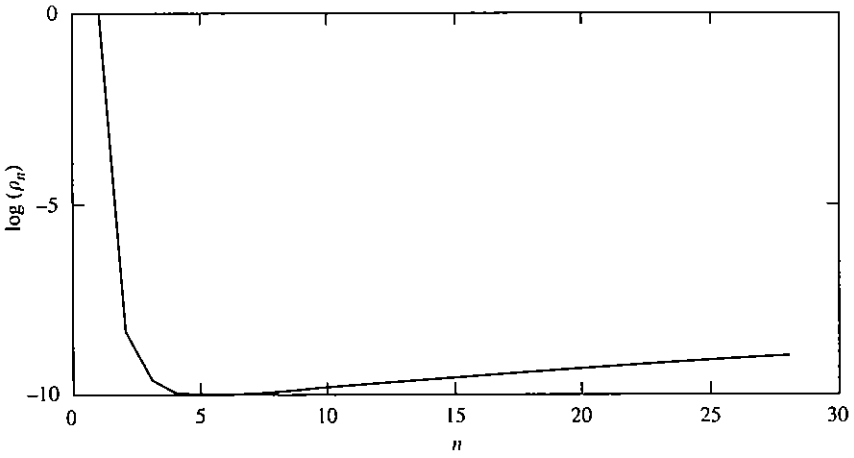


Figure 16.2

Even at the high temperature of the Sun's photosphere only the ground electronic state is significantly populated. This leads us to expect that at more ordinary temperatures only the ground state of atom and molecules are populated at equilibrium. It would be a mistake to thoughtlessly apply equilibrium populations to a study of the Sun's photosphere, however. It is bombarded with extremely high energy radiation from the direction of the Sun's core while radiating at a much lower energy. The photosphere may show significant deviations from equilibrium.

See S. J. Strickler, *J. Chem. Ed.*, *43*, 364 (1966).

P16.24 (a) $$q = 1 + \sum_{i=1}^{n} N_i K_i$$

But, $K_1 = \sigma e^{-\Delta G/RT} = \sigma s$

$K_2 = K_1 s = \sigma s^2$

$K_3 = K_1 s^2 = \sigma s^3$

$\vdots$

$K_i = K_1 s^{i-1} = \sigma s^i$

Therefore,

$$q = 1 + \sum_{i=1}^{n} N_i \sigma s^i$$

To show that $N_i = n - i + 1$ consider the following figure of n positions having an "X" label.

1	2	3	...	y_L					
X	X	X	...	X	...	X	...	X	X
						y_R	...	$n-1$	n

Starting from the left, there are a total of y_L groups of i positions where y_L is limited because an additional group of i would extend beyond the nth position. There are more groups of i. We may start from the right and count off groups of i until reaching position y_R where y_R is limited because an additional group of i would be identical to the group starting at y_L. In fact, $y_R = n - y_L + (i-1)\}$. Consequently,

$$N_i = y_L + y_R = y_L + n - \{y_L + (i-1)\} = n - i + 1$$

(b) $$q = 1 + \sum_{i=1}^{n} N_i \sigma s^i$$

$$\frac{dq}{ds} = \sum_{i=1}^{n} i N_i \sigma s^{i-1} = s^{-1} \sum_{i=1}^{n} i N_i \sigma s^i$$

and $$\sum_{i=1}^{n} i N_i \sigma s^i = \frac{dq}{ds}$$

We may substitute the above expression into the equation for the degree of conversion, θ, that is given in the box.

$$\theta = \left(\frac{1}{nq}\right) \sum_{i=1}^{n} i\, N_i \sigma s^i = \frac{s}{nq} \frac{dq}{ds}$$

Since $dq/q = d(\ln q)$ and $ds/s = d(\ln s)$, the expression becomes

$$\theta = \left(\frac{1}{n}\right) \frac{d(\ln\, q)}{d(\ln\, s)}$$