Chapter 8

An introduction to molecular structure

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Exercises

8.1 Substitution of the trial wavefunction $\psi\psi_N$ into eqn 8.2, and using eqn 8.1b, yields

$$(T_e + T_N + V)\psi\psi_N = E\psi\psi_N$$

Since the nuclear wavefunction does not depend on electronic coordinates whereas the electronic wavefunction depends (parametrically) on nuclear coordinates, we can write

$$(\psi_N T_e \psi + T_N \psi\psi_N + V\psi\psi_N) = E\psi\psi_N$$

Consider the term $T_N \psi\psi_N$.

$$
\begin{aligned}
T_N \psi\psi_N &= -\sum_{I=1}^{2} \frac{\hbar^2}{2m_I} \frac{\partial}{\partial Z_I} \frac{\partial}{\partial Z_I} \psi\psi_N = -\sum_{I=1}^{2} \frac{\hbar^2}{2m_I} \frac{\partial}{\partial Z_I} \psi \frac{\partial \psi_N}{\partial Z_I} - \sum_{I=1}^{2} \frac{\hbar^2}{2m_I} \frac{\partial}{\partial Z_I} \psi_N \frac{\partial \psi}{\partial Z_I} \\
&= -2\sum_{I=1}^{2} \frac{\hbar^2}{2m_I} \frac{\partial \psi}{\partial Z_I} \frac{\partial \psi_N}{\partial Z_I} - \sum_{I=1}^{2} \frac{\hbar^2}{2m_I} \psi \frac{\partial^2 \psi_N}{\partial Z_I^2} - \sum_{I=1}^{2} \frac{\hbar^2}{2m_I} \psi_N \frac{\partial^2 \psi}{\partial Z_I^2} \\
&= W + \psi T_N \psi_N
\end{aligned}
$$

where we have used the definition of W in the equation following eqn 8.4. We therefore obtain

$$(\psi_N T_e \psi + W + \psi T_N \psi_N + V\psi\psi_N) = E\psi\psi_N$$

which is eqn 8.4.

8.2 The Schrödinger equation for the total wavefunction Ψ of the hydrogen molecule-ion is

$$-\frac{\hbar^2}{2m_e}\nabla_e^2\Psi - \sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\nabla_I^2\Psi + V\Psi = E\Psi$$

where the laplacian in the first (second) term is with respect to electronic (nuclear) coordinates and the potential energy V is given by

$$V = \frac{e^2}{4\pi\varepsilon_0|R_1 - R_2|} - \sum_{I=1}^{2}\frac{e^2}{4\pi\varepsilon_0|r_e - R_I|}$$

The Schrödinger equation for the electronic wavefunction ψ, within the Born-Oppenheimer approximation, is

$$-\frac{\hbar^2}{2m_e}\nabla_e^2\psi + V\psi = E_e\psi$$

and that for the nuclear wavefunction ψ_N is

$$-\sum_{I=1}^{2}\frac{\hbar^2}{2m_I}\nabla_I^2\psi_N + E_e\psi_N = E\psi_N$$

8.3 The secular determinant is given in Section 8.3(a), immediately preceding eqn 8.16.

Expanding the determinant yields

$$(\alpha - E)(\alpha - E) - (\beta - ES)(\beta - ES) = 0$$

Therefore

$$(\alpha - E)^2 = (\beta - ES)^2$$

with roots

$$\alpha - E = \beta - ES \quad \Rightarrow \quad E_- = \frac{\alpha - \beta}{(1 - S)}$$

$$\alpha - E = -(\beta - ES) \quad \Rightarrow \quad E_+ = \frac{\alpha + \beta}{(1 + S)}$$

To find the coefficients c_A and c_B, we use eqn 8.14. For energy E_-,

$$c_A(\alpha - E_-) + c_B(\beta - E_- S) = 0$$

$$c_A\left(\frac{\alpha - \alpha S}{(1 - S)} - \frac{\alpha - \beta}{(1 - S)}\right) + c_B\left(\frac{\beta - \beta S}{(1 - S)} - \frac{\alpha S - \beta S}{(1 - S)}\right) = 0$$

$$c_A(\beta - \alpha S) + c_B(\beta - \alpha S) = 0$$

$$c_A = -c_B$$

and requiring that the wavefunction $c_A(\chi_A - \chi_B)$ be normalized yields:

$$\int c_A^2(\chi_A^2 - 2\chi_A\chi_B + \chi_B^2)d\tau = 1$$

$$c_A^2(1 - 2S + 1) = 1$$

$$c_A = \frac{1}{\sqrt{2(1 - S)}}$$

Similarly for energy E_+,

$$c_A(\alpha - E_+) + c_B(\beta - E_+ S) = 0$$

$$c_A\left(\frac{\alpha + \alpha S}{(1 + S)} - \frac{\alpha + \beta}{(1 + S)}\right) + c_B\left(\frac{\beta + \beta S}{(1 + S)} - \frac{\alpha S + \beta S}{(1 + S)}\right) = 0$$

$$c_A(\alpha S - \beta) + c_B(\beta - \alpha S) = 0$$

$$c_A = c_B$$

and requiring that the wavefunction $c_A(\chi_A + \chi_B)$ be normalized yields:

$$\int c_A^2(\chi_A^2 + 2\chi_A\chi_B + \chi_B^2)d\tau = 1$$

$$c_A^2(1 + 2S + 1) = 1$$

$$c_A = \frac{1}{\sqrt{2(1+S)}}$$

8.4   First, since each electron is in a σ-orbital, $\lambda_1 = \lambda_2 = 0$, so $\Lambda = 0$, corresponding to a Σ term.

Second, with regard to the overall parity of the state, since g × u = u, the term must be u parity.

Third, if the two electrons have opposite spins, the term has $S = 0$ and is a singlet (multiplicity of 1); if the two electrons have the same spins, the term has $S = 0$ and is

a triplet (multiplicity of 3).

Finally, each σ-orbital has a character of +1 under reflection in a plane that contains the internuclear axis and since (+1) × (+1) = +1, the term includes a right superscript of +.

As a result, the terms that arise are $^1\Sigma_u^+$ and $^3\Sigma_u^+$.

8.5

$$\Psi\left(1,2; {}^1\Sigma_u^+\right) = \left(\tfrac{1}{2}\right)^{1/2}\left\{\psi_+(1)\psi_-(2)+\psi_+(2)\psi_-(1)\right\}\sigma_-(1,2)$$
$$\Psi\left(1,2; {}^3\Sigma_u^+\right) = \left(\tfrac{1}{2}\right)^{1/2}\left\{\psi_+(1)\psi_-(2)-\psi_+(2)\psi_-(1)\right\}\sigma_+(1,2)$$

where ψ_+ and ψ_- are defined in eqns 8.24(a) and 8.24(b) and the spin states σ_- and σ_+

are defined in Section 7.11. Note that there are three possible σ_+ states corresponding to

values of M_S of +1, 0 or −1.

8.6 The question refers to the orbital part of $c_1\Psi_1 + c_3\Psi_3$ which we denote ψ. Noting, and

therefore ignoring, the spin factors that are common to Ψ_1 and Ψ_3, we obtain, denoting

$a = \chi_A, b = \chi_B$, and $1\sigma = (a+b)/\sqrt{2}, 2\sigma = (a-b)/\sqrt{2}]$

$$\psi = c_1 1\sigma(1)1\sigma(2) + c_3 2\sigma(1)2\sigma(2)$$

$$= \tfrac{1}{2}c_1\{a(1)+b(1)\}\{a(2)+b(2)\} + \tfrac{1}{2}c_3\{a(1)-b(1)\}\{a(2)-b(2)\}$$

$$= \tfrac{1}{2}c_1\{a(1)a(2) + b(1)b(2) + a(1)b(2) + b(1)a(2)\}$$

$$+ \tfrac{1}{2}c_3\{a(1)a(2) + b(1)b(2) - a(1)b(2) - b(1)a(2)\}$$

$$= \tfrac{1}{2}(c_1 + c_3)\{a(1)a(2) + b(1)b(2)\} + \tfrac{1}{2}(c_1 - c_3)\{a(1)b(2) + b(1)a(2)\}$$

as in eqn 8.30.

8.7   Expansion of the secular determinant in eqn 8.32 and setting the overlap S to zero

yields

$$(\alpha_A - E)(\alpha_B - E) - \beta^2 = 0$$

which produces the following quadratic energy for the energy:

$$E^2 + E(-\alpha_A - \alpha_B) + (\alpha_A\alpha_B - \beta^2) = 0$$

The roots to the above equation are

$$E = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\sqrt{(\alpha_A + \alpha_B)^2 - 4(\alpha_A\alpha_B - \beta^2)}$$

$$= \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2}$$

$$= \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\sqrt{(\alpha_A - \alpha_B)^2\left\{1 + \frac{4\beta^2}{(\alpha_A - \alpha_B)^2}\right\}}$$

$$= \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}|\alpha_A - \alpha_B|\sqrt{1 + 4\beta^2/(\alpha_A - \alpha_B)^2}$$

When the two orbitals have greatly differing energies, $|\alpha_A - \alpha_B| \gg \beta$, and using the

approximation $(1 + x)^{1/2} = 1 + \tfrac{1}{2}x$, we obtain

$$E = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}|\alpha_A - \alpha_B|\left\{1 + \frac{2\beta^2}{(\alpha_A - \alpha_B)^2}\right\}$$

$$= \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}|\alpha_A - \alpha_B| \pm \frac{\beta^2}{|\alpha_A - \alpha_B|}$$

With α_B greater than α_A, we have the roots

$$E_+ = \alpha_B + \frac{\beta^2}{|\alpha_A - \alpha_B|}$$

$$E_- = \alpha_A - \frac{\beta^2}{|\alpha_A - \alpha_B|}$$

as in eqn 8.33.

8.8 Refer to Fig. 8.18 of the text.

(a) $C_2 : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4, {}^1\Sigma_g^+$

(b) $C_2^+ : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^3, {}^2\Pi_u$

(c) $C_2^- : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^1, {}^2\Sigma_g^+$

(d) $N_2^+ : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^1, {}^2\Sigma_g^+$

(e) $N_2^- : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2 1\pi_g^{*1}, {}^2\Pi_g$

(f) $F_2^+ : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2 1\pi_g^{*3}, {}^2\Pi_g$

(g) $Ne_2^+ : 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2 1\pi_g^{*4} 2\sigma_u^{*1}, {}^2\Sigma_u^+$

where the superscript * indicates an antibonding molecular orbital.

Exercise: Predict the ground configurations of Na_2, S_2 and HCl and decide which terms lie lowest.

8.9 We use the results of Exercise 8.8; only the molecular orbitals formed from the $n = 2$ atomic orbitals need be considered since the lower energy molecular orbitals (from $n = 1$ atomic orbitals) are completely filled and thus have equal number of bonding and antibonding electrons. In Exercise 8.8, the antibonding molecular orbitals are designated with a * superscript.

(a) C_2: bond order = $\frac{1}{2}(6 - 2) = 2$ HOMO = $1\pi_u$; LUMO = $2\sigma_g$

(b) C_2^+: bond order $= \frac{1}{2}(5 - 2) = 1.5$ $HOMO = 1\pi_u$; $LUMO = 2\sigma_g$

(c) C_2^-: bond order $= \frac{1}{2}(7 - 2) = 2.5$ $HOMO = 2\sigma_g$; $LUMO = 1\pi_g$

(d) N_2^+: bond order $= \frac{1}{2}(7 - 2) = 2.5$ $HOMO = 2\sigma_g$; $LUMO = 1\pi_g$

(e) N_2^-: bond order $= \frac{1}{2}(8 - 3) = 2.5$ $HOMO = 1\pi_g$; $LUMO = 2\sigma_u$

(f) F_2^+: bond order $= \frac{1}{2}(8 - 5) = 1.5$ $HOMO = 1\pi_g$; $LUMO = 2\sigma_u$

(g) Ne_2^+: bond order $= \frac{1}{2}(8 - 7) = 0.5$ $HOMO = 2\sigma_u$; $LUMO = 3\sigma_g$

Exercise: Find the bond orders of the dications C_2^{2+} and F_2^{2+} as well as the dianions C_2^{2-} and F_2^{2-}.

8.10   The secular determinant for the cyclopropenyl radical is

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

Expanding the determinant results in the following cubic equation:

$$(\alpha - E)^3 - 3(\alpha - E)\beta^2 + 2\beta^3 = 0$$

which, with $x = \alpha - E$, can be written as

$$x^3 - 3\beta^2 x + 2\beta^3 = 0$$

$$(x - \beta)^2(x + 2\beta) = 0$$

Therefore, roots are $x = \beta, \beta, -2\beta$. The energy levels are $E = \alpha - \beta, \alpha - \beta, \alpha + 2\beta$. The total π-electron energy is $2(\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta$ and the delocalization energy is

$$E_{deloc} = 3\alpha + 3\beta - 3(\alpha + \beta) = 0$$

and the radical is not predicted to be stable.

8.11 The Hückel molecular orbital energy level diagram for benzene is shown in Fig. 8.30 of

the text. Whereas benzene has six π-electrons, its cation has five and its dianion has

eight. To compute the delocalization energy, recall that each π-electron in an

unconjugated system contributes an energy of $\alpha + \beta$.

(a) The benzene cation has a ground-state electron configuration

$a_{2u}^2 e_{1g}^3$ and a total π-electron energy of $2(\alpha + 2\beta) + 3(\alpha + \beta) = 5\alpha + 7\beta$. Therefore the

delocalization energy is

$$5\alpha + 7\beta - 5(\alpha + \beta) = \underline{2\beta}$$

(b) The benzene dianion has a ground-state electron configuration

$a_{2u}^2 e_{1g}^4 e_{2u}^2$ and a total π-electron energy of $2(\alpha + 2\beta) + 4(\alpha + \beta) + 2(\alpha - \beta) = 8\alpha + 6\beta$.

Therefore the delocalization energy is

$$8\alpha + 6\beta - 8(\alpha + \beta) = \underline{-2\beta}$$

and the dianion is predicted to be unstable.

Exercise: Repeat the problem for $C_4H_4^+$ and $C_4H_4^{2-}$.

8.12

Complex	Number unpaired electrons	S_{TOT}	Multiplicity
d^4	2	1	3
d^5	1	½	2
d^6	0	0	1
d^7	1	½	2

8.13

Complex	Number unpaired electrons	S_{TOT}	Multiplicity
d^4	4	2	5
d^5	5	5/2	6

8.14 (a) In a tetrahedral environment (symmetry group T_d), the d-orbitals span $E(d_{z^2}, d_{x^2-y^2})$

and $T_2(d_{xy}, d_{xz}, d_{yz})$. [Refer to the T_d character table; $d_{xy} \propto xy$ etc.]

Exercise: Determine which symmetry species are spanned by the f-orbitals in a

tetrahedral complex.

(b) See Problem 5.16(b) in Chapter 5. The symmetry species spanned by f-orbitals in

the rotational subgroup T are A + 2T.

8.15 From Section 8.11, we have the following two equations:

(a) $u_k(x) = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x}$

(b) $u_k(x) = Ce^{(\beta-ik)x} + De^{-(\beta+ik)x}$

Differentiation of the above equatioins produces

(a) $u_k'(x) = iA(\alpha - k)e^{i(\alpha-k)x} - iB(\alpha + k)e^{-i(\alpha+k)x}$

(b) $u_k'(x) = C(\beta - ik)e^{(\beta-ik)x} - D(\beta + ik)e^{-(\beta+ik)x}$

The conditions $u_k(a) = u_k(-b)$ and $u_k'(a) = u_k'(-b)$ then lead to the four statements in

Section 8.11 of the text, and hence to the determinant in eqn 8.44. For the equivalence

to eqn 8.45, use symbolic algebra software.

Problems

8.1

$$j'/j_0 = (1/R)\{1 - (1 + s)e^{-2s}\}, \quad s = R/a_0, \ j_0 = e^2/4\pi\varepsilon_0$$

$$k'/j_0 = (1/a_0)\{1 + s\}e^{-s}, \quad S = \{1 + s + \tfrac{1}{3}s^2\}e^{-s}$$

$$E_+ - E_{1s} = j_0/R - (j' + k')/(1 + S) \quad \text{[eqn 8.23a]}$$

$$E_- - E_{1s} = j_0/R + (j' - k')/(1 - S) \quad \text{[eqn 8.23b]}$$

$$(E_+ - E_{1s})/j_0 = (1/R) - \left\{ \frac{(1/R)[1 - (1+s)e^{-2s}] + (1/a_0)[1+s]e^{-s}}{1 + [1 + s + \frac{1}{3}s^2]e^{-s}} \right\}$$

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

$$(E_+ - E_{1s})(a_0/j_0) = \left\{ \frac{(1 - \frac{2}{3}s^2) + (1+s)e^{-s}}{1 + (1 + s + \frac{1}{3}s^2)e^{-s}} \right\} \left(\frac{e^{-s}}{s} \right)$$

$$(E_- - E_{1s})(a_0/j_0) = \left\{ \frac{2 - [(1 - 2s - \frac{4}{3}s^2) + (1+s)e^{-s}]e^{-s}}{1 - (1 + s + \frac{1}{3}s^2)e^{-s}} \right\} \left(\frac{1}{s} \right)$$

$$(\alpha - E_{1s})(a_0/j_0) = [-j' + (j_0/R)](a_0/j_0) \quad \text{[eqn 8.20]}$$

$$= (1 + s)(e^{-2s}/s)$$

$$(\beta - E_{1s}S)(a_0/j_0) = [-k' + (j_0S/R)](a_0/j_0) \quad \text{[eqn 8.21a]}$$

$$= (1 - \frac{2}{3}s^2)(e^{-s}/s)$$

The $E_\pm - E_{1s}$ values are plotted in Fig. 8.1; the α and β integrals are plotted in Fig. 8.2. The E_+ curve has a minimum (the equilibrium bond length) at $R \approx 130$ pm ($s \approx 2.5$) corresponding to $E_+ - E_{1s} = -1.22 \times 10^{-3} j_0$ pm^{-1}. Because $j_0 = 2.31 \times 10^{-28}$ J m, we have

$$\underline{E_+ - E_{1s} = -2.81 \times 10^{-19} \text{ J } (1.76 \text{ eV}, 170 \text{ kJ mol}^{-1})}$$

Therefore the dissociation energy (neglecting the zero-point vibrational energy) is 170 kJ mol^{-1}.
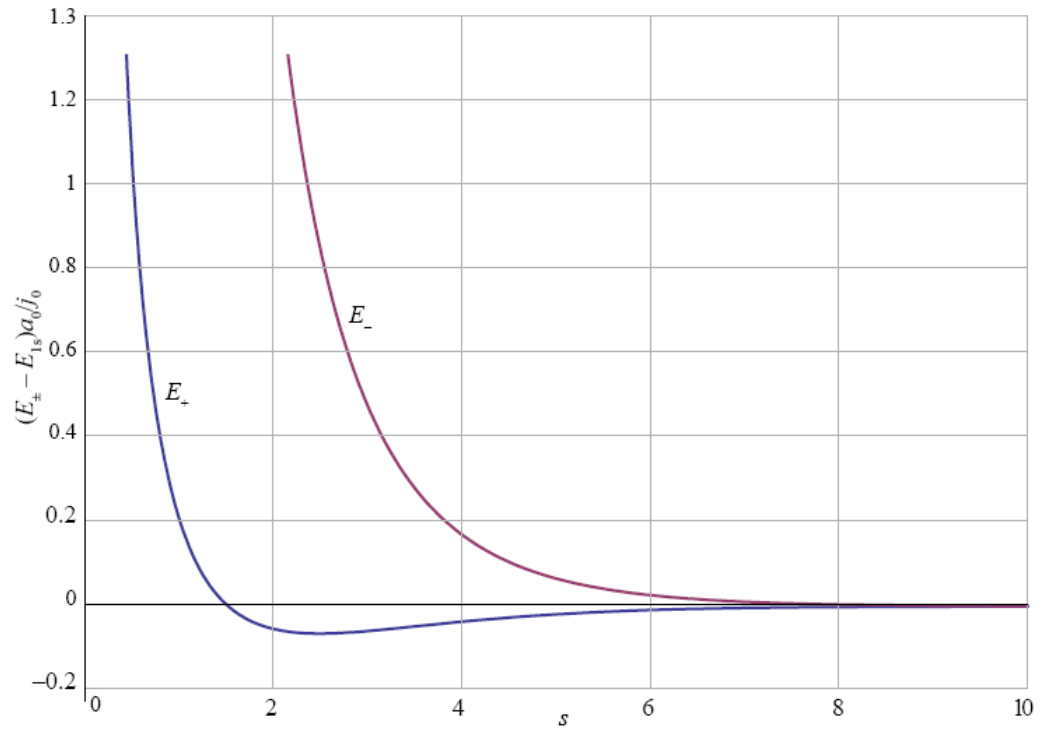
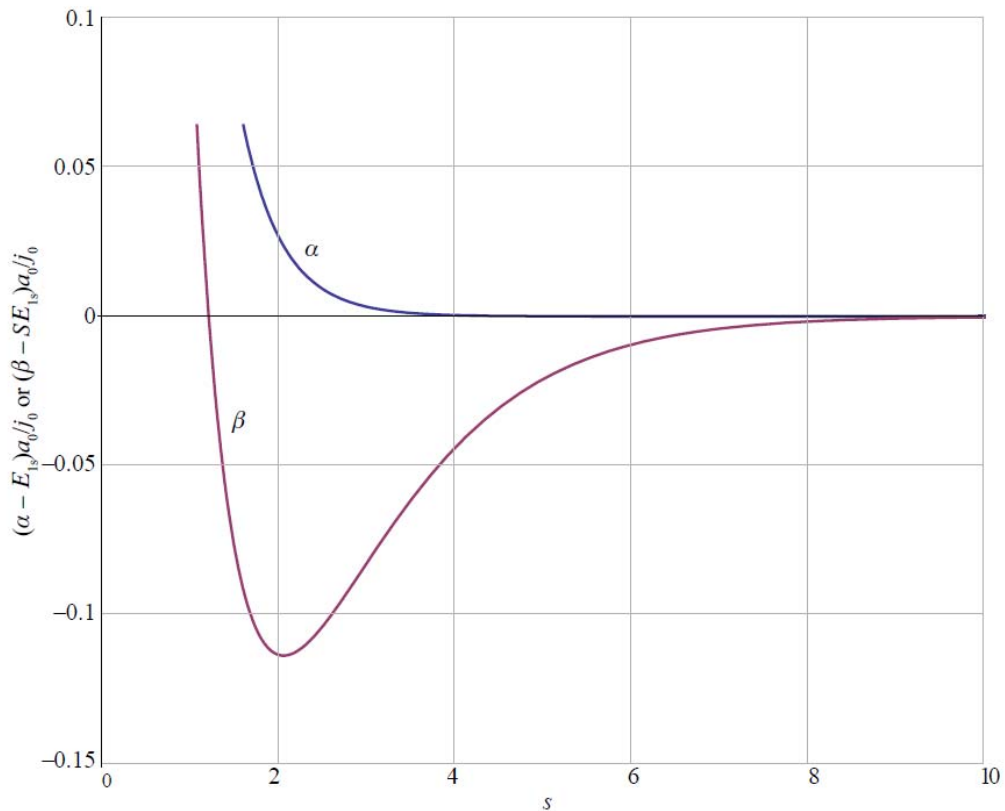Figure 8.1: The values of $E_\pm - E_{1s}$ calculated in Problem 8.1.

Figure 8.2: The dependence of the integrals α and β with distance ($s = R/a_0$).

Exercise: Plot the molecular potential energy curves for He_2^{3+} and estimate its bond length and dissociation energy if you find it to be stable. $[s \to ZR/a_0]$

8.4

$$k_f = (d^2E/dR^2)_0 = (1/a_0^2)(d^2E/dx^2)_0 \quad [x = R/a_0]$$

The 0 indicates the minimum of the curve, which occurs at close to $x = 2.5$ [Section 8.3, Fig. 8.12 of the text].

$$E = E_{1s} + j_0/xa_0 - \left(\frac{j' + \dot{k}'}{1 + S}\right) \quad \text{[eqn 8.23a]}$$

$$= E_{1s} + j_0/xa_0 - \frac{(j_0/xa_0)\{1-(1+x)e^{-2x}\}+(j_0/a_0)(1+x)e^{-x}}{1+(1+x+\frac{1}{3}x^2)e^{-x}}$$

$$= E_{1s} + \frac{j_0}{a_0}\left\{\frac{1}{x} - \frac{(1/x)\{1-(1+x)e^{-2x}\}+(1+x)e^{-x}}{1+(1+x+\frac{1}{3}x^2)e^{-x}}\right\}$$

$$k_f = \left(\frac{j_0}{a_0^3}\right)\frac{d^2}{dx^2}\{\ldots\} \text{ evaluated at } x = 2.5$$

$$= 0.061\,884 j_0/a_0^3 \quad \text{[mathematical software second derivative evaluator]}$$

The vibrational frequency is therefore

$$\omega = \left(\frac{2k_f}{m_H}\right)^{1/2} = \left(\frac{0.061\,884e^2}{2\pi\varepsilon_0 m_H a_0^3}\right)^{1/2}$$

$$= \left(\frac{2\times 0.061\,884\hbar^2}{m_e m_H a_0^4}\right)^{1/2} [a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2] = \frac{0.35181\hbar}{(m_e m_H)^{1/2}a_0^2}$$

$$= \underline{3.41 \times 10^{14} \text{ s}^{-1}}\ (\nu = 54.3 \text{ THz})$$

8.7 The Hamiltonian for the hydrogen molecule is given in eqn 8.25a and can be written as

$$H = \Omega_0 + \Omega_1 + \Omega_2$$

where

$$\Omega_0 = \frac{j_0}{R}$$

$$\Omega_1 = \Omega_1(1) + \Omega_1(2),\ \ \Omega_1(i) = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{j_0}{r_{Ai}} - \frac{j_0}{r_{Bi}}$$

$$\Omega_2 = \frac{j_0}{r_{12}}$$

The ground-state energy is given by $< \Psi(1,2)\,|\,H\,|\,\Psi(1,2) >$ where Ψ is the two-electron

Slater determinant (eqn 7.42a) composed of the spinorbitals

$$\varphi_1(i) = N\{A(i) + B(i)\}\alpha(i)$$

$$\varphi_2(i) = N\{A(i) + B(i)\}\beta(i)$$

where (see eqn 8.24a) $A(i) = \chi_A(i)$, $B(i) = \chi_B(i)$, $N = \{2(1 + S)\}^{-1/2}$, and $S = <A \mid B>$.

The Slater-Condon rules appear in eqns 7.44 and 7.45.

$$\langle\Psi|H|\Psi\rangle = \Omega_0 + \sum_i \langle\varphi_i(1)|\Omega_1(1)|\varphi_i(1)\rangle$$
$$+ \frac{1}{2}\sum_{i \neq j}\{\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_i(1)\varphi_j(2)\rangle - \langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_j(1)\varphi_i(2)\rangle\}$$

where the first term (Ω_0) results because Ψ is normalized and independent of R. The second term develops as follows since the spin states α and β are normalized:

$$\sum_i \langle\varphi_i(1)|\Omega_1(1)|\varphi_i(1)\rangle = 2\langle\varphi_1(1)|\Omega_1(1)|\varphi_1(1)\rangle$$
$$= 2N^2\langle A(1) + B(1)|\Omega_1(1)|A(1) + B(1)\rangle$$
$$= 2N^2\{2\langle A(1)|\Omega_1(1)|A(1)\rangle + 2\langle A(1)|\Omega_1(1)|B(1)\rangle\} \text{ (by symmetry)}$$

$$= 4N^2\left\{E_{1s} - j_0\left\langle A(1)\left|\frac{1}{r_{B1}}\right|A(1)\right\rangle - j_0\left\langle A(1)\left|\frac{1}{r_{A1}}\right|B(1)\right\rangle + E_{1s}\langle A(1)|B(1)\rangle\right\}$$

$$= 4N^2 E_{1s}(1 + S) - 4N^2(j' + k') = 2E_{1s} - 2(j' + k')/(1 + S)$$

Similarly, the third term develops as follows:

$$\frac{1}{2}\sum_{i \neq j}\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_i(1)\varphi_j(2)\rangle = \langle\varphi_1(1)\varphi_2(2)|\Omega_2|\varphi_1(1)\varphi_2(2)\rangle$$
$$= N^4\langle\{A(1) + B(1)\}\{A(2) + B(2)\}|\Omega_2|\{A(1) + B(1)\}\{A(2) + B(2)\}\rangle$$
$$= N^4\{\langle A(1)A(2)|\Omega_2|A(1)A(2)\rangle + \langle A(1)A(2)|\Omega_2|A(1)B(2)\rangle$$
$$+ \langle A(1)A(2)|\Omega_2|B(1)A(2)\rangle + \langle A(1)A(2)|\Omega_2|B(1)B(2)\rangle$$
$$+ \langle A(1)B(2)|\Omega_2|A(1)A(2)\rangle + \langle A(1)B(2)|\Omega_2|A(1)B(2)\rangle$$
$$+ \langle A(1)B(2)|\Omega_2|B(1)A(2)\rangle + \langle A(1)B(2)|\Omega_2|B(1)B(2)\rangle$$
$$+ \langle B(1)A(2)|\Omega_2|A(1)A(2)\rangle + \langle B(1)A(2)|\Omega_2|A(1)B(2)\rangle$$
$$+ \langle B(1)A(2)|\Omega_2|B(1)A(2)\rangle + \langle B(1)A(2)|\Omega_2|B(1)B(2)\rangle$$
$$+ \langle B(1)B(2)|\Omega_2|A(1)A(2)\rangle + \langle B(1)B(2)|\Omega_2|A(1)B(2)\rangle$$
$$+ \langle B(1)B(2)|\Omega_2|B(1)A(2)\rangle + \langle B(1)B(2)|\Omega_2|B(1)B(2)\rangle\}$$

Recognizing that many of the matrix elements are equal by symmetry, we obtain:

$$\frac{1}{2}\sum_{i\neq j}\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_i(1)\varphi_j(2)\rangle$$

$$= N^4\{2\langle A(1)A(2)|\Omega_2|A(1)A(2)\rangle + 8\langle A(1)A(2)|\Omega_2|A(1)B(2)\rangle$$
$$+ 2\langle A(1)B(2)|\Omega_2|A(1)B(2)\rangle + 4\langle A(1)A(2)|\Omega_2|B(1)B(2)\rangle\}$$

Using the definitions in eqns 8.28a-d, we obtain

$$\frac{1}{2}\sum_{i\neq j}\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_i(1)\varphi_j(2)\rangle = 2N^4\{m+4l+j+2k\} = \frac{m+4l+j+2k}{2(1+S)^2}$$

We now explore the final term and show that it vanishes:

$$-\frac{1}{2}\sum_{i\neq j}\{\langle\varphi_i(1)\varphi_j(2)|\Omega_2|\varphi_j(1)\varphi_i(2)\rangle\} =$$

$$-\frac{1}{2}\{\langle\varphi_1(1)\varphi_2(2)|\Omega_2|\varphi_2(1)\varphi_1(2)\rangle + \langle\varphi_2(1)\varphi_1(2)|\Omega_2|\varphi_1(1)\varphi_2(2)\rangle\}$$

The first term on the right is proportional to $<\alpha(1)\,|\,\beta(1)>$ and the second term is

proportional to $<\beta(1)\,|\,\alpha(1)>$ and since both of these vanish due to orthogonality of

the spin states, the final term is zero. Therefore, upon collecting all terms:

$$E = \langle\Psi|H|\Psi\rangle = \frac{j_0}{R} + 2E_{1s} - \frac{2(j'+k')}{1+S} + \frac{m+4l+j+2k}{2(1+S)^2}$$

which is eqn 8.27.

8.10 (a) CO : $1\sigma^2 2\sigma^{*2}1\pi^4 3\sigma^2$, $^1\Sigma^+$ [isoelectronic with N_2]

Bond order = $(8-2)/2 = 3$ HOMO = 3σ; LUMO = 2π

(b) NO : . . . $1\pi^4 3\sigma^2 2\pi^{*1}$, $^2\Pi$ [isoelectronic with O_2^+]

Bond order = $(6-1)/2 = 2.5$ HOMO = 2π; LUMO = 4σ

where the * superscript indicates an antibonding molecular orbital.

Exercise: Predict the ground configurations of (a) O_2, (b) O_2^+, and (c) O_2^-.

8.13 To construct the symmetry-adapted linear combinations (SALCs) for methane, we

identify the four hydrogen atoms as equivalent atoms in the molecule and proceed to

form linear combinations of the atomic orbitals that belong to a specific symmetry

species. In the case of a minimal basis set, we consider only 1s orbitals on the hydrogen

atoms, denoting them s_A, s_B, s_C, s_D. We then follow the method set out in Example 5.9.

The effect of the operations of the group T_d (the point group for methane, $h = 24$) on the

basis set of four hydrogen atomic orbitals is given in the following table:

Operation in T_d	s_A	s_B	s_C	s_D
E	s_A	s_B	s_C	s_D
C_3^+ (one of 4 C_3 axes)	s_A	s_C	s_D	s_B
C_3^- (one of 4 C_3 axes)	s_A	s_D	s_B	s_C
C_3^+ (second)	s_D	s_B	s_A	s_C
C_3^- (second)	s_C	s_B	s_D	s_A
C_3^+ (third)	s_B	s_D	s_C	s_A
C_3^- (third)	s_D	s_A	s_C	s_B
C_3^+ (fourth)	s_C	s_A	s_B	s_D
C_3^- (fourth)	s_B	s_C	s_A	s_D
C_2 (one of 3 C_2 axes)	s_B	s_A	s_D	s_C
C_2 (second)	s_C	s_D	s_A	s_B
C_2 (third)	s_D	s_C	s_B	s_A
σ_d (one of six planes)	s_A	s_B	s_D	s_C
σ_d (second)	s_A	s_D	s_C	s_B
σ_d (third)	s_A	s_C	s_B	s_D
σ_d (fourth)	s_D	s_B	s_C	s_A
σ_d (fifth)	s_C	s_B	s_A	s_D
σ_d (sixth)	s_B	s_A	s_C	s_D

S_4^+ (one of 3 S_4 axes)	s_C	s_D	s_B	s_A
S_4^- (one of 3 S_4 axes)	s_D	s_C	s_A	s_B
S_4^+ (second)	s_B	s_D	s_A	s_C
S_4^- (second)	s_C	s_A	s_D	s_B
S_4^+ (third)	s_D	s_A	s_B	s_C
S_4^- (third)	s_B	s_C	s_D	s_A

For the irreducible representation of symmetry species A_1 (see the character table), $d = 1$ and all $\chi(R) = 1$. The first column therefore gives

$$1/24\,(6s_A + 6s_B + 6s_C + 6s_D) = 1/4\,(s_A + s_B + s_C + s_D)$$

and all three other columns gives the same result. For the irreducible representation of symmetry species T_2 (see the character table), $d = 3$ and the characters are $(3, 0, -1, 1, -1)$. The first column therefore gives

$3/24\,(3s_A + 0 - s_B - s_C - s_D + s_A + s_A + s_A + s_D + s_C + s_B - s_C - s_D - s_B - s_C - s_D - s_B) =$
$3/24\,(6s_A - 2s_B - 2s_C - 2s_D)$.

The second column gives

$3/24\,(3s_B + 0 - s_A - s_D - s_C + s_B + s_D + s_C + s_B + s_B + s_A - s_D - s_C - s_D - s_A - s_A - s_C) =$
$3/24\,(6s_B - 2s_A - 2s_C - 2s_D)$.

The third column gives

$3/24\,(3s_C + 0 - s_D - s_A - s_B + s_D + s_C + s_B + s_C + s_A + s_C - s_B - s_A - s_A - s_D - s_B - s_D) =$
$3/24\,(6s_C - 2s_A - 2s_B - 2s_D)$.

The fourth column gives

$3/24\,(3s_D + 0 - s_C - s_B - s_A + s_C + s_B + s_D + s_A + s_D + s_D - s_A - s_B - s_C - s_B - s_C - s_A) =$
$3/24\,(6s_D - 2s_A - 2s_B - 2s_C)$.

The four linear combinations are not linearly independent (the sum of all four is zero) but we can form three linear independent combinations using
    (result from columns 1 + 2),
    (result from columns 2 + 3),
    (result from columns 3 + 4).
We therefore have the following SALCs, indicating also the atomic orbitals on the carbon atom ($2s$, $2p_x$, $2p_y$, $2p_z$) that have the correct symmetry to form molecular orbitals with the SALCs:

A_1: SALC $= s_A + s_B + s_C + s_D$; can overlap with C $2s$

T_2: SALCS = (i) $s_A + s_B - s_C - s_D$, (ii) $s_B + s_C - s_A - s_D$, (iii) $s_C + s_D - s_A - s_B$;

Each can overlap with carbon $2p_x$, $2p_y$, $2p_z$.

Note that we can show that for all other irreducible representations (that is, A_2, E, T_1), no columns survive.

8.16 In the allyl radical, each carbon atom contributes one p-orbital and one p-electron to the π-electron framework. We follow the procedure of Example 8.4; the secular equation to solve is

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

This expands to

$$(\alpha - E)^3 - 2\beta^2(\alpha - E) = 0$$

or

$$(\alpha - E)[(\alpha - E)^2 - 2\beta^2] = 0$$

which has the following three roots:

$$E = \alpha \quad E = \alpha + \sqrt{2}\beta \quad E = \alpha - \sqrt{2}\beta$$

For the allyl radical, two electrons are in the lowest energy molecular orbital (of energy $\alpha + \sqrt{2}\beta$) and one electron is in the molecular orbital of energy α. The total π-electron energy using the Hückel approximation is therefore

$$2(\alpha + \sqrt{2}\beta) + \alpha = \underline{3\alpha + 2\sqrt{2}\beta}$$

Exercise: Estimate the delocalization energy for the allyl radical. Comment on its predicted stability.

8.19 The basis p_1, p_2, p_3, $p_4 \equiv p_N$, p_5, p_6 transforms as follows in C_{2v} (write the C_2 axis cutting through p_1 and p_N):

	p_1	p_2	p_3	p_N	p_5	p_6	χ
E	p_1	p_2	p_3	p_N	p_5	p_6	6
C_2	$-p_1$	$-p_6$	$-p_5$	$-p_N$	$-p_3$	$-p_2$	-2
σ'_v	$-p_1$	$-p_2$	$-p_3$	$-p_N$	$-p_5$	$-p_6$	-6
σ_v	p_1	p_6	p_5	p_N	p_3	p_2	2

The characters 6, -2, -6, 2 span $2A_2 + 4B_1$. The unnormalized symmetry-adapted linear combinations are

$$\pi(A_2) = p_{A_2}p_2 = p_2 - p_6; \quad (p_2 - p_6)/\sqrt{2} \text{ when normalized}$$

$$\pi(A_2) = p_{A_2}p_3 = p_3 - p_5; \quad (p_3 - p_5)/\sqrt{2} \text{ when normalized}$$

$$\pi(B_1) = p_{B_1}p_1 = p_1;$$

$$\pi(B_1) = p_{B_1}p_2 = p_2 + p_6; \quad (p_2 + p_6)/\sqrt{2} \text{ when normalized}$$

$$\pi(B_1) = p_{B_1}p_3 = p_3 + p_5; \quad (p_3 + p_5)/\sqrt{2} \text{ when normalized}$$

$$\pi(B_1) = p_{B_1}p_N = p_N$$

The A_2 determinant in the Hückel approximation involves the matrix elements

$$\tfrac{1}{2}\langle p_2 - p_6|H|p_2 - p_6\rangle = \tfrac{1}{2}\langle p_3 - p_5|H|p_3 - p_5\rangle = \alpha_C \equiv \alpha$$

$$\tfrac{1}{2}\langle p_2 - p_6|H|p_3 - p_5\rangle = \tfrac{1}{2}\{\langle p_2|H|p_3\rangle + \langle p_6|H|p_5\rangle - \langle p_6|H|p_3\rangle - \langle p_2|H|p_5\rangle\}$$

$$= \tfrac{1}{2}\{\beta + \beta - 0 - 0\} = \beta$$

The A_2 secular determinant is therefore

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0; \quad \text{consequently } \underline{E = \alpha \pm \beta}$$

The B_1 determinant involves

$$\langle p_1 | H | p_1 \rangle = \alpha$$

$$\tfrac{1}{2} \langle p_2 + p_6 | H | p_2 + p_6 \rangle = \alpha = \tfrac{1}{2} \langle p_3 + p_5 | H | p_3 + p_5 \rangle$$

$$\langle p_N | H | p_N \rangle = \alpha_N \approx \alpha + \tfrac{1}{2}\beta$$

$$\langle p_1 | H | p_2 + p_6 \rangle / \sqrt{2} = (\beta + \beta)/\sqrt{2} = \beta\sqrt{2}$$

$$\langle p_1 | H | \text{all others} \rangle = 0$$

$$\tfrac{1}{2} \langle p_2 + p_6 | H | p_3 + p_5 \rangle = \tfrac{1}{2}(\beta + \beta) = \beta$$

$$\langle p_2 + p_6 | H | p_N \rangle / \sqrt{2} = 0$$

$$\langle p_3 + p_5 | H | p_N \rangle / \sqrt{2} = \beta_{CN}\sqrt{2} \approx \beta\sqrt{2}$$

The determinant itself is therefore

$$\begin{vmatrix} \alpha - E & \beta\sqrt{2} & 0 & 0 \\ \beta\sqrt{2} & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta\sqrt{2} \\ 0 & 0 & \beta\sqrt{2} & \alpha + \tfrac{1}{2}\beta - E \end{vmatrix}$$

$$= (\alpha - E)^3(\alpha + \tfrac{1}{2}\beta - E) - 2\,(\alpha - E)^2\beta^2 - (\alpha - E)(\alpha + \tfrac{1}{2}\beta - E)\beta^2$$

$$- 2\beta^2(\alpha - E)(\alpha + \tfrac{1}{2}\beta - E) + 4\beta^4 = 0$$

Write $(\alpha - E)/\beta = x$; then solve

$$x^3(x + \tfrac{1}{2}) - 2x^2 - x(x + \tfrac{1}{2}) - 2x(x + \tfrac{1}{2}) + 4 = 0$$

or

$$x^4 + \tfrac{1}{2}x^3 - 5x^2 - \tfrac{3}{2}x + 4 = 0$$

The roots of this equation (determined numerically) are

$$x = 0.8410, \quad 1.9337, \quad -1.1672, \quad -2.1074$$

so, in this approximation, the energies of the B_1 orbitals lie at

$$E = \alpha - 1.9337\beta, \; \alpha - 0.8410\beta, \; \alpha + 1.1672\beta, \; \alpha + 2.1074\beta$$

The π-electron energy is therefore

$$E_\pi = 2(\alpha + 2.1074\beta) + 2(\alpha + \beta) + 2(\alpha + 1.1672\beta) = 6\alpha + 8.5492\beta$$

The delocalization energy is

$$E_{\text{deloc}} = 6\alpha_C + 8.5492\beta - \{5\alpha_C + \alpha_N + 6\beta\} = 2.0492\beta$$

Exercise: Find the Hückel molecular orbitals energies of pyrazine using the same set of approximations.

8.22 The Clebsch–Gordan series for $f^2(l = 3)$ is

$$3 \times 3 = 6 + 5 + \cdots + 0$$

so $f^2 \rightarrow$ I, H, G, F, D, P, S. As the orbitals are equivalent, I must be ^{1}I [Pauli principle], and so the permitted terms for the free ion are

$$^1\text{I}, \; ^3\text{H}, \; ^1\text{G}, \; ^3\text{F}, \; ^1\text{D}, \; ^3\text{P}, \; ^1\text{S}$$

[either note that terms alternate in general, or else evaluate the symmetrized and anti-symmetrized direct products].

For the second part, use eqn 5.47b:

$$\chi(C_\alpha) = \frac{\sin[(L + \tfrac{1}{2})\alpha]}{\sin \tfrac{1}{2}\alpha}$$

with $\alpha = 0(E)$, $2\pi/3(C_3)$, $\pi(C_2)$, $\pi/2(C_4)$, $\pi(C_2')$. Draw up the following Table:
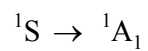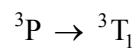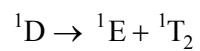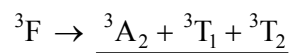
Term	E	C_3	C_2	C_4	C_2'	Decomposition
I	13	1	1	−1	1	$A_1 + A_2 + E + T_1 + 2T_2$
H	11	−1	−1	1	−1	$E + 2T_1 + T_2$
G	9	0	1	1	1	$A_1 + E + T_1 + T_2$
F	7	1	−1	−1	−1	$A_2 + T_1 + T_2$
D	5	−1	1	−1	1	$E + T_2$
P	3	0	−1	1	−1	T_1
S	1	1	1	1	1	A_1

For the decompositions use

$$a_l = (1/h)\sum_c g(c)\chi^{(l)}(c)\chi(c) \quad \text{[eqn 5.23]}$$

$$= (1/24)\,\{\chi^{(l)}(E)\chi(E) + 8\chi^{(l)}(C_3)\chi(C_3) + 3\chi^{(l)}(C_2)\chi(C_2)$$

$$+ 6\chi^{(l)}(C_4)\chi(C_4) + 6\chi^{(l)}(C_2')\chi(C_2')\}$$

in conjuction with the O character table. The multiplicities carry over. Therefore:

$$^1I \rightarrow \underline{^1A_1 + {}^1A_2 + {}^1E + {}^1T_1 + 2{}^1T_2}$$

$$^3H \rightarrow \underline{^3E + 2\,^3T_1 + {}^3T_2}$$

$$^1G \rightarrow \underline{^1A_1 + {}^1E + {}^1T_1 + {}^1T_2}$$

$$^3F \rightarrow \underline{^3A_2 + {}^3T_1 + {}^3T_2}$$

$$^1D \rightarrow \underline{^1E + {}^1T_2}$$

$$^3P \rightarrow \underline{^3T_1}$$

$$^1S \rightarrow \underline{^1A_1}$$
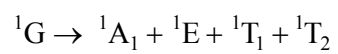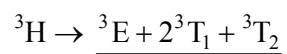
Exercise: What terms does a g^2 configuration give rise to **(a)** in a free atom, **(b)** an octahedral complex?

8.25 Once again, it is helpful to have a model of the tetrahedral system labelled with the orbitals. Use the same cube as in Problem 8.24, but labelled as in Fig. 8.11.
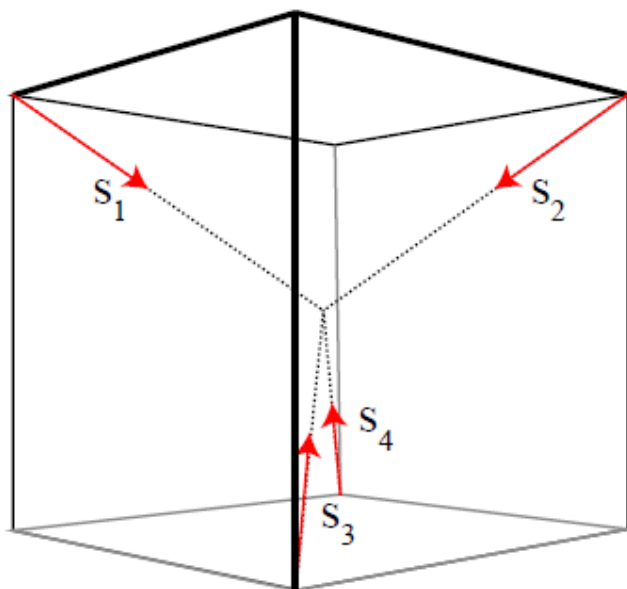
Figure 8.11: A representation of the s-orbital basis in a tetrahedral complex.

The s-orbital linear combinations can be constructed as follows. Consider s_1; under the operations of the group (Fig. 8.12) it transforms as follows:
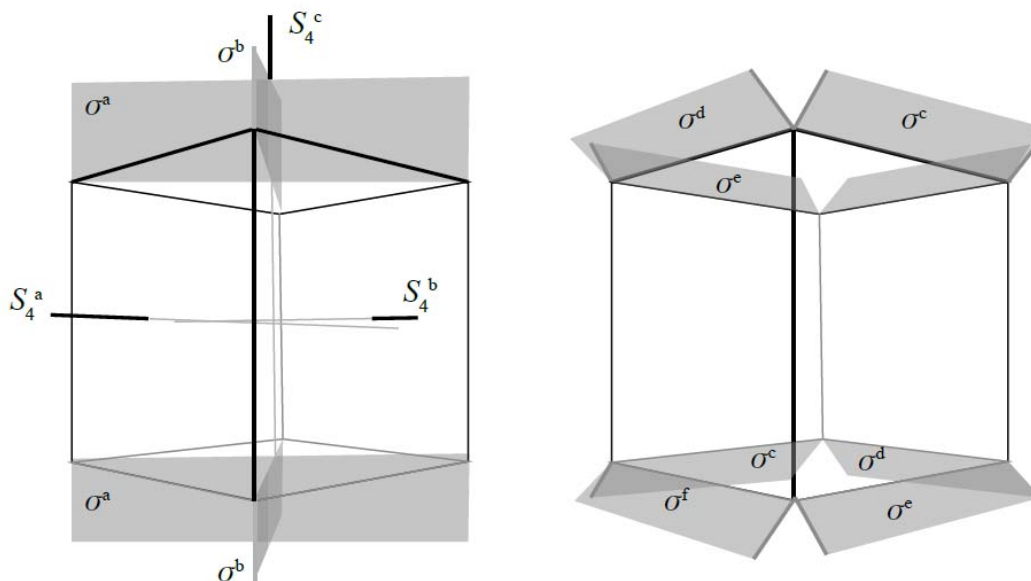

Figure 8.12: The operations of the group T_d.

R	E	C_3^{+a}	C_3^{+b}	C_3^{+c}	C_3^{+d}	C_3^{-a}	C_3^{-b}	C_3^{-c}	C_3^{-d}	C_2^a	C_2^b	C_2^c
Rs_1	s_1	s_3	s_2	s_1	s_3	s_4	s_4	s_1	s_2	s_3	s_4	s_2

R	σ_d^a	σ_d^b	σ_d^c	σ_d^d	σ_d^e	σ_d^f	S_4^a	S_4^b	S_4^c	S_4^{-a}	S_4^{-b}	S_4^{-c}
Rs_1	s_1	s_2	s_4	s_1	s_1	s_3	s_4	s_3	s_3	s_2	s_2	s_4

Application of the projection operators to s_1 then leads to:

$$p_{A_1}s_1 = (1/24)\{s_1 + s_3 + s_2 + \cdots + s_3 + s_2 + s_4\}$$

$$= (1/4)\{s_1 + s_2 + s_3 + s_4\}$$

$$p_{T_2}s_1 = (1/4)\{3s_1 - s_2 - s_3 - s_4\}$$

$$p_{T_2}s_2 = (1/4)\{3s_2 - s_3 - s_4 - s_1\} \quad \text{[by symmetry]}$$

$$p_{T_2}s_3 = (1/4)\{3s_3 - s_4 - s_1 - s_2\}$$

$$p_{T_2}s_4 = (1/4)\{3s_4 - s_1 - s_2 - s_3\}$$

Ignoring normalization, we take the following linear combinations (chosen, Fig. 8.13, so as to have the symmetries of p_x, p_y, p_z):

$$\left.\begin{array}{l} p_{T_2}s_1 + p_{T_2}s_2 = s_1 + s_2 - s_3 - s_4 \\ p_{T_2}s_2 + p_{T_2}s_3 = s_2 + s_3 - s_4 - s_1 \\ p_{T_2}s_1 + p_{T_2}s_3 = s_1 + s_3 - s_2 - s_4 \end{array}\right\} T_2$$
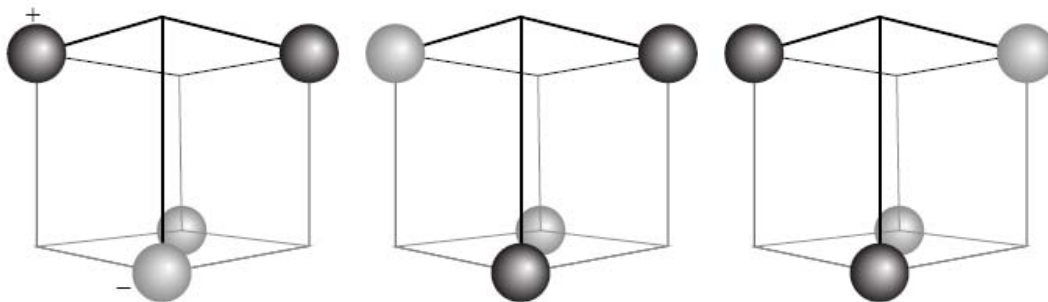

Figure 8.13: The symmetry-adapted linear combinations of s-orbitals of T_2 symmetry.

The p-orbital basis (Fig. 8.14) transforms under the operations of the group (T) as illustrated by the following behaviour of p_1:
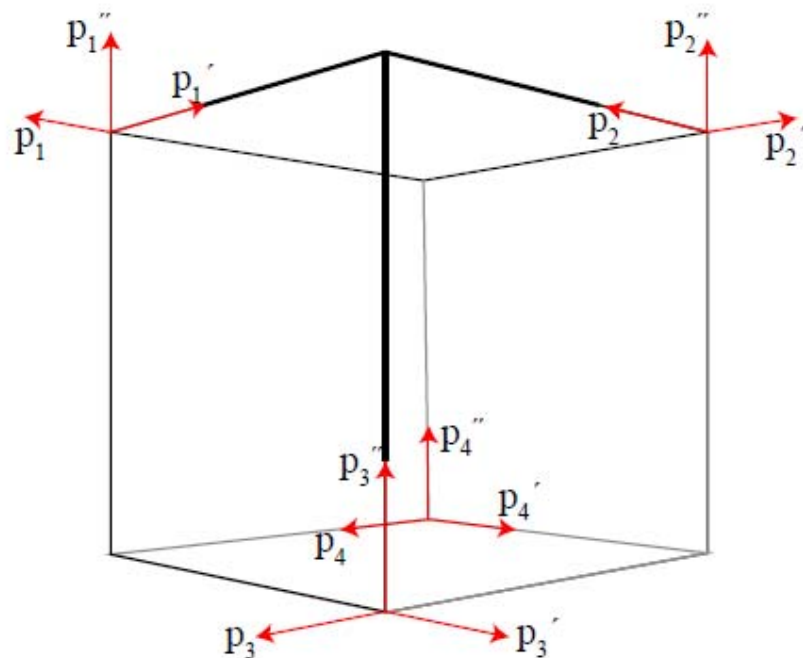
Figure 8.14: The p-orbital basis in a tetrahedral molecule.

R	E	C_3^a	C_3^b	C_3^c	C_3^d	C_3^{-a}	C_3^{-b}	C_3^{-c}	C_3^{-d}	C_2^a	C_2^b	C_2^c
Rp_1	p_1	$-p_3''$	p_2'	p_1''	p_3'	$-p_4'$	$-p_4''$	$-p_1'$	p_2''	p_3	$-p_4$	$-p_2$

R	σ_d^a	σ_d^b	σ_d^c	σ_d^d	σ_d^e	σ_d^f	S_4^a	S_4^b	S_4^c	S_4^{-a}	S_4^{-b}	S_4^{-c}
Rp_1	$-p_1'$	p_2'	$-p_4''$	p_1	p_1''	p_3	$-p_4$	$-p_3''$	$-p_4'$	$-p_2$	p_2''	p_3'

Since we have taken the p-orbital basis, which spans $A_1 + E + 2T_2$, there will be $A_1 + T_2$ components (corresponding to the s-basis, as in the first part of the Problem) as well as

C08   p. 26

E + T₁ + T₂ components. We shall construct only the E p-orbital combinations. The projection operator gives

$$p_{\mathrm{E}}p_1 = (2/24)\{2p_1 + p_3'' - p_2' - p_1'' - p_3' + p_4' + p_4'' + p_1' - p_2'' + 2p_3 - 2p_4 - 2p_2\}$$

The remaining $p_{\mathrm{E}}p_j$ may be constructed similarly.

Exercise: Find the remaining E, T₁, and T₂ symmetry-adapted combinations.

8.28 The plots corresponding to Fig. 8.43 of the text but with (a) $\gamma = \underline{\pi}$, (b) $\gamma = 2\pi$ are shown in Fig. 8.16. The allowed solutions lie within the tinted band. Evaluate the function for a range of values of γ, $0 < \gamma < \frac{1}{2}\pi$.
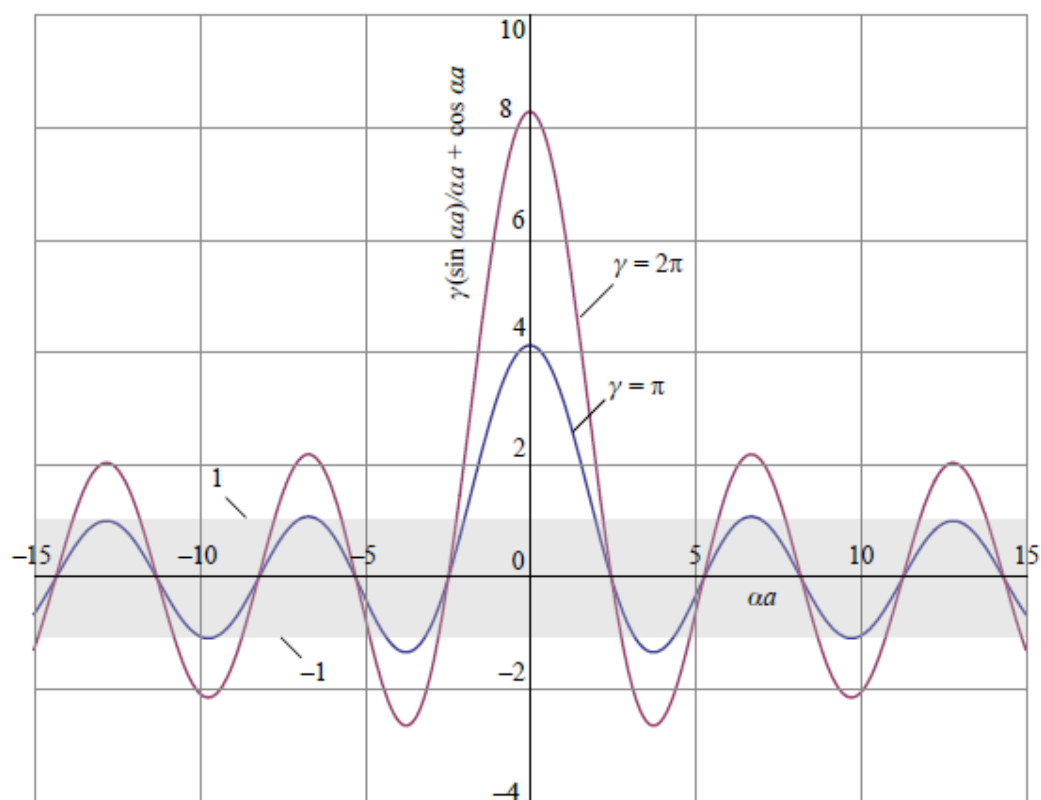

Figure 8.16: The determination of the bands of allowed energies for $\gamma = \pi$ and $\gamma = 2\pi$.