Answers to the Problems in Chapter 12

Problem 12.1.

The Hückel matrix is shown on the left below. Subtract E from each on-diagonal element, divide every element by β and set $(\alpha - E)/\beta = 0$ to give the matrix on the right.

	1	2	3	4
1	α	β	0	0
2	β	α	β	β
3	0	β	α	β
4	0	β	β	α

	1	2	3	4
1	x	1	0	0
2	1	x	1	1
3	0	1	x	1
4	0	1	1	x

When the matrix on the right is multiplied out as a determinant (remember the sign convention!) and set equal to zero we obtain the polynomial $x^4 - 4x^2 + 2x + 1 = 0$. The roots of this equation and the Hückel coefficients are given in the question.

The molecule has 4 carbon atoms which provide 4 π electrons so that the lowest two energy levels are occupied; $E = \alpha + 2.170\beta$ and $\alpha + 0.311\beta$ (remember that $\beta < 0$). Therefore, using the equations on p. 361:

$Q_1 = 2\{(0.282)^2 + (0.815)^2\} = 2\{0.080 + 0.664\} = 1.488$

$P_{12} = 2\{0.282 \times 0.612 + (-0.815) \times (-0.254)\} = 0.759$

If the ion $[C_4H_4]^+$ was formed from the molecule the electron would be lost from the highest occupied molecular orbital; $E = \alpha + 0.311\beta$. Therefore, the positive charge would be distributed in the same way as an electron is distributed in that orbital, i.e. $(-0.815)^2$ on carbon atom 1, $(-0.254)^2$ on atom 2, etc.

Similarly, if the ion $[C_4H_4]^-$ was formed from the molecule the electron would be located in the lowest unoccupied molecular orbital, $E = \alpha - 1.000\beta$. Therefore, its distribution would be confined to atoms 3 and 4, each of which would have a charge of $(0.707)^2 = 0.5$ electrons.

Problem 12.2.
Your bond-length / bond-order table should read:

	P_π	L/pm	P_π data from:
Ethane	0.0	153.4	
Benzene	0.667	139.7	Figure 11.5
Ethene	1.0	133.9	
Ethyne	2.0	120.4	
Butadiene 2-3	0.447	148.3	Table 12.4
Butadiene 1-2	0.894	133.7	Table 12.4

The estimated length for the butadiene 2-3 bond is about 143 pm which is some 5 pm shorter than the experimental value. Alternatively, one might say that the calculated π-bond order is too large. Similarly, the calculated π-bond order for the 1-2 bond appears to be too small. This would seem to be a consequence of the fact that the Hückel procedure assumes that all C=C bonds have the same resonance integral, which is definitely not true for butadiene for which β_{12} should be greater than β_{23}.

Problem 12.3.

Using the values of h_0 and k_0 given, the Hückel method gives the secular determinant:

$$\begin{matrix} \alpha_C & \beta_{CO} \\ \beta_{CO} & \alpha_O \end{matrix} \Rightarrow \begin{matrix} \alpha_C - E & 2\beta_C \\ 2\beta_C & \alpha_C + 1.2\beta_C - E \end{matrix} \Rightarrow \begin{matrix} x & 2 \\ 2 & x+1.2 \end{matrix} = 0$$

We divide each element by β_C, set $(\alpha_C - E)/\beta_C = x$ and multiply out the determinant to obtain the polynomial $x^2 + 1.2x - 4 = 0$.

The roots of this equation are $x = -2.688$ and $+1.488$ which lead to values of E of $\alpha_C + 2.688\beta_C$ and $\alpha_C - 1.488\beta_C$ respectively.

To obtain the coefficients for the orbital for which $x = -2.688$ we return to the original secular equations (see p. 355) and replace x by –2.688 to give:

$-2.688C_C + 2C_O = 0$ or $C_C = 0.744C_O$
or from the other secular equation:
$2C_C + (-2.688 + 1.2)C_O = 0$ or $C_C = 0.744C_O$

We see that we can obtain the ratio of C_C to C_O, but not their absolute values.

But we have the normalising condition; $(C_C)^2 + (C_O)^2 = 1.0$.

Substituting for C_C we obtain $C_O = \pm 0.802$ and from that $C_C = \pm 0.597$ and it is important to note that the two coefficients have the same sign.
The calculation for the other orbital follows in exactly the same way.

Readers may find it of interest to obtain these results by applying the matrix method of Appendix 3 to the energy matrix

$$\begin{matrix} \alpha_C & 2\beta_C \\ 2\beta_C & \alpha_C + 1.2\beta_C \end{matrix}$$

The methanal molecule has two π electrons. The two electrons are paired in the lowest orbital and:
$Q_O = 2\times0.802\times0.802 = 1.286$, $Q_C = 2\times0.597\times0.597 = 0.713$ and
$P_{CO} = 2\times0.802\times0.597 = 0.958$.

Problem 12.4.

All the wavefunctions |ψ> in Table 12.5 are eigenfunctions of the operators $\hat{l}_z$ and $\hat{s}_z$ and, therefore, the results in columns 2 and 3, when multiplied by a magnetic field, *B*, are energy eigenvalues. This is also true for the wavefunctions |+1±½> and |–1±½> in this problem, but not for the wavefunctions $|d_{xy}\pm½\rangle$ which have been formed by the mixing of |+2±½> and |–2±½> by the strong octahedral field. Therefore, in order to obtain energies, we first need to calculate:

$$\langle xy+½|\hat{l}_z + 2\hat{s}_z|xy+½\rangle = -(i/\sqrt{2})^2\langle 2+½|\hat{l}_z + 2\hat{s}_z|2+½\rangle - (i/\sqrt{2})^2\langle -2+½|\hat{l}_z + 2\hat{s}_z|-2+½\rangle$$

$$= ½(2+1) + ½(-2+1) = +1$$

We need to consider only two of the possible four terms because the operators do not change the wavefunctions |+2+½> and |–2+½> and <+2±½|–2±½> = 0.

Similarly, $\langle xy-½|\hat{l}_z + 2\hat{s}_z|xy-½\rangle = -1$ and the required table is:

|ψ>	$\langle\psi\|(\hat{l}_z + 2\hat{s}_z)\|\psi\rangle$	μ/μ_B	$E = -\mu\bullet B$
|+1+½>	+2	–2	+2*B*
|+1–½>	0	0	0
|–1+½>	0	0	0
|–1–½>	–2	+2	–2*B*
|xy–½>	–1	+1	–*B*
|xy+½>	+1	–1	+*B*

$$\overline{\mu} = \frac{\sum_i \mu_i \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} = \frac{-2e^{-2x} + 2e^{+2x} + e^{+x} - e^{-x}}{e^{-2x} + e^{+2x} + e^{+x} + e^{-x} + 2e^{0}} \quad [x = B/kT]$$

$$= \{4\sinh(2x) + 2\sinh(x)\}/\{2\cosh(2x) + 2\cosh(x) + 2\}$$

$$= \{2\sinh(2x) + \sinh(x)\}/\{\cosh(2x) + \cosh(x) + 1\}$$

Problem 12.5.

The Hamiltonian operator is:

$$\hat{H} = -2K\hat{S}_1 \bullet \hat{S}_2 = -2K\{\hat{S}_{1z}\hat{S}_{2z} + \tfrac{1}{2}(\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+})\}$$

It is useful to draw up the table:

	$\hat{S}_{1z}\hat{S}_{2z}$	$\frac{1}{2}\hat{S}_{1+}\hat{S}_{2-}$	$\frac{1}{2}\hat{S}_{1-}\hat{S}_{2+}$
|+½+1>	+½|+½+1>	0	0
|+½ 0>	0	0	+√½|–½ 0>
|–½+1>	–½|–½+1>	+√½|+½ 0>	0
|+½–1>	–½|+½–1>	0	+√½|–½ 0>
|–½ 0>	0	+√½|+½ –1>	0
|–½–1>	+½|–½–1>	0	0

The $\hat{S}_1 \bullet \hat{S}_2$ matrix is:

	|+½+1>	|+½ 0>	|–½+1>	|+½–1>	|–½ 0>	|–½–1>
<+½+1|	+½	0	0	0	0	0
<+½ 0|	0	0	+√½	0	0	0
<–½+1|	0	+√½	–½	0	0	0
<+½–1|	0	0	0	–½	+√½	0
<–½ 0|	0	0	0	+√½	0	0
<–½–1|	0	0	0	0	0	+½

The energies which we require are the eigenvalues of this matrix multiplied by –2K. They are:

+½×(–2K) = –K (4-fold) and –1×(–2K) = +2K (2-fold).

[Compare the four $^2P_{3/2}$ ($E = +\zeta/2$) and the two $^2P_{1/2}$ levels ($E = -\zeta$) of a p^1 atom with spin-orbit coupling ζ.]

Problem 12.6.

$$\langle \Psi_m | \Psi_n \rangle = \frac{1}{2L}\int_{\alpha-L}^{\alpha+L}\{e^{-i\pi mx/L}\cdot e^{+i\pi nx/L}\}dx$$

$$= \frac{1}{2L}\int_{\alpha-L}^{\alpha+L} e^{+i\pi(n-m)x/L}dx \equiv \frac{1}{2L}\int_{\alpha-L}^{\alpha+L} e^{+i\pi Mx/L}dx$$

where $M \equiv n-m$ is a non-zero integer if $n \neq m$.

$$= \frac{1}{2iM\pi}\left[e^{+i\pi Mx/L}\right]_{\alpha-L}^{\alpha+L}$$

$$= \frac{1}{2iM\pi}\left\{e^{+i\pi M(\alpha+L)/L} - e^{+i\pi M(\alpha-L)/L}\right\}$$

$$= \frac{1}{2iM\pi}\left\{\begin{array}{l}\cos\left(\dfrac{M\pi(\alpha+L)}{L}\right)+i\sin\left(\dfrac{M\pi(\alpha+L)}{L}\right)\\ -\cos\left(\dfrac{M\pi(\alpha-L)}{L}\right)-i\sin\left(\dfrac{M\pi(\alpha-L)}{L}\right)\end{array}\right\}$$

By using the formulae for the difference of two sines and of two cosines the above expression can be reduced to:

$$\frac{1}{2iM\pi}\bullet 2\sin\{M\pi\}\left\{-\sin\left(\frac{M\pi\alpha}{L}\right)+i\cos\left(\frac{M\pi\alpha)}{L}\right)\right\}$$

Since M is a non-zero integer, sin(Mπ) is always zero which proves the required orthogonality.

It is interesting to note that, at first glance, we appear to have proved that the normalisation integral (n = m) is also zero. But we also have M (= n–m) on the bottom line above so that when n = m the result is zero divided by zero which is not 1 but indeterminate. To prove that the functions are normalised we have to enter n = m at the start and perform the integration as on p. 382.

Problem 12.7.

The general matrix element of the potential V is:

$$\left\langle \Psi_m \left| \hat{V} \right| \Psi_n \right\rangle = \frac{-v}{2L}\int_{\alpha-L}^{\alpha+L} e^{-i\pi mx/L} \cdot \cos\left(\frac{2N\pi x}{L}\right) \cdot e^{+i\pi nx/L} dx$$

$$= \frac{-v}{2L}\int_{\alpha-L}^{\alpha+L} e^{+i\pi(-m+n)x/L} \cdot \cos\left(\frac{2N\pi x}{L}\right) dx$$

$$= \frac{-v}{2L}\int_{\alpha-L}^{\alpha+L} \left\{\cos\left(\frac{[-m+n]\pi x}{L}\right) + i\sin\left(\frac{[-m+n]\pi x}{L}\right)\right\} \cdot \cos\left(\frac{2N\pi x}{L}\right) dx$$

$$= \frac{-v}{4L}\int_{\alpha-L}^{\alpha+L} \left\{\cos\left(\frac{[2N-m+n]\pi x}{L}\right) + \cos\left(\frac{[2N+m-n]\pi x}{L}\right)\right\} dx$$

$$\frac{-iv}{4L}\int_{\alpha-L}^{\alpha+L} \left\{\sin\left(\frac{[2N-m+n]\pi x}{L}\right) + \sin\left(\frac{[2N+m-n]2\pi x}{L}\right)\right\} dx.$$

2N–m+n and 2N+m–n are integers. Call the integer M and examine the various sine and cosine integrals; e.g.

$$\int_{\alpha-L}^{\alpha+L} \cos\left(\frac{M\pi x}{L}\right) dx = \left[\sin\left(\frac{M\pi x}{L}\right) \bullet \frac{L}{M\pi}\right]_{\alpha-L}^{\alpha+L}$$

$$= \frac{L}{M\pi}\left\{\sin\left(\frac{M\pi[\alpha+L]}{L}\right) - \sin\left(\frac{M\pi[\alpha-L]}{L}\right)\right\}$$

$$= \frac{L}{M\pi}\left\{\begin{array}{l} \sin\left(\frac{M\pi\alpha}{L}\right)\cos(M\pi) + \cos\left(\frac{M\pi\alpha}{L}\right)\sin(M\pi) \\ -\sin\left(\frac{M\pi\alpha}{L}\right)\cos(M\pi) + \cos\left(\frac{M\pi\alpha}{L}\right)\sin(M\pi) \end{array}\right\} = 0$$

A similar result holds for the sine integrals. But, for the reason outlined in problem 12.6, if M = 2N–m+n or 2N+m–n = 0 (i.e. n–m = ±2N) the result is not necessarily zero. But to determine it we have to enter the related values of N, m and n at the start of the calculation. In the example shown in detail on p. 383, for example, we have m = –n and we find that for a non-zero result we must have N = m. Thus N = m = –n or m–n = 2N.