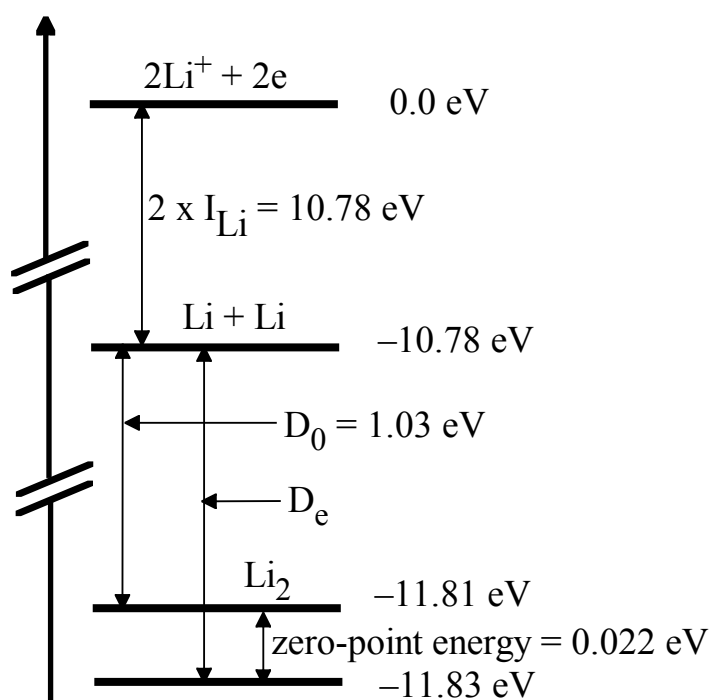


Answers to the Problems in Chapter 6

Problem 6.1.

Energy levels for  $2\text{Li}^+ + 2e$ ,  $2\text{Li}$  and  $\text{Li}_2$ .



$$D_e = D_0 + \frac{1}{2}h\nu = 1.030 + 0.022 = 1.052 \text{ eV}$$

Problem 6.2.

I don't think that I can add much useful information about this problem here. It may be helpful to know that, using the data given, I find  $\beta = 8.703 \times 10^7 \text{ cm}^{-1}$  and  $\nu = 105.36 \times 10^{11} \text{ s}^{-1}$ .

Problem 6.3.

The same is true here. It is simply a case of inserting values into an equation and plotting.

Problem 6.4.

The  $sp^2$  hybrid orbitals are:

$$\Psi_1 = (1/\sqrt{6})\{\sqrt{2}\phi_s - \phi_x + \sqrt{3}\phi_y\}$$

$$\Psi_2 = (1/\sqrt{6})\{\sqrt{2}\phi_s - \phi_x - \sqrt{3}\phi_y\}$$

$$\Psi_3 = (1/\sqrt{3})\{\phi_s + \sqrt{2}\phi_x\}$$

The individual atomic orbitals are normalised and orthogonal so that, for example:

Normalisation

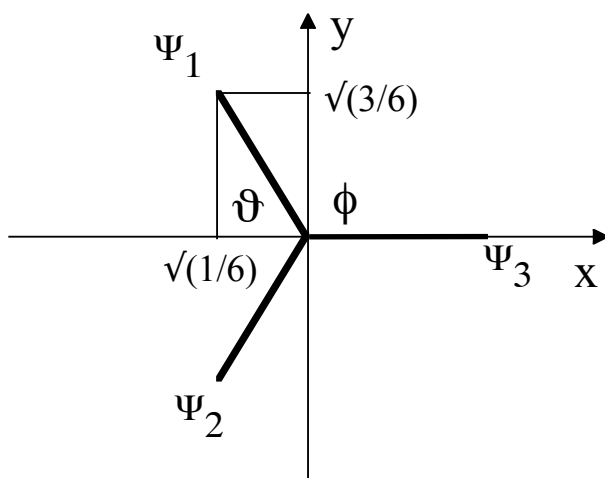
$$\int \Psi_1^* \Psi_1 d\tau = (1/6) \{2\int \phi_s^* \phi_s d\tau + \int \phi_x^* \phi_x d\tau + 3\int \phi_y^* \phi_y d\tau\} = (1/6) \{2+1+3\} = 1.0$$

Orthogonality

$$\int \Psi_1^* \Psi_2 d\tau = (1/6) \{2\int \phi_s^* \phi_s d\tau + \int \phi_x^* \phi_x d\tau - 3\int \phi_y^* \phi_y d\tau\} = (1/6) \{2+1-3\} = 0.0$$

Orientation

We envisage the three hybrid orbitals as vectors in the xy-plane formed from the two orthogonal p orbitals,  $\phi_x$  and  $\phi_y$ , and  $\phi_s$ . Since the s orbital has no directional properties we need not consider it further. In this *vector view*,  $\Psi_1$  has a component of  $-\sqrt{1/6}$  along the x axis and  $+\sqrt{3/6}$  along the y.  $\Psi_2$  has a component of  $-\sqrt{1/6}$  along the x axis and  $-\sqrt{3/6}$  along the y. See diagram below. Therefore,  $\vartheta = \tan^{-1}\{\sqrt{3/6}/\sqrt{1/6}\} = \tan^{-1}\{\sqrt{3}\} = 60^\circ$ . Therefore, the angle between  $\Psi_1$  and  $\Psi_2$  is  $2 \times 60^\circ = 120^\circ$ .



Problem 6.5.

The Hamiltonian operator,  $\hat{H}$  in atomic units, and the wavefunction are given in the question. The normalising constant is calculated in Box 6.1, it is  $\{2(1+S^2)\}^{-1/2}$ . The expectation value of the energy,  $\bar{E}$ , is:

$$\bar{E} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{2 + 2S^2}$$

If we expand  $\Psi$ , the numerator of the above expression comprises two terms of the form  $\langle \phi_A(1)\phi_B(2) | \hat{H} | \phi_A(1)\phi_B(2) \rangle$  which we call J' and two of the form  $\langle \phi_A(1)\phi_B(2) | \hat{H} | \phi_B(1)\phi_A(2) \rangle$  which we call K'. These terms differ in that J' has the same electrons in the same orbitals on either side of the operator whereas in K' they change over. We evaluate J' as follows:

$$\begin{aligned} J' &= \langle \phi_A(1) | -\nabla_1^2 - 1/r_{A1} | \phi_A(1) \rangle \cdot \langle \phi_B(2) | \phi_B(2) \rangle && [E_{1s}] \\ &+ \langle \phi_B(2) | -\nabla_2^2 - 1/r_{B2} | \phi_B(2) \rangle \cdot \langle \phi_A(1) | \phi_A(1) \rangle && [E_{1s}] \\ &+ \langle \phi_B(2) | -1/r_{A2} | \phi_B(2) \rangle \cdot \langle \phi_A(1) | \phi_A(1) \rangle && [Q] \\ &+ \langle \phi_A(1) | -1/r_{B1} | \phi_A(1) \rangle \cdot \langle \phi_B(2) | \phi_B(2) \rangle && [Q] \\ &+ \langle \phi_A(1)\phi_B(2) | 1/r_{12} | \phi_A(1)\phi_B(2) \rangle && [J] \\ &+ \langle \phi_A(1)\phi_B(2) | 1/R_{AB} | \phi_A(1)\phi_B(2) \rangle && [1/R] \\ &= 2E_{1s} + 2Q + J + 1/R \end{aligned}$$

The integrations above are always over all the electron(s) within the  $\langle \rangle$  sign.

Similarly,

$$\begin{aligned} K' &= \langle \phi_A(1) | -\nabla_1^2 - 1/r_{B1} | \phi_B(1) \rangle \cdot \langle \phi_B(2) | \phi_A(2) \rangle && [S^2 E_{1s}]^\dagger \\ &+ \langle \phi_B(2) | -\nabla_2^2 - 1/r_{A2} | \phi_A(2) \rangle \cdot \langle \phi_A(1) | \phi_B(1) \rangle && [S^2 E_{1s}] \\ &+ \langle \phi_B(2) | -1/r_{B2} | \phi_A(2) \rangle \cdot \langle \phi_A(1) | \phi_B(1) \rangle && [SQ'] \\ &+ \langle \phi_A(1) | -1/r_{A1} | \phi_B(1) \rangle \cdot \langle \phi_B(2) | \phi_A(2) \rangle && [SQ'] \\ &+ \langle \phi_A(1)\phi_B(2) | 1/r_{12} | \phi_B(1)\phi_A(2) \rangle && [K] \\ &+ \langle \phi_A(1)\phi_B(2) | 1/R_{AB} | \phi_B(1)\phi_A(2) \rangle && [S^2/R] \\ &= 2 S^2 E_{1s} + 2 SQ' + K + S^2/R \end{aligned}$$

$^\dagger S^2$  because  $\langle \phi_A(1) | -\nabla_1^2 - 1/r_{B1} | \phi_B(1) \rangle = \langle \phi_A(1) | E_{1s} | \phi_B(1) \rangle = E_{1s} \langle \phi_A(1) | \phi_B(1) \rangle = E_{1s} S$ .

Thus

$$\frac{J'+K'}{1+S^2} = \frac{2E_{1s}(1+S^2) + 2Q + 2SQ' + J + K}{1+S^2} + \frac{1+S^2}{R(1+S^2)} = 2E_{1s} + \frac{2Q + 2SQ' + J + K}{1+S^2} + \frac{1}{R}$$

If the wavefunction is  $\Psi' = N' \{ \phi_A(1)\phi_B(2) \}$  then  $N' = 1.0$  and

$$\bar{E}' = \langle \phi_A(1)\phi_B(2) | \hat{H} | \phi_A(1)\phi_B(2) \rangle = J' \text{ as above.}$$

For the wavefunction  $\Psi'' = N'' \{ \phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2) \}$   $N'' = \{2(1-S^2)\}^{-1/2}$  and

$$\begin{aligned} \bar{E}'' &= \frac{J'-K'}{1-S^2} = \frac{2E_{1s}(1-S^2)}{1-S^2} + \frac{2Q - 2SQ' + J - K}{1-S^2} + \frac{1-S^2}{R(1-S^2)} \\ &= 2E_{1s} + \frac{2Q - 2SQ' + J - K}{1-S^2} + \frac{1}{R} \end{aligned}$$

Problem 6.6

When the rows and columns of the matrix are combined to form  $\phi_1$ ,  $(\phi_2 + \phi_3)/\sqrt{2}$  and  $(\phi_2 - \phi_3)/\sqrt{2}$  it takes the following form:

$$\begin{array}{cccc}
 & \phi_1 & (\phi_2 + \phi_3)/\sqrt{2} & (\phi_2 - \phi_3)/\sqrt{2} \\
 \phi_1 & \alpha & \sqrt{2}\beta & 0 \\
 (\phi_2 + \phi_3)/\sqrt{2} & \sqrt{2}\beta & \alpha + \gamma & 0 \\
 (\phi_2 - \phi_3)/\sqrt{2} & 0 & 0 & \alpha - \gamma
 \end{array}$$

One eigenvalue is  $E_1 = \alpha - \gamma$

The  $2 \times 2$  matrix gives eigenvalues of  $E_2 = [2\alpha + \gamma + \{\gamma^2 + 8\beta^2\}^{1/2}]/2$  and  $E_3 = [2\alpha + \gamma - \{\gamma^2 + 8\beta^2\}^{1/2}]/2$

At the extremes we have:

$$\begin{array}{llll}
 \gamma = 0 & E_1 = \alpha, & E_2 = \alpha + \sqrt{2}\beta, & E_3 = \alpha - \sqrt{2}\beta \\
 \gamma = \beta & E_1 = \alpha - \beta, & E_2 = \alpha + \beta, & E_3 = \alpha - 2\beta
 \end{array}$$

Use a spread sheet to construct a diagram correlating these two extremes over the values indicated in the question.

Since  $\beta$  and  $\gamma$  are negative quantities we make the following correspondence between the experimental data and the theoretical eigenvalues.

$$E_3 = [2\alpha + \gamma - \{\gamma^2 + 8\beta^2\}^{1/2}]/2 = -4.2 \text{ eV}$$

$$E_1 = \alpha - \gamma = +0.8 \text{ eV} \quad E_2 = [2\alpha + \gamma + \{\gamma^2 + 8\beta^2\}^{1/2}]/2 = +3.4 \text{ eV}$$

a) With these assignments we have  $(E_1 - E_3)/(E_2 - E_1) = 5.0/2.6 \approx 2$

If we look for this ratio of energy differences on the correlation diagram we find it in the region of  $\gamma = -3$

b) Since  $\beta = -10.0$  all across the diagram, the ratio  $\gamma/\beta = -3/-10 = 0.3$

c)  $E_2 + E_3 = 2\alpha + \gamma = 3.4 - 4.2 = -0.8 \text{ eV}$  and  $E_1 = \alpha - \gamma = +0.8 \text{ eV}$

Therefore,  $E_1 + E_2 + E_3 = 3\alpha = 0.0$  so that,  $\alpha = -0.0 \text{ eV}$

$E_2 + E_3 - 2E_1 = 3\gamma = -0.8 - 1.6 = -2.4$ , so that,  $\gamma = -0.8 \text{ eV}$

$\gamma/\beta = -0.3$  and  $\gamma = -0.8$ , therefore,  $\beta = -0.8/0.3 = -2.67 \text{ eV}$

Check

$$\{\gamma^2 + 8\beta^2\}^{1/2} = 7.594 \text{ eV}$$

$$E_2 = (0.0 - 0.8 + 7.594)/2 = 3.395 \text{ eV}$$

$$E_1 = 0.0 + 0.8 = 0.8 \text{ eV}$$

$$E_3 = (0.0 - 0.8 - 7.594)/2 = -4.195 \text{ eV}$$