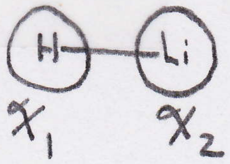
Answers - Chapter 2

1. (a)



$\langle \chi_1 | \chi_2 \rangle = S_{12} = 0.3609$

$H_{11} = e_1^\circ = -13.60$ eV

$H_{22} = e_2^\circ = -5.40$ eV

Wolfsberg-Helmholtz approximation:

$$H_{12} = \Delta_{12} = K \frac{(H_{11} + H_{22})}{2} S_{12}$$

$$= \frac{1.75}{2}(-19.0)(0.3609) = -6.00 \text{ eV}$$

Secular determinant:

$$\begin{vmatrix} e_1^\circ - e_i & \Delta_{12} - e_i S_{12} \\ \Delta_{12} - e_i S_{12} & e_2^\circ - e_i \end{vmatrix}$$

$$e_1 = \frac{-b - \sqrt{D}}{2a} \qquad e_2 = \frac{-b + \sqrt{D}}{2a}$$

$a = 1 - S_{12}^2 = 0.8698$

$b = 2\Delta_{12} S_{12} - e_1^\circ - e_2^\circ = 14.6692$ eV

$D = b^2 - 4ac$

$c = e_1^\circ e_2^\circ - \Delta_{12}^2 = 37.44 \text{ eV}^2$

$\therefore D = 84.9242 \text{ eV}^2$

$e_1 = -13.73$ eV

$e_2 = -3.14$ eV

The two wavefunctions are of the form

$$\psi_1 = c_{11}\chi_1 + c_{21}\chi_2 \qquad \psi_2 = c_{12}\chi_1 + c_{22}\chi_2$$

$$c_{11} = \frac{1}{\sqrt{1+2tS_{12}+t^2}} \qquad t = \frac{\Delta_{12} - e_1^\circ S_{12}}{e_1^\circ - e_2^\circ} = 0.1331$$

$\therefore c_{11} = 0.9475$

$c_{21} = t c_{11} = 0.1261$

$$c_{22} = \frac{1}{\sqrt{1+2t'S_{12}+t'^2}} \qquad t' = \frac{\Delta_{12} - e_2^\circ S_{12}}{e_2^\circ - e_1^\circ} = -0.4940$$

$\therefore c_{22} = 1.0615$

$c_{12} = t' c_{22} = -0.5244$

(b) For the population analysis n_i for $\psi_1 = 2$
n_i for $\psi_2 = 0$

$\therefore P_{11} = (2)(0.9475)^2 = 1.7955$

$P_{22} = (2)(0.1261)^2 = 0.0318$

$P_{12} = (2)(2)(0.9475)(0.1261)(0.3609) = 0.1725$

$\therefore q_1 = 1.7955 + \frac{1}{2}(0.1725) = 1.8818$ $\therefore$ charge on H $= -0.8818$

$q_2 = 0.0318 + \frac{1}{2}(0.1725) = 0.1182$ $\therefore$ charge on Li $= +0.8818$

(while there are 3 protons on Li
we have neglected the 2 electrons
in the 1s shell)

$\mu^* = 2.54(0.8818)(3.015) = 6.75$ Debyes

(c) The primary reason why our calculation, above, is different from that found at the ab initio levels is that we have neglected the 2p A.O.'s on Li! Consider the following which uses a more complete basis on Li wich include the 2p AOs.

The inclusion of the p A.O. on Li will cause some p character on Li to mix into ψ_1 therefore, the electron density on Li will increase and Q_{Li} will decrease. For the same reason Q_H becomes less negative and P_{Li-H} increases. An equivalent way of putting this is that there is more covalent character in the Li-H bond. Naturally, the value of μ^* must decrease. On going from the minimal to extended basis levels, the extra functions serve to increase the ionic character – the charges become larger, P_{LiH} decreases, and μ^* increases.

The dipole moment is really the gradient of the charge density over all space. In a diatomic molecule one would normally assume that most of the charge would lie between the nuclei and hence could be evaluated in terms of point charges centered on the nuclei. However, there is in this case considerable mixing of the lithium p A.O. into ψ_1. Consequently some electron density extends beyond lithium away from hydrogen and therefore the effective distance of the charge gradient is increased dramatically. The reason why e_1 lies at so much higher energy in the two ab initio calculations is due to electron-electron repulsion (see Chapter 8 - especially p. 123-4). Li is very electropositive and the two core 1s electrons very effectively shield the charge from the protons at the nucleus. Furthermore, the majority of the electron density is concentration in the vicinity of H which only has one proton. Therefore, this increased $e^- - e^-$ repulsion pushes e_1 up. Notice that putting more flexability into the basis set allows the two electrons to "spread out" in space more so that e_1 in the extended basis set is lowered.

2. Let $S_{12} > 0$ and, therefore, $H_{12} < 0$. For the $3e^- - 2e$ bond the energy of interaction, ΔE, is given by

$$\Delta E = 2e_1 + e_2 - 3e_1^\circ .$$

Here if $\Delta E < 0$ there is stabilization by if $\Delta E > 0$ then there is net destabilization. Recall that

$$e_1 = \frac{e_1^\circ + H_{12}}{1+S_{12}} \quad \& \quad e_2 = \frac{e_1^\circ - H_{12}}{1-S_{12}}$$

and substituting this into the equation above:

$$\Delta E = \frac{2(e_1^\circ + H_{12})(1-S_{12}) + (e_1^\circ - H_{12})(1+S_{12}) - 3e_1^\circ(1-S_{12}^2)}{1-S_{12}^2}$$

For convience let $H_{12} = K S_{12}$ then

$$\Delta E = \frac{(K - e_1^\circ) S_{12} (1 - 3S_{12})}{1 - S_{12}^2}$$

normally $K < e_1^\circ$ and since $S_{12} > 0$

then in order for $\Delta E < 0$;

$$(1 - 3S_{12}) > 0 \quad \text{or} \quad S_{12} < 1/3$$

Alternatively one could use the Wolfsberg-Helmholz approximation

$$H_{12} = \frac{K(2e_1^\circ)S_{12}}{2} = K e_1^\circ S_{12}$$

letting $K \approx 2$ then $H_{12} = 2e_1^\circ S_{12}$ or $K = 2e_1^\circ$

so

$$\Delta E = \frac{e_1^\circ S_{12}(1 - 3S_{12})}{1 - S_{12}^2}$$

An S_{12} less than 1/3 means that a $3e^- - 2c$ bond will be long. Using the STO for H in problem 1, the computed $S_{12} = 0,596$ for an H-H distance of 0.8 Å. Even at a distance of 1.1 Å, $S_{12} = 0,359$. H_2^- will not exist. There are, however, a number of compounds with $3e^- - 2c$ bonds.