

Q 12-6

Yes. Since the electrostatic potential is shown as contour map, the bigger apparent size of the atom indicates the higher electron charge around H and being an electron acceptor in the molecule (i.e. in LiH, H is electron acceptor and has oxidized Li; hence it has a higher electron charge around and looks bigger).

Q 12.8

AO → a one electron wave function for an atom

MO → a one electron wave function that is generally expressed as a linear combination of atomic orbitals.

Molecular wave function → an N electron wave function that is expressed in terms of molecular orbitals

Basis set → the set of AOs used to construct the MOs

Minimal basis set → the smallest set of AOs for doing a calculation (generally core AOs plus occupied and unoccupied valence AOs)

P 12.8

MO	σ or π	bonding or antibonding	image
3	σ	bonding	f
4	σ	antibonding	b
5	π	bonding	c
6	σ	bonding	a
7	π	bonding	e
8	π	antibonding	d

Since the AO coefficients from N and O are not the same for MO 5 and 7, their energies are different. These coefficients affect the size of π lobe around each atom.

P 12.14

Probabilities of finding the electron on the H and F atoms:

$$p_H = (c_{11})^2 + c_{11}c_{21}S_{12} = 0.34^2 + 0.34 \times 0.84 \times 0.30 = 0.201$$

$$p_F = (c_{11})^2 + c_{11}c_{21}S_{12} = 0.84^2 + 0.34 \times 0.84 \times 0.30 = 0.791$$

For calculating the dipole moment: (z is the charge on the atom)

$$\mu = e(z_2 - z_1)r = 1.609 \times 10^{-19}C \times 91.7 \times 10^{-12}m \times |0.791 - 0.201| = 8.71 \times 10^{-30} = 2.62 D$$

This result is relatively close to the experimental value.

P 13.10

BH₂ has 5 and NH₂ has 7 valence electrons. The valence electron HOMO for BH₂ is 2a₁ and for NH₂ is 1b₁. Hence the NH₂ molecule adopts a more bent structure to lower the energy and BH₂ molecule has the larger bond angle.

P 6

Butadiene has a C₂ symmetry axis (the Huckel model does not distinguish between cis, trans or linear configurations).

$$\Psi = c_1p_1 + c_2p_2 + c_3p_3 + c_4p_4$$

And:

$$\begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0$$

From SALCs (symmetry adapted linear combination) of atomic orbitals we can write:

$$\chi_1 = \frac{1}{\sqrt{2}}(p_1 + p_4), \quad \chi_2 = \frac{1}{\sqrt{2}}(p_2 + p_3), \quad \chi_3 = \frac{1}{\sqrt{2}}(p_2 - p_3), \quad \chi_4 = \frac{1}{\sqrt{2}}(p_1 - p_4)$$

$$\Psi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

With respect to C₂ operation, χ_1 and χ_2 are symmetric and χ_3 and χ_4 are asymmetric and H_{ij} and S_{ij} vanish if i and j have different symmetry. The block diagonalized matrix then will be:

$$\begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha + \beta - E & 0 & 0 \\ 0 & 0 & \alpha - \beta - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0$$

By solving the 2x2 determinants:

$$(\alpha - E)(\alpha + \beta - E) - \beta^2 = 0 \Rightarrow E_1 = \alpha + 1.62\beta, \quad E_3 = \alpha - 0.62\beta$$

$$(\alpha - E)(\alpha - \beta - E) - \beta^2 = 0 \Rightarrow E_2 = \alpha + 0.62\beta, \quad E_4 = \alpha - 1.62\beta$$