Answer on Question #82730 - Chemistry - Physical Chemistry

Question:

When using an independent particle model, an MO ψ is expressed in LCAO form, i.e. as a linear combination of atomic orbitals {φ_1, φ_2, . . . , φ_K}, (1)

and the expansion coefficients are determined from secular equation: the Hamiltonian is the one electron operator h and the "orbital energy" ε. Find the MOs and orbital energies for a linear

polyene (Cn Hn+2), taking φ_μ to be 2p_z AOs on C and including only nearest-neighbor matrix

element, with

(φ_μ|h|φ_μ) = α, (φ_μ|h|φ_μ±1) = β (2)

and with the neglect of the overlap.

Give explicitly the MOs and orbital energies for N = 3 and N = 4.

Solution:

$$\langle \varphi_i | \mathbf{H} | \varphi_i \rangle = \alpha_i$$
$$\langle \varphi_i | \mathbf{H} | \varphi_j \rangle = \beta_{ij}$$
$$\langle \varphi_i | \varphi_j \rangle = S_{ij}$$

where αi is termed the Coulomb integral, βij the resonance integral and Sij the overlap integral. We are using normalized AOs, so Sii . Furthermore, the two atoms are identical, so

α1 = α2;

β12 = β21;

$$(c_1^2 + c_2^2)\alpha + 2c_1c_2\beta - E(c_1^2 + c_2^2 + 2c_1c_2S) = 0$$

$$\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$$

$$(\alpha - E)c_1 + (\beta - ES)c_2 = 0$$
$$(\beta - ES)c_1 + (\alpha - E)c_2 = 0$$

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$E_1 = \frac{\alpha + \beta}{1 + S} \quad \text{and} \quad E_2 = \frac{\alpha - \beta}{1 - S}$$

$$\langle \Psi_i | \Psi_i \rangle = c_{i1}^2 + c_{i2}^2 + 2c_{i1}c_{i2}S = 1$$

$$\Psi_1 = \frac{1}{\sqrt{2(1+S)}}(\varphi_1 + \varphi_2) \quad \text{and} \quad \Psi_2 = \frac{1}{\sqrt{2(1+S)}}(\varphi_1 - \varphi_2)$$