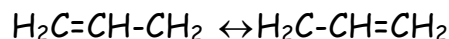


Solutions to problem from previous final exam

Problem from previous final exam - SOLUTIONS

The allyl cation $\text{H}_2\text{C}-\text{CH}-\text{CH}_2^{(+)}$ has resonance structures



which indicate that the pi electrons are delocalized across the entire molecule. The $2p_z$ orbitals from all three C atoms can be used to form delocalized pi MOs:

$$\phi_\pi = c_A 2p_{zA} + c_B 2p_{zB} + c_C 2p_{zC} \equiv c_A \chi_A + c_B \chi_B + c_C \chi_C$$

where the new symbols χ_A, χ_B, χ_C are adopted purely for notational convenience.

a) (5 pts) Write in determinant form the expression from which the MO energies can be calculated. Don't make any assumptions yet about which terms in the determinant might be equal to each other or might be equal to zero. You can write terms like H_{AA} and S_{AB} without them. You don't need to write the Hamiltonian explicitly for this part or for any part of this problem.

$$\begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} & H_{AC} - ES_{AC} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} & H_{BC} - ES_{BC} \\ H_{CA} - ES_{CA} & H_{CB} - ES_{CB} & H_{CC} - ES_{CC} \end{vmatrix} = 0$$

b. (4 pts) Simplify your expression from (a) by using the symmetry of the molecule to determine which terms are equal to each other. Simplify further by neglecting overlap between orbitals on the different atoms, and by assuming that the atomic orbitals are normalized. Simplify further by neglecting any interactions involving greater than nearest neighbor separation. You should end up with only integrals of the form H_{11} and H_{12} , which you should relabel as α and β respectively.

Solutions to problem from previous final exam

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

c. (8 pts) Solve for the MO energies, using the simplified determinant expression from part (b). Write solutions in the form $E = \alpha + x\beta$, where x takes on a different value for each of the MOs. Noting that $\beta < 0$, sketch an energy level diagram indicating the MOs and their energies. Note on your diagram the position of energy α , which is the energy of an electron localized on an atomic orbital (i.e. the energy with no pi bonding).

$$(\alpha - E)[(\alpha - E)^2 - \beta^2] - \beta[\beta(\alpha - E) - 0] + 0 = 0$$

$$(\alpha - E)^3 - 2\beta^2(\alpha - E) = 0$$

$$(\alpha - E)[(\alpha - E)^2 - 2\beta^2] = 0$$

Solutions are

$$\alpha - E = 0$$

$$\alpha - E = \pm\sqrt{2}\beta$$

$$E = \alpha + \sqrt{2}\beta, 0, \alpha - \sqrt{2}\beta$$

Energy level diagram

$$- E = \alpha - \sqrt{2}\beta$$

$$- E = \alpha$$

$$- E = \alpha + \sqrt{2}\beta$$

d. (5 pts) Neglecting electron-electron repulsions, give the total pi bonding energy for the allyl cation which has two pi electrons. Noting that the pi MO energies for a localized pi bond, at this same level of treatment, are $E = \alpha \pm \beta$,

Solutions to problem from previous final exam

compare your result to the total pi bonding energy that you would get if there were no delocalization but just a single pi bond localized on two of the C atoms. Indicate the *delocalization energy*, that is, the extra pi bonding energy due to delocalization of the pi MO across all three atoms.

Total pi bonding energy is $E_\pi = 2(\sqrt{2}\beta)$ compared to 2β for the localized pi bond, yielding a delocalization energy of $2(\sqrt{2}-1)\beta$

e. (16 pts) Recall that the secular determinant comes from a matrix equation

$$\begin{bmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} & H_{AC} - ES_{AC} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} & H_{BC} - ES_{BC} \\ H_{CA} - ES_{CA} & H_{CB} - ES_{CB} & H_{CC} - ES_{CC} \end{bmatrix} \begin{bmatrix} c_A \\ c_B \\ c_C \end{bmatrix} = 0$$

Use your simplified determinant from part (b) (in terms of only α and β) to write a simplified matrix equation for the constants, and use each of the energy solutions from part (c) to determine the constants c_i for the corresponding MO. Re-draw your energy level sketch, this time writing the (normalized) wavefunctions associated with each energy level and sketching the wavefunctions. Note that normalization $\Rightarrow c_A^2 + c_B^2 + c_C^2 = 1$.

$$\begin{bmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{bmatrix} \begin{bmatrix} c_A \\ c_B \\ c_C \end{bmatrix} = 0$$

Symmetry gives $c_A = \pm c_C$ for all MOs

Solution $E = \alpha$: top row gives $\beta c_B = 0 \Rightarrow c_B = 0$

Second row gives $\beta(c_A + c_C) = 0 \Rightarrow c_A = -c_C$

Normalization gives $(c_A, c_B, c_C) = \left(\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}} \right)$

Wavefunction $\phi_0 = \frac{1}{\sqrt{2}}(\chi_A - \chi_C)$

Solutions to problem from previous final exam

Solution $E = \alpha - \sqrt{2}\beta$:

Top row gives $\sqrt{2}\beta c_A + \beta c_B = 0 \Rightarrow c_B = -\sqrt{2}c_A$

Third row gives $\beta c_B + \sqrt{2}\beta c_C = 0 \Rightarrow c_B = -\sqrt{2}c_C$

Normalization gives $(c_A, c_B, c_C) = \frac{1}{2}(1, -\sqrt{2}, 1)$

Wavefunction $\phi_- = \frac{1}{2}(\chi_A - \sqrt{2}\chi_B + \chi_C)$

Solution $E = \alpha + \sqrt{2}\beta$:

Top row gives $-\sqrt{2}\beta c_A + \beta c_B = 0 \Rightarrow c_B = \sqrt{2}c_A$

Third row gives $\beta c_B - \sqrt{2}\beta c_C = 0 \Rightarrow c_B = \sqrt{2}c_C$

Normalization gives $(c_A, c_B, c_C) = \frac{1}{2}(1, \sqrt{2}, 1)$

Wavefunction $\phi_+ = \frac{1}{2}(\chi_A + \sqrt{2}\chi_B + \chi_C)$

Energy level diagram

