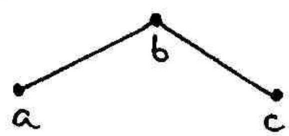
Problem Set 7

1. Consider H_3^+, an interstellar molecule.

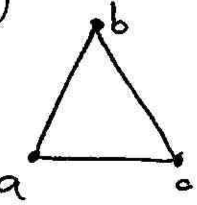
Consider two possible geometries for this molecule

Ⓐ



&

Ⓑ



(equilateral triangle)

Let's call the 3 atomic orbitals in both cases $\vec{\phi}_a$, $\vec{\phi}_b$ & $\vec{\phi}_c$. Assume $\vec{\phi}_a^\dagger \mathbb{H} \vec{\phi}_b = \vec{\phi}_b^\dagger \mathbb{H} \vec{\phi}_c = \beta$ but that in case Ⓐ $\vec{\phi}_a^\dagger \mathbb{H} \vec{\phi}_c = 0$ while in case Ⓑ $\vec{\phi}_a^\dagger \mathbb{H} \vec{\phi}_c = \beta$.

(i) Write the 3×3 Hamiltonian for these two cases.

(ii) Show for Ⓐ $\begin{pmatrix} 1/2 \\ \sqrt{2}/2 \\ 1/2 \end{pmatrix}$, $\begin{pmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{pmatrix}$ & $\begin{pmatrix} 1/2 \\ -\sqrt{2}/2 \\ 1/2 \end{pmatrix}$ are eigenvectors. Find the corresponding eigenvalues.

Show for Ⓑ $\begin{pmatrix} 1/\sqrt{3} \\ 1/\sqrt{3} \\ 1/\sqrt{3} \end{pmatrix}$, $\begin{pmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{pmatrix}$ & $\begin{pmatrix} \frac{1}{\sqrt{6}} \\ -\frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{6}} \end{pmatrix}$ are eigenvectors. Find the corresponding eigenvalue.

(iii) Draw an MO diagram for H_3^+ and H_3^- in both geometry Ⓐ & Ⓑ. Based on this MO diagram conclude if in its ground state if H_3^+ is in geometry Ⓐ or Ⓑ. How about H_3^-? State your reasoning.

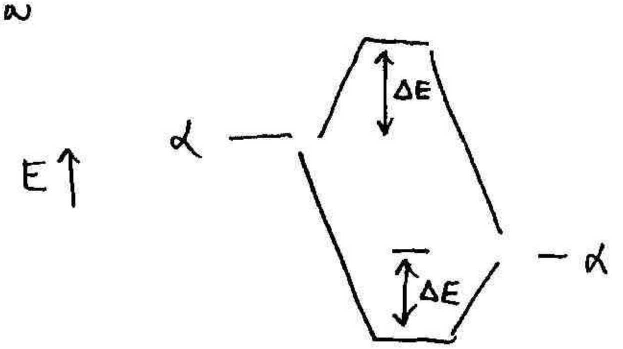
2. Consider the matrix, $\mathbb{H} = \begin{pmatrix} \alpha & \beta \\ \beta & -\alpha \end{pmatrix}$, $\alpha > 0$

Note that if $\begin{pmatrix} a \\ b \end{pmatrix}$ is an eigenvector of $\mathbb{H}$ so is $t\begin{pmatrix} a \\ b \end{pmatrix}$. Choose as $t = 1/a$

$$t\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 1 \\ tb \end{pmatrix} \equiv \begin{pmatrix} 1 \\ x \end{pmatrix}$$

(ii) Find the values of x which correspond to eigenvalues of H. What are the corresponding eigenvalues?

(iii) Consider the two asymptotic cases : $\alpha = 0$ & $|\alpha| >> |\beta|$ [Choose $|\alpha| = 10^2 |\beta|$] & Find in both cases ΔE, where ΔE is shown pictorially below



In which case is $|\Delta E|$ bigger? What bearing does this finding have on the 2nd rule for the making of M.O. diagrams?

3. In quantum mechanics we always find:

$$\vec{\phi}_a^{\,\dagger}\, \mathbb{H}\, \vec{\phi}_b = \left(\vec{\phi}_b^{\,\dagger}\, \mathbb{H}\, \vec{\phi}_a\right)^* = \vec{\phi}_b^{\,\dagger}\, \mathbb{H}\, \vec{\phi}_a \text{ (if real)}$$

In math language we say $\mathbb{H}$ is Hermatian.

Let's see why this property is necessary.

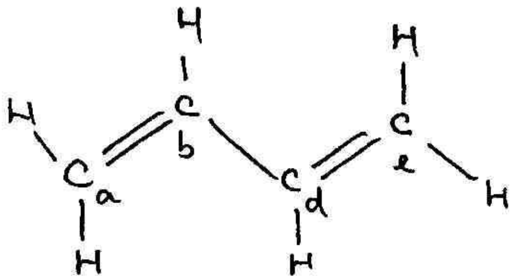
Consider a non-Hermetian matrix:

$$\mathbb{H} = \begin{pmatrix} 0 & 1 \\ \beta & 0 \end{pmatrix} \qquad \begin{array}{ll} \vec{\phi}_a^{\,\dagger}\, \mathbb{H}\, \vec{\phi}_a = \vec{\phi}_b \mathbb{H} \vec{\phi}_b = 0 & \\ \vec{\phi}_b^{\,\dagger}\, \mathbb{H}\, \vec{\phi}_a = \beta & \vec{H}_a^{\,\dagger}\, \mathbb{H}\, \vec{\phi}_b = 1 \end{array}$$

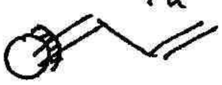
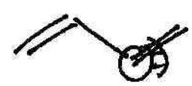
& β is a real number, not equal to 1.

(ii) Consider an eigenvector $\begin{pmatrix} 1 \\ x \end{pmatrix}$. Show for $\beta \neq 1$ there is no such eigenvector. Consider an eigenvector of the form $\begin{pmatrix} 0 \\ x \end{pmatrix}$. Again show there is no such eigenvector. Can this $\mathbb{H}$ exist in quantum mechanics?

4. Consider the C p_z orbitals of butadiene

 abbreviated as 

$\vec{\phi}_a = \begin{pmatrix}1\\0\\0\\0\end{pmatrix}$ $\vec{\phi}_b = \begin{pmatrix}0\\1\\0\\0\end{pmatrix}$ $\vec{\phi}_d = \begin{pmatrix}0\\0\\1\\0\end{pmatrix}$ $\vec{\phi}_e = \begin{pmatrix}0\\0\\0\\1\end{pmatrix}$

Assume $\vec{\phi}_a^{\,\dagger} \mathbb{H} \vec{\phi}_b = \vec{\phi}_b^{\,\dagger} \mathbb{H} \vec{\phi}_d = \vec{\phi}_d^{\,\dagger} \mathbb{H} \vec{\phi}_e = \beta$

Express the 4x4 $\mathbb{H}$ matrix.

Show $\begin{pmatrix}1\\ \frac{1+\sqrt{5}}{2}\\ \frac{1+\sqrt{5}}{2}\\ 1\end{pmatrix}$, $\begin{pmatrix}1\\ -\frac{1+\sqrt{5}}{2}\\ +\frac{1+\sqrt{5}}{2}\\ -1\end{pmatrix}$, $\begin{pmatrix}\frac{1+\sqrt{5}}{2}\\ 1\\ -1\\ -\frac{1+\sqrt{5}}{2}\end{pmatrix}$ & $\begin{pmatrix}\frac{1+\sqrt{5}}{2}\\ -1\\ -1\\ \frac{1+\sqrt{5}}{2}\end{pmatrix}$

are eigenvectors. Find their corresponding eigenvalues. Draw the full MO diagram.

5. Show that the eigenvectors of butadiene π M.O.s are orthogonal. Show the M.O.'s of HF are orthogonal.