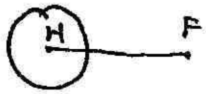
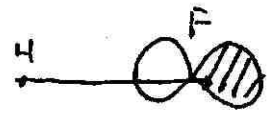
Lecture 21. HF

① As before we consider only two atomic orbitals, the 1s H orbital and the $2p_z$ F orbital.

$\vec{\phi}_{1s}$ $\qquad\qquad\qquad\qquad$ $\vec{\phi}_{2p_z}$





$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad\qquad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

② We now need to construct the $\mathbb{H}$ matrix.

$\vec{\phi}_{1s}^{\,+} \mathbb{H} \vec{\phi}_{1s}$ = average energy of the $\mathbb{H}$ 1s orbital $= -13.6$ eV $= \alpha_H$

$\vec{\phi}_{2p_z}^{\,+} \mathbb{H} \vec{\phi}_{2p_z}$ = average energy of the $\mathbb{F}$ $2p_z$ orbital $\simeq -18.1$ eV $= \alpha_F$

③ Consider now $\vec{\phi}_{1s}^{\,+} \mathbb{H} \vec{\phi}_{2p_z}$ vs. $\vec{\phi}_{2p_z}^{\,+} \mathbb{H} \vec{\phi}_{1s}$.

The first term corresponds to the probability amp. that in the environment of HF molecule, measurement of the energy of a state in the F $2p_z$ orbital turns this orbital into the H 1s orbital. The 2^{nd} term is the converse, the P.A. that a H 1s orbital is turned into a F $2p_z$ orbital (by measurement of the energy). As we discuss in Problem Set 7, problem 3 $\vec{\phi}_{1s}^{\,+} \mathbb{H} \vec{\phi}_{2p_z} = \vec{\phi}_{2p_z}^{\,+} \mathbb{H} \phi_{1s}$.

③ We could call this equality a quantum mechanical micro-reversibility. You will study micro-reversibility elsewhere in the chemistry curriculum.

Let's call $\vec{\phi}_{1s}^{\dagger} \mathbb{H} \vec{\phi}_{2p_z} = \vec{\phi}_{2p_z}^{\dagger} \mathbb{H} \vec{\phi}_{1s} = \beta$

With these definitions:

$$\mathbb{H} = \begin{pmatrix} -13.6 & \beta \\ \beta & -18.1 \end{pmatrix} = \begin{pmatrix} \alpha_H & \beta \\ \beta & \alpha_F \end{pmatrix}$$

④ In defining energies, energies are evaluated with respect to a reference energy. We usually set energy $= 0$ for electrons which are not moving and are ∞ far away from other charges. But for this problem, let's set $E = 0$ for the average of -13.6 & -18.1 eV, -15.85 eV.

With respect to this energy: $15.85 - 13.6 = 2.25$ eV

$18.1 - 15.85 = 2.25$ eV

Assume $|\alpha| > |\beta|$ $\quad \therefore \frac{|\beta|}{|\alpha|} < 1 \quad$ & $\frac{|\beta^2|}{|\alpha|} \ll 1$

$$\mathbb{H} = \begin{pmatrix} \alpha & \beta \\ \beta & -\alpha \end{pmatrix}$$

where $\alpha = 2.25$ eV

Note changing the zero energy does not affect probability amplitudes.

⑤ To find eigenvectors we need to find vectors such that

$$\begin{pmatrix} \alpha & \beta \\ \beta & -\alpha \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix} = t\begin{pmatrix} u \\ v \end{pmatrix}$$

If $\begin{pmatrix} u \\ v \end{pmatrix}$ is an eigenvector so is $a\begin{pmatrix} u \\ v \end{pmatrix}$.

$\therefore$ choose $a = \frac{1}{u}$ & $\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 1 \\ a\,v \end{pmatrix} \equiv \begin{pmatrix} 1 \\ x \end{pmatrix}$

We need to find a vector $\begin{pmatrix} 1 \\ x \end{pmatrix}$ such that

$$\begin{pmatrix} \alpha & \beta \\ \beta & -\alpha \end{pmatrix}\begin{pmatrix} 1 \\ x \end{pmatrix} = \begin{pmatrix} \alpha + \beta x \\ \beta - \alpha x \end{pmatrix} = t\begin{pmatrix} 1 \\ x \end{pmatrix} = \begin{pmatrix} t \\ tx \end{pmatrix}$$

$$\therefore \quad \frac{\beta - \alpha x}{\alpha + \beta x} = \frac{tx}{t} = x$$

$$\alpha x + \beta x^2 = \beta - \alpha x$$

$$\beta x^2 + 2\alpha x - \beta = 0$$

$$x = \frac{-2\alpha \pm \sqrt{4\alpha^2 + 4\beta^2}}{2\beta}$$

$$x = \frac{-\alpha \pm \sqrt{\alpha^2 + \beta^2}}{\beta} = +\frac{\alpha}{\beta}\left[-1 \pm \sqrt{1 + \frac{\beta^2}{\alpha^2}}\right]$$

(6)

$$\begin{pmatrix} \alpha & \beta \\ \beta & -\alpha \end{pmatrix}\begin{pmatrix} 1 \\ x \end{pmatrix} = \begin{pmatrix} \alpha + \beta x \\ \beta - \alpha x \end{pmatrix} = \begin{pmatrix} t \\ tx \end{pmatrix}$$

$$t = \alpha + \beta x$$

Substituting the values we found for x

$$t = \alpha + \beta x = \alpha + \beta \left[\frac{\alpha}{\beta}\right]\left\{-1 \pm \sqrt{1 + \beta^2/\alpha^2}\right\}$$

$$= \alpha + \alpha \left\{-1 \pm \sqrt{1 + \beta^2/\alpha^2}\right\}$$

$$= \pm \alpha \sqrt{1 + \beta^2/\alpha^2}$$

(7) A rule from calculus:

$y \ll 1$ $$(1 + y)^{\omega} \simeq 1 + \omega y$$

$$\therefore t \simeq \pm\alpha \left(1 + \frac{1}{2}\frac{\beta^2}{\alpha^2}\right) = \pm\left[\alpha + \frac{1}{2}\frac{\beta^2}{\alpha}\right]$$

$$x \simeq \frac{\alpha}{\beta}\left\{-1 \pm \left[1 + \frac{1}{2}\frac{\beta^2}{\alpha^2}\right]\right\} = -\frac{\alpha}{\beta} \pm \left[\frac{\alpha}{\beta} + \frac{1}{2}\frac{\beta}{\alpha}\right]$$

$$= \begin{cases} \frac{1}{2}\frac{\beta}{\alpha} \\ -\frac{2\alpha}{\beta} - \frac{1}{2}\frac{\beta}{\alpha} \end{cases}$$

⑧ We consider just one of the eigenvectors here:

$$\begin{pmatrix} 1 \\ \frac{1}{2}\frac{\beta}{\alpha} \end{pmatrix} \quad \text{with eigenvalue} \quad \alpha + \frac{1}{2}\frac{\beta^2}{\alpha}.$$

Let's check this is an approximate eigenvector.

$$\begin{pmatrix} \alpha & \beta \\ +\beta & -\alpha \end{pmatrix}\begin{pmatrix} 1 \\ \frac{1}{2}\frac{\beta}{\alpha} \end{pmatrix} = \begin{pmatrix} \alpha + \frac{1}{2}\frac{\beta^2}{\alpha} \\ +\beta - \frac{1}{2}\beta \end{pmatrix} = \begin{pmatrix} \alpha + \frac{1}{2}\frac{\beta^2}{\alpha} \\ \beta/2 \end{pmatrix}$$

$$= \left(\alpha + \frac{1}{2}\frac{\beta^2}{\alpha}\right)\begin{pmatrix} 1 \\ \dfrac{\beta/2}{\alpha + \frac{1}{2}\frac{\beta^2}{\alpha}} \end{pmatrix}$$

Consider lower term:

$$\left[\alpha + \frac{1}{2}\frac{\beta^2}{\alpha}\right]^{-1} \simeq [\alpha]^{-1} \qquad |\beta| < |\alpha| \;\therefore\; |\beta|^2 \ll \alpha$$

$\therefore$ lower term

$$\simeq \frac{\beta}{2\alpha}$$

& the vector $\begin{pmatrix} 1 \\ \frac{1}{2}\beta/\alpha \end{pmatrix}$ is an approximate eigenvector.
Note β is a neg. number

(9) Consider the other approximate eigenvector

$$\begin{pmatrix} 1 \\ -\frac{2\alpha}{\beta} - \frac{1}{2}\frac{\beta}{\alpha} \end{pmatrix} \simeq \begin{pmatrix} 1 \\ -\frac{2\alpha}{\beta} \end{pmatrix}$$

Recall $a \begin{pmatrix} 1 \\ -\frac{2\alpha}{\beta} \end{pmatrix}$ would also be an eigenvector

Choose $a = -\frac{\beta}{2\alpha}$ $\therefore$ we have as an

approximate eigenvector : $\begin{pmatrix} -\frac{\beta}{2\alpha} \\ 1 \end{pmatrix}$

$$\begin{pmatrix} \alpha & \beta \\ +\beta & -\alpha \end{pmatrix} \begin{pmatrix} -\frac{\beta}{2\alpha} \\ 1 \end{pmatrix} = \begin{pmatrix} -\beta/2 + \beta \\ -\frac{\beta^2}{2\alpha} - \alpha \end{pmatrix} = \begin{pmatrix} +\beta/2 \\ -\alpha - \frac{\beta^2}{2\alpha} \end{pmatrix}$$

For this vector to be an eigenvector with eigenvalue

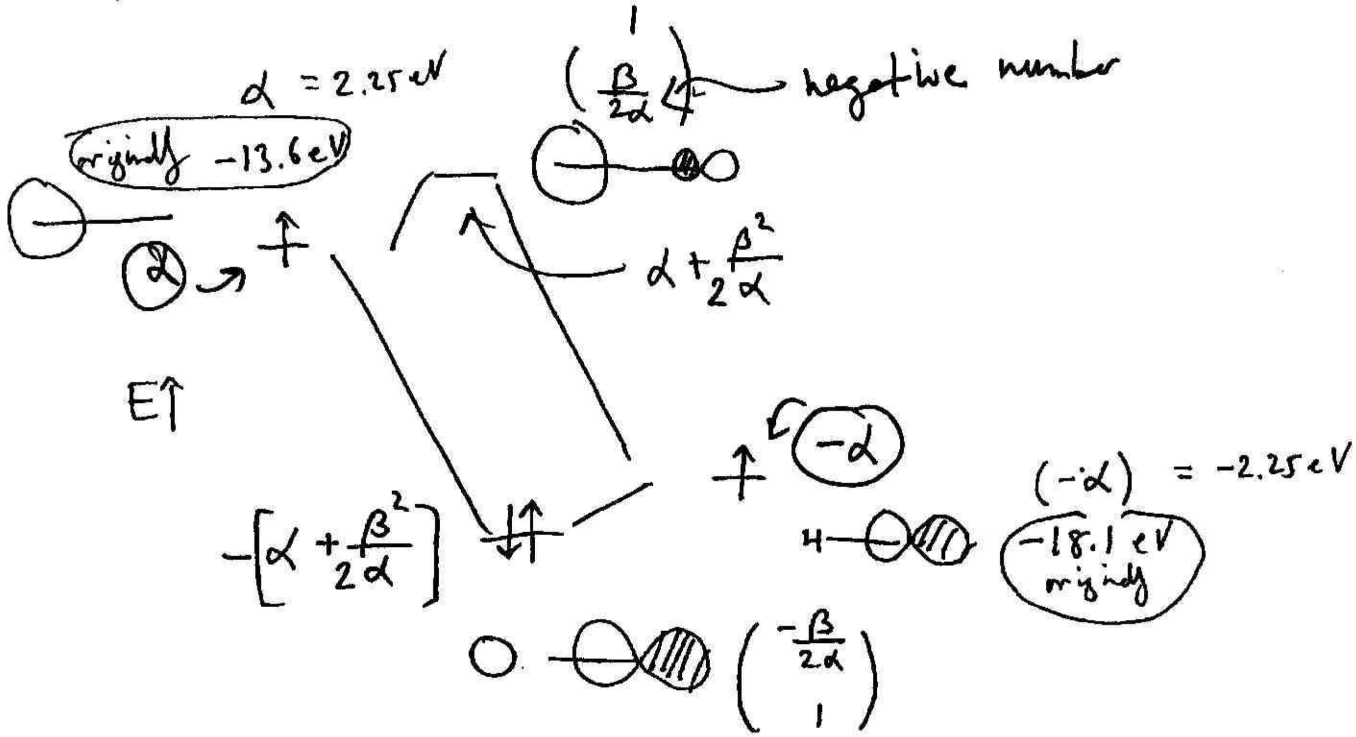
$$t = -\left[\alpha + \frac{1}{2}\frac{\beta^2}{\alpha}\right]$$

$$\begin{pmatrix} \beta/2 \\ \alpha - \beta^2/2\alpha \end{pmatrix} \overset{\text{must}}{=} \begin{pmatrix} -\beta/2\alpha \\ 1 \end{pmatrix} \left[-\alpha - \frac{1}{2}\frac{\beta^2}{\alpha}\right]$$

Note $\left[-\alpha - \frac{1}{2}\frac{\beta^2}{\alpha}\right]\left[-\frac{\beta}{2\alpha}\right] \simeq [-\alpha]\left[-\frac{\beta}{2\alpha}\right] = \frac{\beta}{2}$

QED.

(10) Graphing these approximate answers:

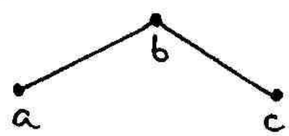


Note bonding orbital resemble more closely the original lower energy orbital while the antibonding orbital resemble more the initial higher energy orbital. How does this fit in with our original rule about making MO diagrams?

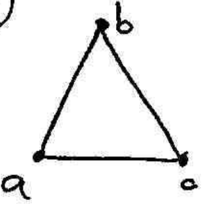
Problem Set 7

1. Consider H_3^+, an interstellar molecule.

Consider two possible geometries for this molecule

(A) 

&

(B)  (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 (A) $\vec{\phi}_a^{\dagger} \mathbb{H} \vec{\phi}_c = 0$ while in case (B) $\vec{\phi}_a^{\dagger} \mathbb{H} \vec{\phi}_c = \beta$.

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

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

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

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

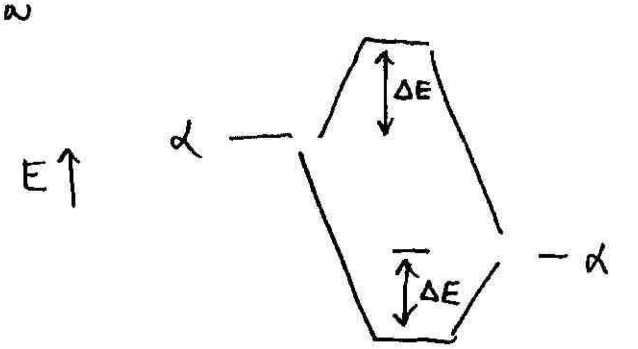
2. Consider the matrix, $\mathbb{H} = \begin{pmatrix} \alpha & \beta \\ \beta & -\alpha \end{pmatrix}$, $\alpha > 0$

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 Hermetian.

Let's see why this property is necessary.

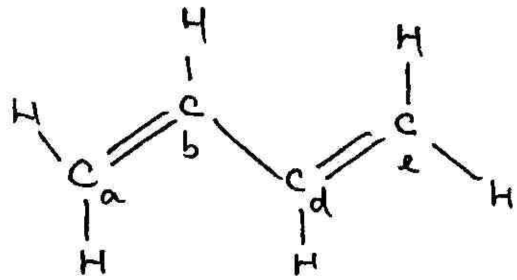
Consider a non-Hermetian matrix:

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

& β is a real number, not equal to 1.

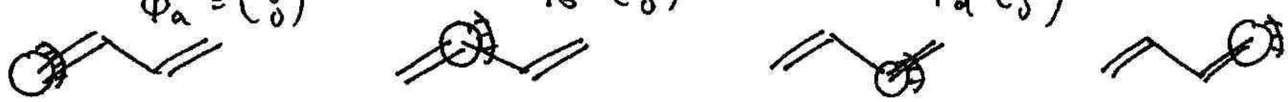
(ii) Consider an eigenvector $\begin{pmatrix} 1 \\ x \end{pmatrix}$. Show for $\beta \neq 1$ there is no such eigenvector. Consider an eigenvector of the form $\begin{pmatrix} 0 \\ x \end{pmatrix}$. Again show there is no such eigenvector. Can this $\mathbb{H}$ exist in quantum mechanics?

4. Consider the C p_z orbitals of butadiene



abbreviated as 

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



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.