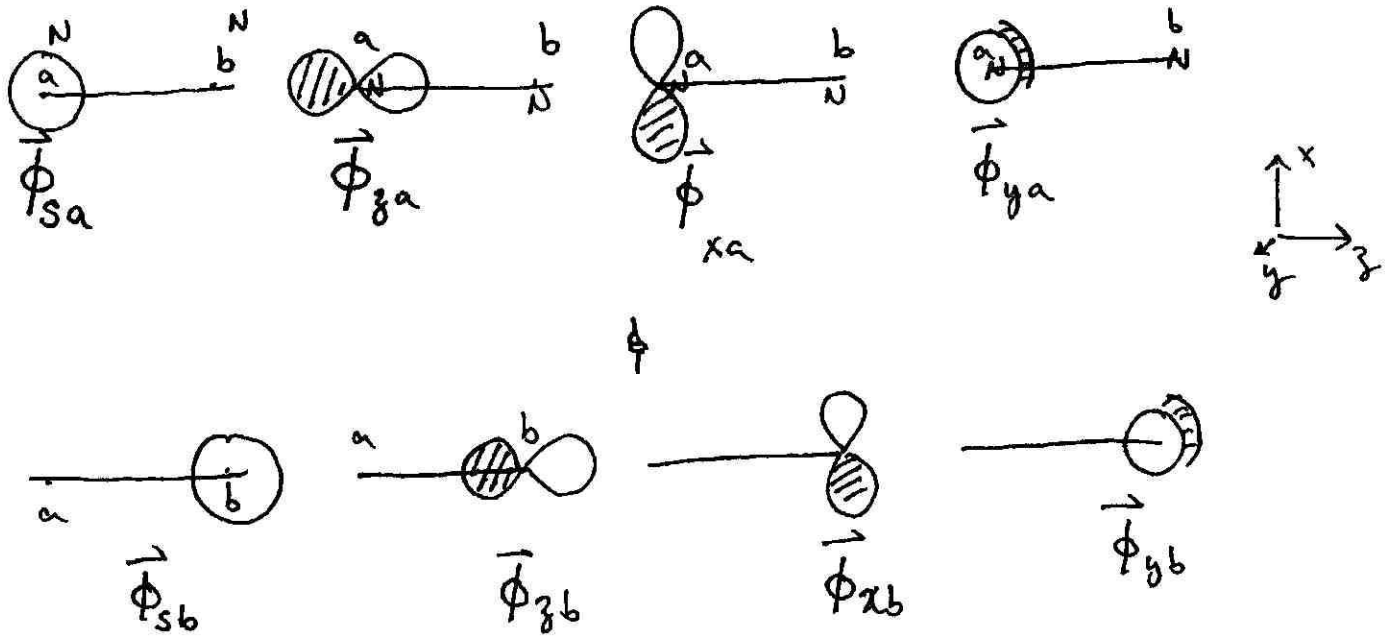
Lecture 20 On to N_2.

① For N_2 the atomic orbitals expressed as vectors are



② Written as vectors they become:

$$\vec{\phi}_{sa} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \vec{\phi}_{sb} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \vec{\phi}_{za} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \vec{\phi}_{zb} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\vec{\phi}_{xa} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \vec{\phi}_{xb} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \quad \vec{\phi}_{ya} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \quad \vec{\phi}_{yb} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

These are 8-dimensional vectors.

③ Just like in the H_2 problem we need to find the Hamiltonian, $\mathbb{H}$. $\mathbb{H}$ will be an 8×8 matrix:

$$\mathbb{H} = \begin{array}{c} \\ \phi_{sa}^\dagger \\ \phi_{sb}^\dagger \\ p_{xa}^\dagger \\ p_{xb}^\dagger \\ p_{ya}^\dagger \\ p_{yb}^\dagger \\ p_{za}^\dagger \\ p_{zb}^\dagger \end{array} \begin{array}{c} \begin{array}{cccccccc} \phi_{sa} & \phi_{sb} & p_{xa} & p_{xb} & p_{ya} & p_{yb} & p_{za} & p_{zb} \end{array} \\ \begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} & H_{15} & H_{16} & H_{17} & H_{18} \\ H_{21} & H_{22} & H_{23} & H_{24} & H_{25} & H_{26} & H_{27} & H_{28} \\ H_{31} & H_{32} & H_{33} & H_{34} & H_{35} & H_{36} & H_{37} & H_{38} \\ H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & H_{46} & H_{47} & H_{48} \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & H_{56} & H_{57} & H_{58} \\ H_{61} & H_{62} & H_{63} & H_{64} & H_{65} & H_{66} & H_{67} & H_{68} \\ H_{71} & H_{72} & H_{73} & H_{74} & H_{75} & H_{76} & H_{77} & H_{78} \\ H_{81} & H_{82} & H_{83} & H_{84} & H_{85} & H_{86} & H_{87} & H_{88} \end{pmatrix} \end{array}$$

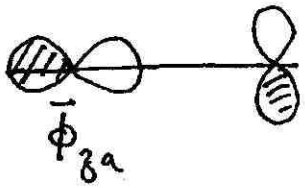
eg $\phi_{sa}^\dagger \mathbb{H} \vec{\phi}_{sb} = H_{12}$

That's 64 terms we need to find.

④ We need clues.

Clue 1. Lots of these orbitals don't interact with eachother.

$\left(\phi_{za}^\dagger \mathbb{H} \vec{\phi}_{xb} = 0 \right)$



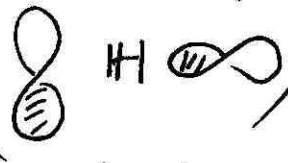
For example $\vec{\phi}_{za}$ and $\vec{\phi}_{xb}$ do not interact.

What does "do not interact" mean in terms of quantum mechanics? Answer: After measurement $\vec{\phi}_{za}$ and $\vec{\phi}_{xb}$ do not ever turn into eachother. That these orbitals "do not interact" means:

$$\vec{\phi}_{za}^{\,\dagger} \vec{\phi}_{xb} = 0 \qquad \vec{\phi}_{xb}^{\,\dagger} \vec{\phi}_{za} = 0$$

$$\vec{\phi}_{za}^{\,\dagger} \mathbb{H} \vec{\phi}_{xb} = 0 \qquad \vec{\phi}_{xb}^{\,\dagger} \mathbb{H} \vec{\phi}_{za} = 0$$

$\left(\phi_{xb}^\dagger \mathbb{H} \phi_{za} \right)$



⑤ Let us recall which atomic orbitals do not interact with eachother.

⑤ continued.

(i) No atomic orbital interacts with another atomic orbital on the same atom. eg. $\vec{\phi}_{sa}^{\dagger} H \vec{\phi}_{za} = 0$.

(ii) p_x orbitals do not interact with p_y or p_z orbitals eg. $\vec{\phi}_{xa}^{\dagger} H \vec{\phi}_{yb}$.

(iii) Similarly p_y orbitals do not interact with p_x or p_z orbitals and p_z orbitals " " " " p_x or p_y " .

(iv) In previously doing the N_2 problem we assumed (we will get rid of this assumption later) that s orbitals do not interact with p orbitals.

Assumption (for now) $\vec{\phi}_{sa}^{\dagger} H \vec{\phi}_{zb} = 0$

⑥ Taking into account all the statements in ⑤:

$$H = \begin{pmatrix} H_{11} & H_{12} & 0 & 0 & 0 & 0 & 0 & 0 \\ H_{21} & H_{22} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & H_{33} & H_{34} & 0 & 0 & 0 & 0 \\ 0 & 0 & H_{43} & H_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{55} & H_{56} & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{65} & H_{66} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & H_{77} & H_{78} \\ 0 & 0 & 0 & 0 & 0 & 0 & H_{87} & H_{88} \end{pmatrix}$$

⑦ Let's look at the terms along the diagonal of this square matrix.

$\vec{\phi}_{sa}^{\dagger} H \vec{\phi}_{sa} = H_{11}$; $\vec{\phi}_{sb}^{\dagger} H \vec{\phi}_{sb} = H_{22}$; $\vec{\phi}_{za}^{\dagger} H \vec{\phi}_{za} = H_{33}$ ...

(see vector list)

⑧ Recall that $\vec{\psi}^{\dagger} \mathbb{M} \vec{\psi}$ is the average measured value of $\mathbb{M}$ for the state $\vec{\psi}$.

$\therefore \vec{\phi}_{2a}^{\dagger} \mathbb{H} \vec{\phi}_{2a}$ is the average energy of the $\vec{\phi}_{2a}$ atomic orbital. This energy is (for Nitrogen) has been found to be -13.4 eV. (The $\vec{\phi}_{sa}$ energy has been found to be -26.0 eV)

So just from looking at the atomic orbital energies we find

$$\vec{\phi}_{sa}^{\dagger} \mathbb{H} \vec{\phi}_{sa} = \vec{\phi}_{sb}^{\dagger} \mathbb{H} \vec{\phi}_{sb} = -26.0 \text{ eV}$$

$$\vec{\phi}_{2a}^{\dagger} \mathbb{H} \vec{\phi}_{2a} = \vec{\phi}_{2b}^{\dagger} \mathbb{H} \vec{\phi}_{2b} = \vec{\phi}_{xa}^{\dagger} \mathbb{H} \phi_{xa} = \ldots = \vec{\phi}_{yb}^{\dagger} \mathbb{H} \vec{\phi}_{yb} = -13.4 \text{ eV}$$

We can call $\vec{\phi}_{sa}^{\dagger} \mathbb{H} \vec{\phi}_{sa} = \alpha_s = -26.0$ eV

and $\vec{\phi}_{2a}^{\dagger} \mathbb{H} \vec{\phi}_{2a} = \alpha_p = -13.4$ eV

⑨ The only terms left to find are:

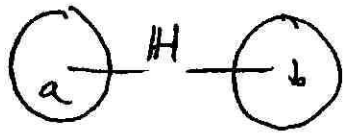
$$\begin{cases} \vec{\phi}_{sa}^{\dagger} \mathbb{H} \vec{\phi}_{sb} \\ \vec{\phi}_{sb}^{\dagger} \mathbb{H} \vec{\phi}_{sa} \end{cases} \quad \begin{cases} \vec{\phi}_{2a}^{\dagger} \mathbb{H} \vec{\phi}_{2b} \\ \vec{\phi}_{2b}^{\dagger} \mathbb{H} \vec{\phi}_{2a} \end{cases} \quad \begin{cases} \vec{\phi}_{xa}^{\dagger} \mathbb{H} \vec{\phi}_{xb} \\ \vec{\phi}_{xb}^{\dagger} \mathbb{H} \vec{\phi}_{xa} \end{cases}$$

$$\begin{cases} \vec{\phi}_{ya}^{\dagger} \mathbb{H} \vec{\phi}_{yb} \\ \vec{\phi}_{yb}^{\dagger} \mathbb{H} \phi_{ya} \end{cases}$$

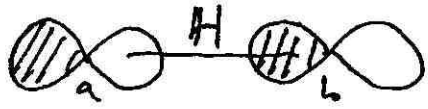
⑩ By symmetry $\vec{\phi}_{sa}^{\,\dagger} H \vec{\phi}_{sb} = \vec{\phi}_{sb}^{\,\dagger} H \vec{\phi}_{sa}$

& similarly all the bracketed pairs are equal. We can draw the four term pictorially.

$\vec{\phi}_{sa}^{\,\dagger} H \vec{\phi}_{sb}$

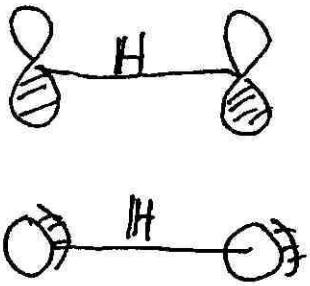


$\vec{\phi}_{za}^{\,\dagger} H \vec{\phi}_{zb}$



$\vec{\phi}_{xa}^{\,\dagger} H \vec{\phi}_{xb}$

$\vec{\phi}_{ya}^{\,\dagger} H \vec{\phi}_{yb}$



⑪ These last two pictures are just rotations of eachother. So $\vec{\phi}_{xa}^{\,\dagger} H \vec{\phi}_{xb} = \vec{\phi}_{ya}^{\,\dagger} H \vec{\phi}_{yb}$

We call the interaction in $\vec{\phi}_{xa} H \vec{\phi}_{xb}$ a π interaction.

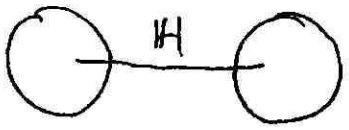
[Looking down the axis of the bond the picture look like  , which looks like a p orbital  & π is greek for p]

Let's call

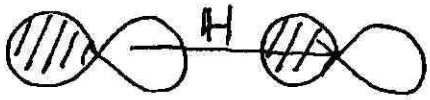
$$\vec{\phi}_{xa}^{\,\dagger} H \vec{\phi}_{xb} = \vec{\phi}_{ya}^{\,\dagger} H \vec{\phi}_{yb} \equiv \beta_\pi$$

β_π

(12) Similarly let's call:



$$\vec{\phi}_{sa}^{\,\dagger} H \vec{\phi}_{sb} = \beta_s$$



$$\vec{\phi}_{\sigma a}^{\,\dagger} H \vec{\phi}_{\sigma b} = -\beta_\sigma$$

We use (−) sign as the orbital is antibading, it makes De Broglie wave length, (I should say effective De Broglie wavelength) shorter & therefore higher in energy. [We use σ as axis of bond, picture looks like (II), as orbital (σ is greek for s)]

(13) The Hamiltonian reduces to

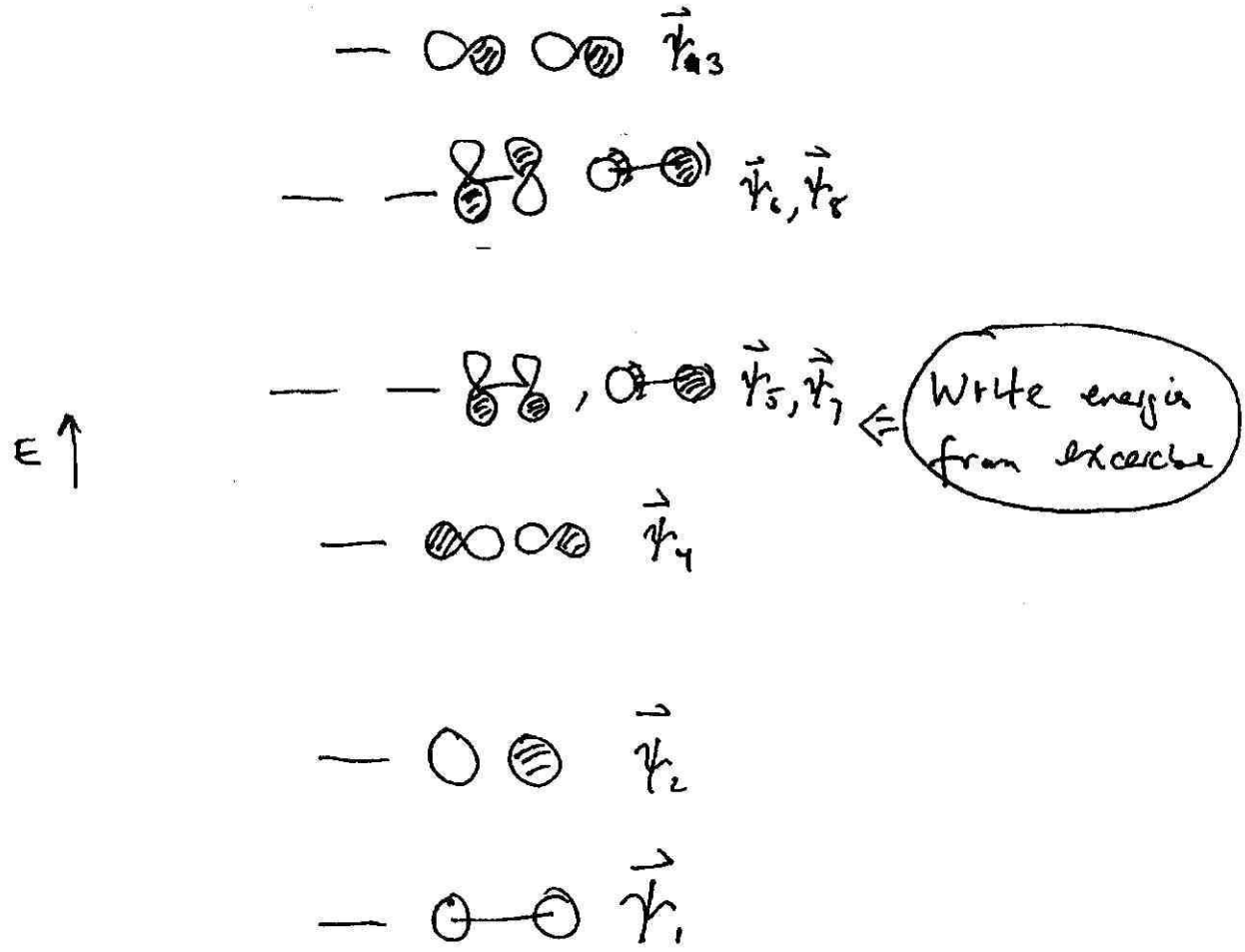
$$H = \begin{pmatrix} \alpha_s & \beta_s & 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_s & \alpha_s & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha_p & -\beta_\sigma & 0 & 0 & 0 & 0 \\ 0 & 0 & -\beta_\sigma & \alpha_p & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha_p & \beta_\pi & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_\pi & \alpha_p & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \alpha_p & \beta_\pi \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta_\pi & \alpha_p \end{pmatrix}$$

(14) Exercise :

Show $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$, $\vec{\psi}_1$, $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$, $\vec{\psi}_2$, $\begin{pmatrix} 0 \\ 0 \\ 1/\sqrt{2} \\ +1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$, $\vec{\psi}_3$, $\begin{pmatrix} 0 \\ 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$, $\vec{\psi}_4$, $\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ +1/\sqrt{2} \\ 0 \\ 0 \end{pmatrix}$, $\vec{\psi}_5$, $\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \\ 0 \\ 0 \end{pmatrix}$, $\vec{\psi}_6$, $\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}$, $\vec{\psi}_7$, & $\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix}$, $\vec{\psi}_8$

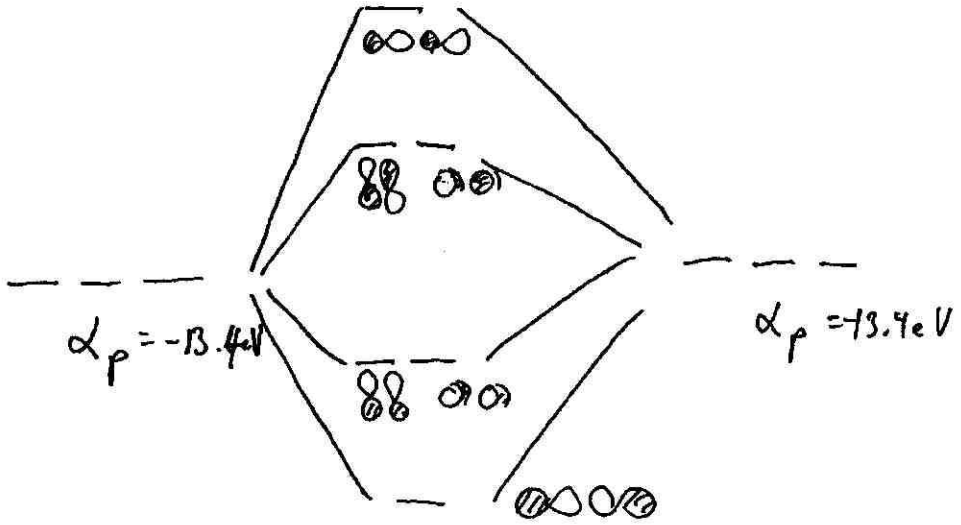
are eigenvectors. Find their eigenvalues.

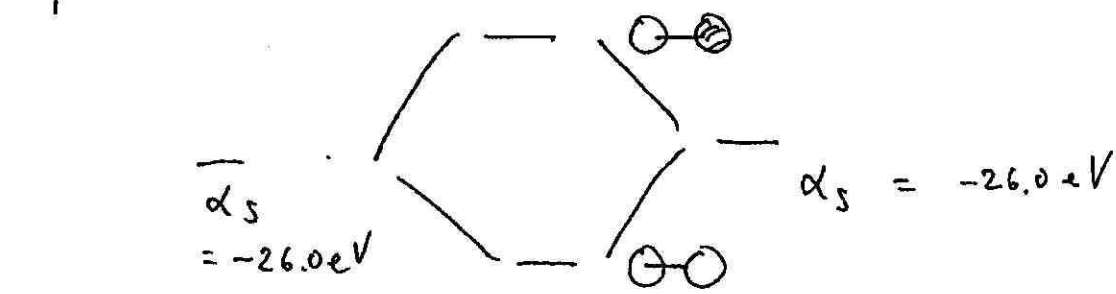
(15) Plotting pictorially :



This is the center portion of the N_2 diagram

(16) Placing the initial atomic energies on the side & lines connecting where orbitals come from:





This is the full MO diagram (assuming no s and p interactions.

(17) We can also use our experience to understand the first rule we put forward for making MO diagrams:
"The number of M.O = The number of A.O"
The M.O's are the eigenvectors of the Hamiltonian. The number of A.O's = the size of the square matrix Hamiltonian. (For N_2 it is 8×8). It turns out there are always at least as many eigenvectors as there are rows or columns in H.