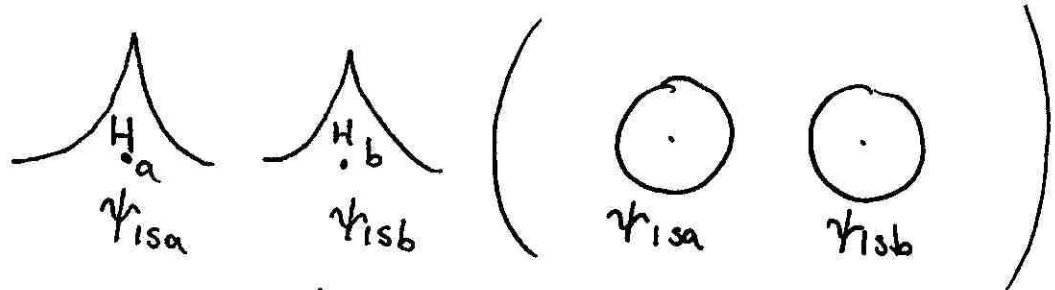
Lect.19 H_2 MO as a quantum matrix mechanics problem $\overset{19.2}{\text{(no page 19.1)}}$

4. We apply the rules of quantum matrix mechanics to the problem of the H_2 molecular orbital diagram.



Let's call $\quad \psi_{1sa} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \vec{\psi}_{1sa}$

$$\psi_{1sb} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \vec{\psi}_{1sb}$$

The measurement we are interested in is the energy. The energy measurement is called the Hamiltonian (after Hamilton). It is abbreviated $\mathbb{H}$.

5. $\mathbb{H}$ can be represented here as a 2×2 square matrix.

$$\mathbb{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

$$\vec{\psi}_{1sa}^{\dagger} \mathbb{H} \vec{\psi}_{1sa} = (1 \quad 0)\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = H_{11} = \text{energy of the } \psi_{1sa} \text{ orbital}$$

$$\vec{\psi}_{1sb}^{\dagger} \mathbb{H} \vec{\psi}_{1sb} = (0 \quad 1)\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = H_{22} = \text{" " " } \psi_{1sb} \text{ orbital.}$$

As these energies are equal $H_{11} = H_{22} = \alpha$.
The use of the letter α here is traditional. α is a real number here.

Excercise 1

Similarly show:

$$\vec{\psi}^{\dagger}_{1Sa} \, \mathbb{H} \, \vec{\psi}_{1Sb} = H_{12} \quad \text{and} \quad \vec{\psi}^{\dagger}_{1Sb} \, \mathbb{H} \, \vec{\psi}_{1Sa} = H_{21}$$

6. The first quantity measures the probability amplitude the $\mathbb{H}\vec{\psi}_{1Sb}$ state behaves like the $\vec{\psi}_{1Sa}$ state.
By symmetry this probability amplitude is the same as the probability amplitude the $\mathbb{H}\vec{\psi}_{1Sa}$ state behave like the $\vec{\psi}_{1Sb}$ state.

$$\therefore \quad H_{12} = H_{21} = \beta$$

β again is a traditional name. It is here also real. (β is actually negative).

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

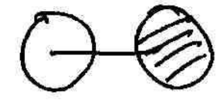
7. Any state, according to rule 2 of matrix mechanics, can be expressed as a linear combination of the eigenstates of $\mathbb{H}$.
What are the eigenstates of $\mathbb{H}$?
By inspection:

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} = (\alpha + \beta) \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

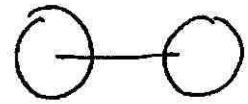
$$\& \quad \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix} = (\alpha - \beta) \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix}$$

(8) The eigenvectors of $\mathbb{H}$ are $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$ and $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$ with eigenvalues of respectively $\alpha+\beta$ & $\alpha-\beta$.

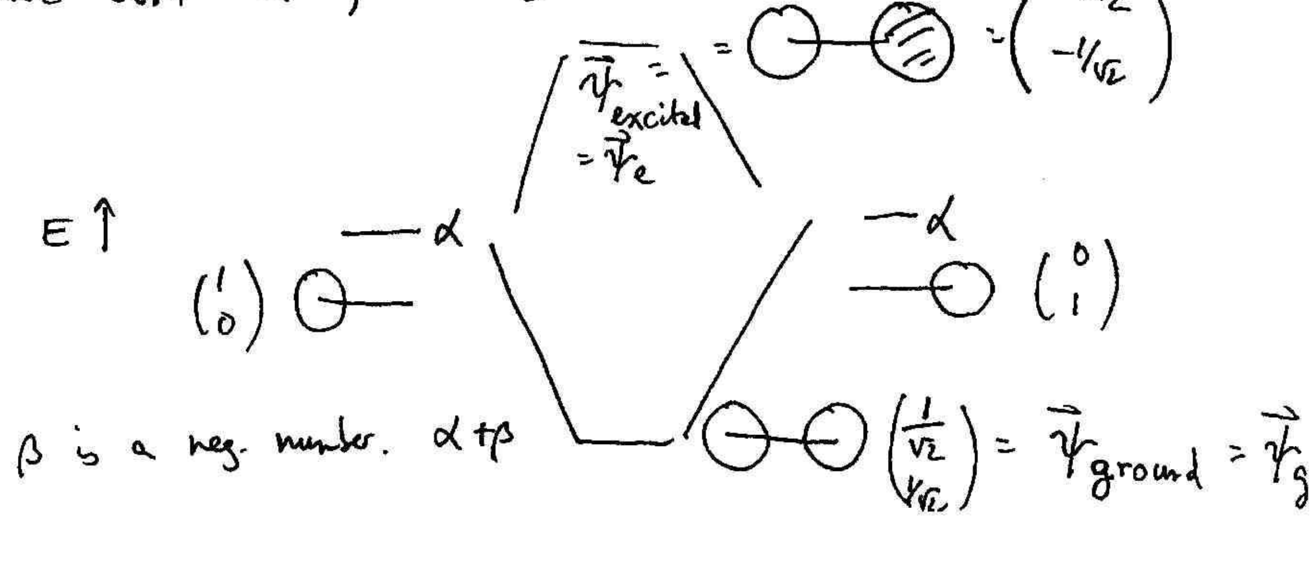
(9) We can draw pictures for the above eigenvectors

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

E $\uparrow$

$\alpha + \beta$ — $\begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}$ 

(10) If we include also our knowledge that the energies of $\vec{\psi}_{1sa}$ & $\vec{\psi}_{1sb}$ $\left[\begin{pmatrix} 1 \\ 0 \end{pmatrix} \& \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right]$ are both α, we find



The MO diagram for H_2 is just a diagram illustrating the energy eigenvectors and eigenvalue.

(11) We now can interpret the meaning of

$$\vec{\psi}_{1sa} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} + \frac{1}{\sqrt{2}}\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -1/\sqrt{2} \end{pmatrix}$$

$$= \frac{1}{\sqrt{2}}\psi_{ground} + \frac{1}{\sqrt{2}}\psi_{excited}.$$

The prob. amplitude that an electron will initial state $\vec{\psi}_{1sa}$ will behave as if it is a $\vec{\psi}_{ground}$ state is $1/\sqrt{2}$. The probability amplitude that an electron in the initial state $\vec{\psi}_{1sa}$ will behave as if it is $\vec{\psi}_{excited}$ is also $1/\sqrt{2}$.

If we measure the energy of the $\vec{\psi}_{1sa}$ state for an H_2 molecule ½ the time we will find the energy is $\alpha+\beta$ & half the time we will find the energy is $\alpha-\beta$.