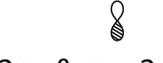


The m.o. on MOs

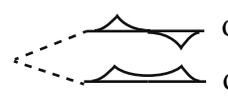
The example here is for 2 electrons, but the same can be done for any number of electrons

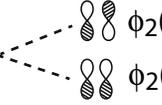
1) Pick an atomic basis; small for calculations by hand, large on the computer

ex:  $\phi_1(\mathbf{r})=1s_A$ & $\phi_2(\mathbf{r})=1s_B$ e.g. minimal basis for H_2
Shown as cut through x axis

ex:  $\phi_1=2p_A$ & $\phi_2=2p_B$ e.g. for a Hückel calculation; or for excited state; or for a bigger atom where p orbitals are partly filled; or just to get high accuracy from a bigger matrix.
Shown as polar plot

2) Combine atomic basis functions $\phi_m(\mathbf{r})$ into 1-electron MO basis functions $\phi_i(\mathbf{r})$, inspired by H_2^+ and adapted to molecular symmetry for larger molecules:

ex:  $\phi_2(\mathbf{r})=1\sigma^*(\mathbf{r})=1/\sqrt{2}\{\phi_1(\mathbf{r})-\phi_2(\mathbf{r})\}$
 $\phi_1(\mathbf{r})=1\sigma(\mathbf{r})=1/\sqrt{2}\{\phi_1(\mathbf{r})+\phi_2(\mathbf{r})\}$
e.g. for σ bond/antibond of H_2

ex:  $\phi_2(\mathbf{r})=\pi^*(\mathbf{r})=1/\sqrt{2}\{\phi_1(\mathbf{r})-\phi_2(\mathbf{r})\}$
 $\phi_1(\mathbf{r})=\pi(\mathbf{r})=1/\sqrt{2}\{\phi_1(\mathbf{r})+\phi_2(\mathbf{r})\}$
e.g. for π bond/antibond of ethylene

3) Multiply together 1-electron MO basis functions to obtain the multi-electron basis functions $\Psi_n(\mathbf{r}_1, \mathbf{r}_2, \dots)$:

ex: $\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1) \alpha_1 \phi_1(\mathbf{r}_2) \beta_2 = \sigma(\mathbf{r}_1) \alpha_1 \sigma(\mathbf{r}_2) \beta_2$ would be the lowest energy multi-electron basis function, each of the two electrons in a sigma-bonding orbital

ex: $\Psi_6(\mathbf{r}_1, \mathbf{r}_2) = \phi_2(\mathbf{r}_1) \alpha_1 \phi_2(\mathbf{r}_2) \beta_2 = \pi^*(\mathbf{r}_1) \alpha_1 \pi^*(\mathbf{r}_2) \beta_2$ would be as much higher energy multi-electron basis function, each of the two electrons in a pi-antibonding orbital

4) Make sure all multi-electron basis functions are antisymmetrized:

ex: $\Psi_0(\mathbf{r}_1, \mathbf{r}_2) \sim \phi_1(\mathbf{r}_1) \alpha_1 \phi_1(\mathbf{r}_2) \beta_2 - \phi_1(\mathbf{r}_2) \alpha_2 \phi_1(\mathbf{r}_1) \beta_1$

Note: this is a difference of products of two MOs, each of which is a sum of two AOs!!

$\Psi_5(\mathbf{r}_1, \mathbf{r}_2) \sim \pi(\mathbf{r}_1) \alpha_1 \pi^*(\mathbf{r}_2) \alpha_2 - \pi^*(\mathbf{r}_2) \alpha_2 \pi(\mathbf{r}_1) \alpha_1$

Note: this is multi-electron basis function for two unpaired electrons, one in a pi bonding orbital, the other in a pi-antibonding orbital

5) Calculate matrix elements of the Hamiltonian with your multielectron wavefunctions:

$$\text{Hamiltonian: } \hat{H} = \hat{h}_1 + \hat{h}_2 + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \leftarrow \begin{array}{l} \text{e-e repulsion} \\ \text{nuclear repulsion} \end{array}$$

$$\hat{h}_i = \frac{1}{2m_e} \hat{p}_i^2 - \frac{e^2}{4\pi\epsilon_0 r_{iA}} - \frac{e^2}{4\pi\epsilon_0 r_{iB}} \leftarrow \text{the "one electron terms"}$$

ex: $H_{00} = \langle \Psi_0 | H | \Psi_0 \rangle = \int dx_1 \int dy_1 \int dz_1 \int ds_1 \int dx_2 \int dy_2 \int dz_2 \int ds_2 \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2) H \Psi_0(\mathbf{r}_1, \mathbf{r}_2) \neq 0$ Note: ds is integration over the spin variable, e.g. $\langle \alpha | \beta \rangle = 0, \langle \alpha | \alpha \rangle = 1$

ex: $H_{05} = \langle \Psi_0 | H | \Psi_5 \rangle = \int dx_1 \int dy_1 \int dz_1 \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2) H \Psi_5(\mathbf{r}_1, \mathbf{r}_2) = 0$ The reason is the integral over $\langle \alpha_2 | \beta_2 \rangle$ etc is zero

6) Diagonalize the matrix:

$$H = \begin{pmatrix} H_{00} & H_{05} \\ H_{05} & H_{55} \end{pmatrix} = \begin{pmatrix} H_{00} & 0 \\ 0 & H_{55} \end{pmatrix}$$

In this example, the matrix is already diagonal, the Ψ_0 and Ψ_5 states don't mix. In fact, the ground (lowest energy) basis function NEVER mixes with singly excited states, so to a good approximation $\Psi_{\text{true}} \approx \Psi_0$ and $E_{\text{true}} \approx H_{00}$ for the ground state of a molecule. Very convenient.

