Basis in the : molecular orbitals (MO)

Next 2 lectures: the most common basis sets used for complete accurate electronic structure calculations

Today: NAOs
Next: Valence bonds (VBs)

$\hat{H} = h_1(\vec{r}_1)$ (H-atom) $+ h_2(\vec{r}_2)$ (H-atom) $+ \frac{e^2}{4\pi\varepsilon_0 r_{12}}$ (e-e repulsion) $+ \frac{e^2}{4\pi\varepsilon_0 R_{ec}}$ (nuclear repulsion) - sec N26.

little r is for distance between e's

Smallest basis: approximate $|1s_A\rangle|\pm\frac{1}{2}\rangle$ and $|1s_B\rangle|\pm\frac{1}{2}\rangle$ [4 functions] ($\pm\frac{1}{2}$: spin α or β)

Using what we learned about H_2^+, combine $|1s_A\rangle$ and $|1s_B\rangle$ into a new basis

$|\sigma^*\rangle = \frac{1}{\sqrt{2}}\{|1s_A\rangle - |1s_B\rangle\}|\pm\frac{1}{2}\rangle$

$|\sigma\rangle = \frac{1}{\sqrt{2}}\{|1s_A\rangle + |1s_B\rangle\}|\pm\frac{1}{2}\rangle$

Minimally we need 2 basis function, if neglected high energy σ^* orbitals

The actual basis functions must be antisymmetric:

$\Psi_1(\vec{r}_1, \vec{r}_2, S=0)$ (overall spin) $\hat{=} |1\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} |\sigma_g\rangle_1\alpha_1 & |\sigma_g\rangle_1\beta_1 \\ |\sigma_g\rangle_2\alpha_2 & |\sigma_g\rangle_2\beta_2 \end{vmatrix}$

$= \frac{1}{\sqrt{2}}\left(\{|\sigma_g\rangle_1|\sigma_g\rangle_2\alpha_1\beta_2 - |\sigma_g\rangle_1|\sigma_g\rangle_2\alpha_2\beta_1\}\right)$

$= \frac{1}{\sqrt{2}}|\sigma_g\rangle_1|\sigma_g\rangle_2\{\alpha_1\beta_2 - \alpha_2\beta_1\}$

$\{\alpha_1\beta_2 - \alpha_2\beta_1\}$: antisymmetric part of the wavefunction

$^1\Sigma$ state: $S=0$ has only one orientation: $S_z = M_S = 0$

made from σ orbitals, no π

both e⁻ in bonding orbital ⇒ lowest E ⇒ Pauli exclusion: must have opposite spin

An example of a higher energy basis function:

$$\psi_2(\vec{r}_1, \vec{r}_2, s=1) \hat{=} |2\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} |\sigma\rangle_1 \alpha_1 & |\sigma^*\rangle \alpha_1 \\ |\sigma\rangle_2 \alpha_2 & |\sigma^*\rangle_2 \alpha_2 \end{vmatrix}$$

$S=1$ has $M_S = \pm 1, 0, -1$

$^3\Sigma$ ← state

↑ note from s orbitals

$$= \frac{1}{\sqrt{2}} \left\{ |\sigma\rangle_1 |\sigma^*\rangle_2 - |\sigma^*\rangle_1 |\sigma\rangle_2 \right\} \alpha_1 \alpha_2$$

e⁻ must be in different spatial ~~orientation~~ orbitals ← same spin

$$\underset{\sim}{H} = \begin{pmatrix} H_{11} & 0 & \cdots \\ 0 & H_{22} & \\ \vdots & & H_{nn} \end{pmatrix} \rightarrow H_{12} = 0 \text{ (look)}$$

↖ very high energy, can leave out

$E_{low} \approx H_{11}$

$E_{high} \approx H_{22}$