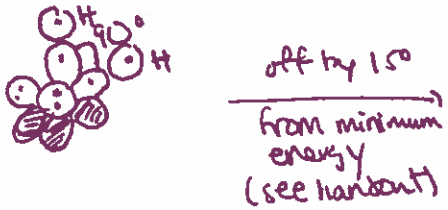
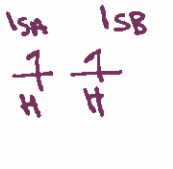
Potential energy surfaces II: H_2O in UB basis

In HF, $e_{1sH} \sim e_{2po2} \; e_{2s0} \gg e_{1s}$ oxygen

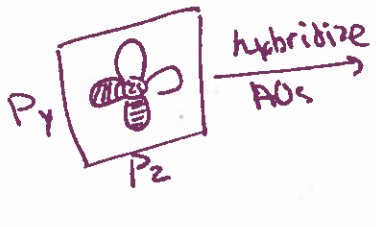
how to combine AOs to make UBs





$\langle 1s_A | \hat{H} | 2p_x \rangle =$ _____

Instead of using $1s_A, 1s_B, 2s, 2p_x, 2p_y \cdots$ mix-combine AOs to build a better basis



$$\phi_2 = \overset{c_1}{0.45}|2s\rangle + \overset{c_2}{0.7}|2p_y\rangle + \overset{c_3}{0.55}|2p\rangle$$

$$\phi_1 = c_1|2s\rangle - c_2|2p_y\rangle + c_3|2p_z\rangle$$

$$\phi_3 = 0.77|2s\rangle - 0.63|2p_z\rangle$$

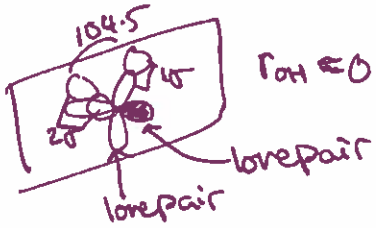
Combine hybrid AOs w/ $|1s_A\rangle$ & $|1s_B\rangle$ to make 2 bonds & 2 antibonds

$$|\sigma\rangle = c_1'|1s_B\rangle + c_2'|\phi_1\rangle$$ (use "−" sign for antibonding)

$$|2\sigma\rangle = c_1'|1s_A\rangle + c_2'|\phi_2\rangle$$

$|\phi_3\rangle$ & $|p_x\rangle$ = lone pairs

optimize all coefficients by HF-SCF



$$\psi_0 = A_{10}|1s^2|\sigma^2 2\sigma^2 \underbrace{2p_x^2 \phi_3^2}_{\text{lone pairs}}$$

Prediction: Both lone pairs are different