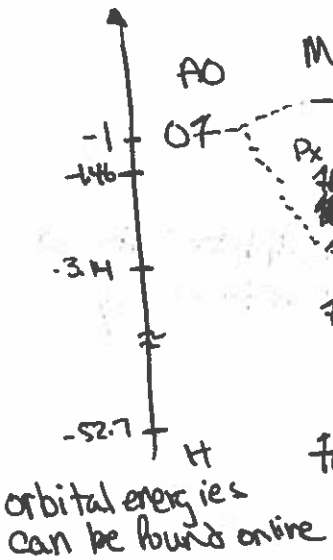
# Potential energy surfaces of molecules: ex: HF with MO basis




$\langle 1s_H | \hat{F} | 2p_{x,y} \rangle = 0$ but

$\langle 1s_H | \hat{F} | 2p_z \rangle \equiv H_{s,p_z} \neq 0$

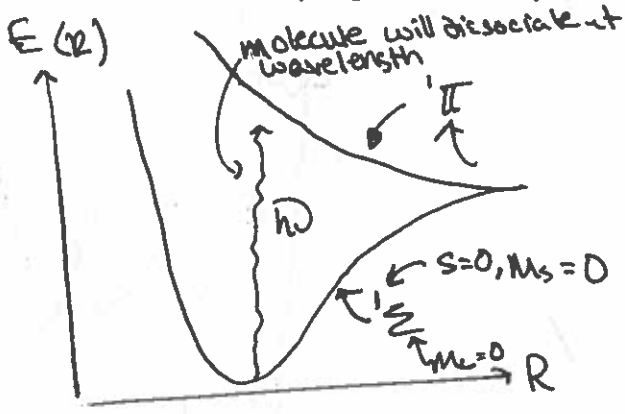
← too low in E

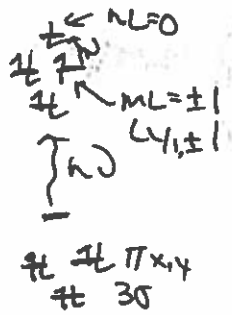
$$\underset{\approx}{\hat{H}}\, 1e^- \approx \begin{pmatrix} H_{1s_H} & H_{s_1p_z} & \text{small} \cdots \\ H_{s_1p_z} & H_{2p_z} & 0 \cdots \\ \text{small} & 0 & H_{2s} \\ \vdots & \vdots & \ddots \end{pmatrix}$$

diagonalize the 2x2 to yield approx $|3\sigma\rangle$ MO basis function

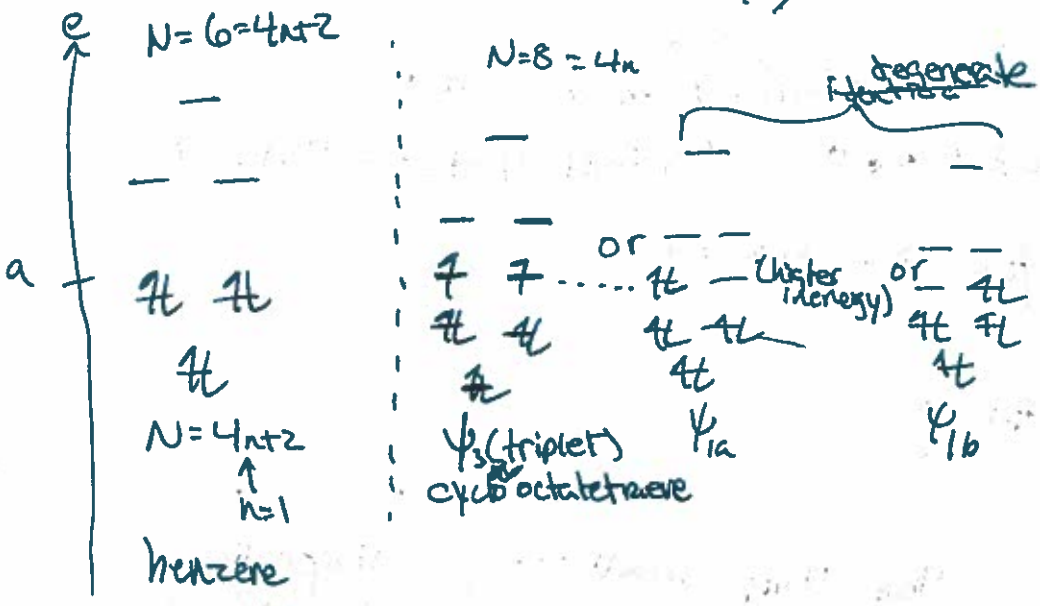
$$|\Psi_{valle}\rangle \sim \hat{A}_{10} \cdot 1s_F^2 2s_F^2 3\sigma^2 \pi_x^2 \pi_y^2$$

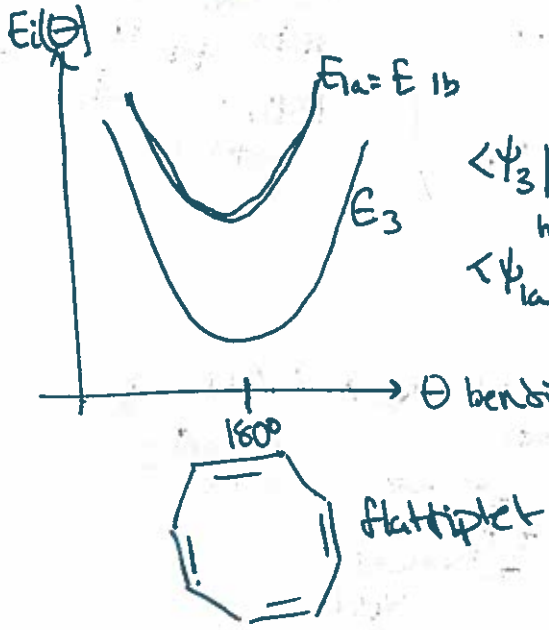
$$|3\sigma\rangle \approx 0.4|1s_H\rangle + 0.91|2p_{MZ}\rangle - \underbrace{0.01|2s\rangle}_{\text{not adding a lot}}$$



ex: cyclooctatetraene $\underset{\approx}{H} = \begin{pmatrix} ab\ 0 \cdots b \\ b\ ab \cdots 0 \\ \vdots \end{pmatrix}$ NxN matrix




$\langle \psi_3 | \hat{H} | \psi_{1ab} \rangle = 0$

however

$\langle \psi_{1a} | \hat{H} | \psi_{1b} \rangle \equiv U_{ab} \longrightarrow \begin{pmatrix} E_{1a} & U_{ab} \\ U_{ab} & E_{1b} \end{pmatrix} \longrightarrow \lambda = E, E'$