Solving the schrödinger equation through linear algebra

- Pick a complete orthonormal basis φ_n so $\psi = \sum c_n \varphi_n$
- calculate "matrix" elements $H_{mn} \hat{=} \langle m|H|n\rangle \hat{=} \int d\vec{r}\, \varphi_m^* H \varphi_n$
- Instead of solving the PDE $\hat{H}\psi = E\psi$ diagonalize the matrix

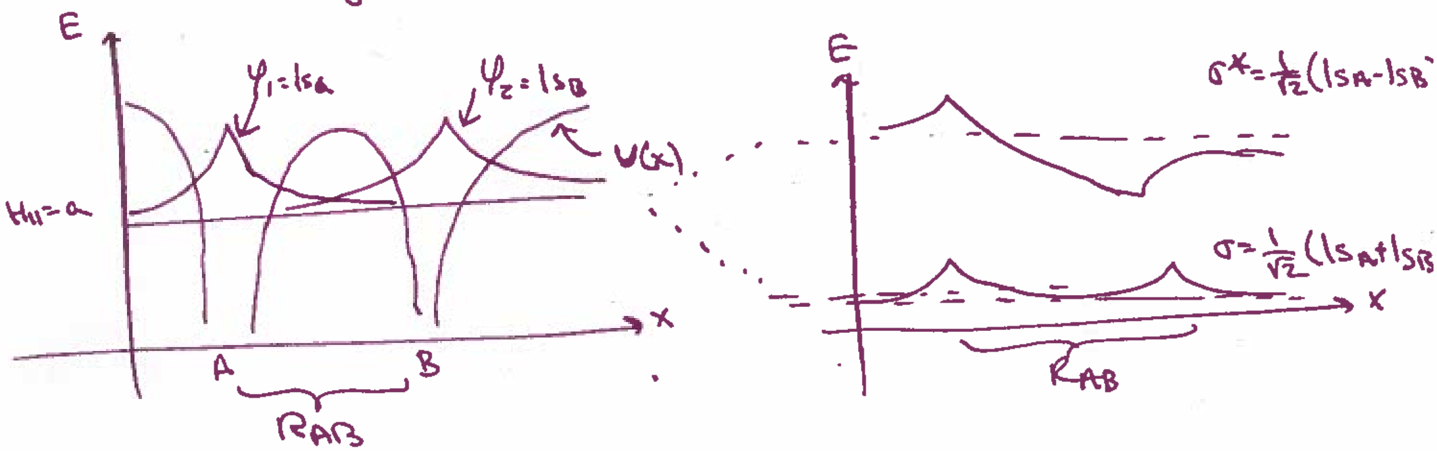
$$\underset{\approx}{H} = \begin{pmatrix} H_{11} & H_{12} & \cdots \\ H_{21} & H_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

solve
$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots \\ H_{21} & H_{22}-E & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0$$

Approximation for H_2^+: cut sum after φ_1 & φ_2:

Before diagonalizing: AO

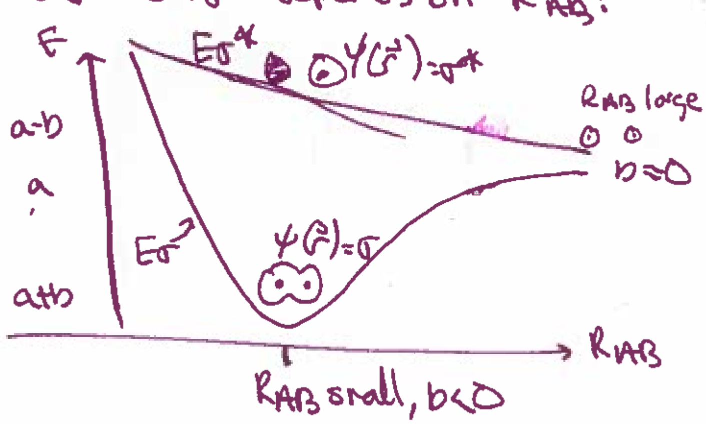
After diagonalizing: MO

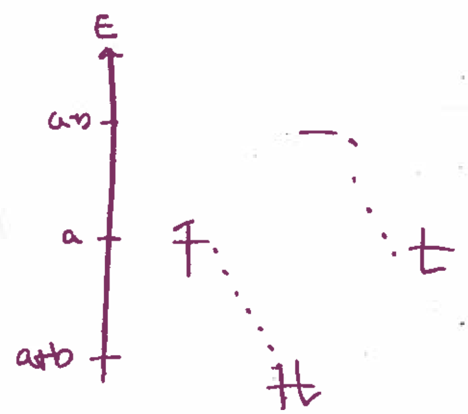


$$\underset{\approx}{H} = \begin{pmatrix} a & b \\ b & a \end{pmatrix}$$

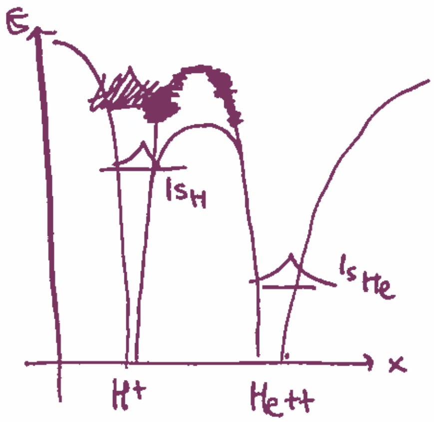
$$\left.\begin{aligned} E_{\sigma^*} &= a-b \\ E_\sigma &= a+b \end{aligned}\right\} \qquad \vec{v}_{\sigma^*} = \begin{pmatrix} +\ 1/\sqrt{2} \\ -\ 1/\sqrt{2} \end{pmatrix} \qquad \vec{v}_\sigma = \begin{pmatrix} +\ 1/\sqrt{2} \\ +\ 1/\sqrt{2} \end{pmatrix}$$

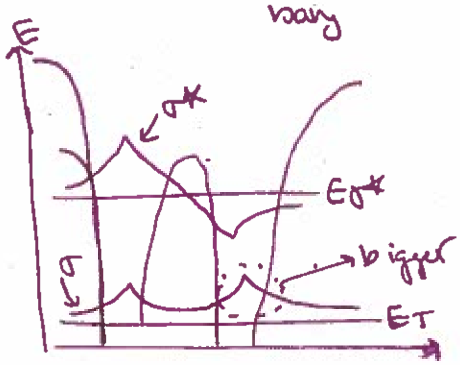
E_σ and E_{σ^*} depends on R_{AB}:

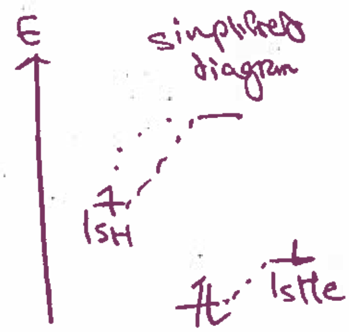




An asymmetric molecule; HeH^{++} or HeH^{+} ← 1st molecule after big bang







$\underset{\sim}{H} = \begin{pmatrix} a & b \\ b & c \end{pmatrix}$ $c<a$ → diagonalize

$V_\sigma \approx \begin{pmatrix} 0.2 \\ 0.98 \end{pmatrix}$ $V_{\sigma^*} \approx \begin{pmatrix} 0.98 \\ -0.3 \end{pmatrix}$