Calculating the molecular orbital of a molecule using "matrix elements" and linear algebra

The method: LA

$$\hat{H}\psi = E\psi$$

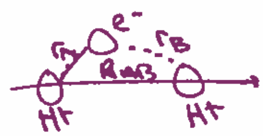
$$\updownarrow$$

$$\vec{v} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \quad \psi = \sum_n c_n \varphi_n(x)$$

$$H_{nm} = \int d\vec{r}\, \varphi_n \hat{H} \varphi_m$$

$\det(\underline{\underline{H}} - \underline{\underline{I}}E) = 0$ solves the matrix eigenvalue problem

The molecule: H_2^+



Minimal atomic basis

$\left.\begin{array}{l} \varphi_1 = 1s_A \sim e^{-r_A/a_0} \\ \varphi_2 = 1s_B \sim e^{-r_B/a_0} \end{array}\right\}$ should Graham Schmidt to get orthogonal basis $|1\rangle, |2\rangle$

Step 1: calculate the matrix

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{AB}}}_{\text{nuclei repulsion}}$$

$$H_{11} = \langle 1|\hat{H}|1\rangle = \int d\vec{r}\, \varphi_1^*(\vec{r})\hat{H}\varphi_1(\vec{r}) = a = H_{22}$$

$$H_{12}\ \langle 1|\hat{H}|2\rangle = \int d\vec{r}\, \varphi_1^*(\vec{r})\hat{H}\varphi_2(\vec{r}) = b = H_{21}^*$$

hole

$a < 0$ $\lim_{R_{AB}\to\infty} a = E_h$; $b < 0$ $\lim_{R_{AB}\to\infty} b = 0$

$$\underline{\underline{H}}\vec{v} = E\vec{v} \Rightarrow \begin{pmatrix} a & b \\ b & a \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

step 2: diagonalize to get eigenvalues & eigenvectors

$$\begin{vmatrix} a-E & b \\ b & a-E \end{vmatrix} = 0 = (a-E)^2 - b^2 \Rightarrow E\ a \pm b$$

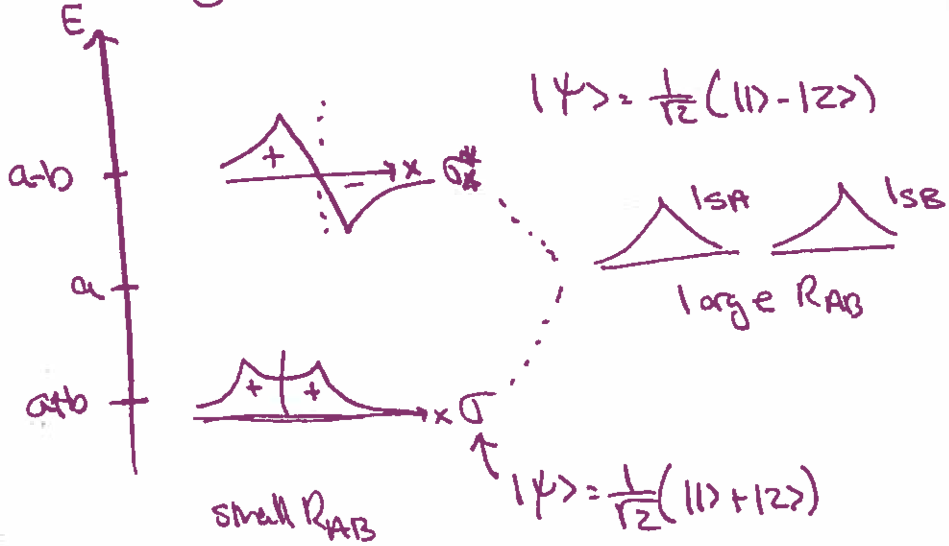
Eigenvectors

$$\left.\begin{array}{l} E_1 = a+b \\ (\underline{\underline{H}} - \underline{\underline{I}}E_1)\vec{v}_1 = 0 \end{array}\right\} \Rightarrow \begin{pmatrix} -b & b \\ b & -b \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \Rightarrow \left\{\begin{array}{l} c_1 = c_2 ;\ |c_1|^2 + |c_2|^2 = 1 \\ \Rightarrow \vec{v}_1 = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \end{array}\right.$$

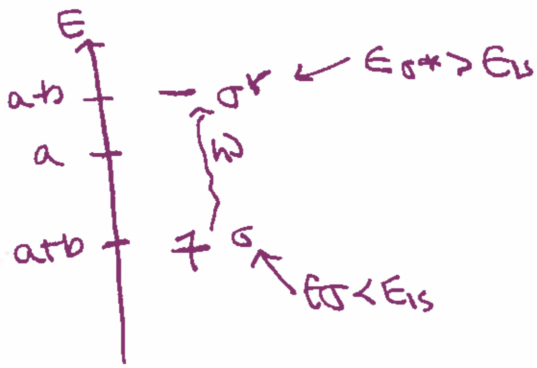
$$E_2 = a-b$$

$$\left.\begin{array}{l} E_2 = a-b \\ (\underset{\approx}{H} - \underset{\approx}{I}E_2)\vec{v}_2 = 0 \end{array}\right\} \begin{pmatrix} +b & b \\ b & +b \end{pmatrix}\begin{pmatrix} c_1' \\ c_2' \end{pmatrix} = 0 \Rightarrow \left\{ \begin{array}{l} c_1' = -c_2' \text{ or} \\ \vec{v}_2 \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix} \end{array}\right.$$

Plotting:



Fill in the e^-:



$$H_2^+ \xrightarrow{h\nu} H + H^+$$