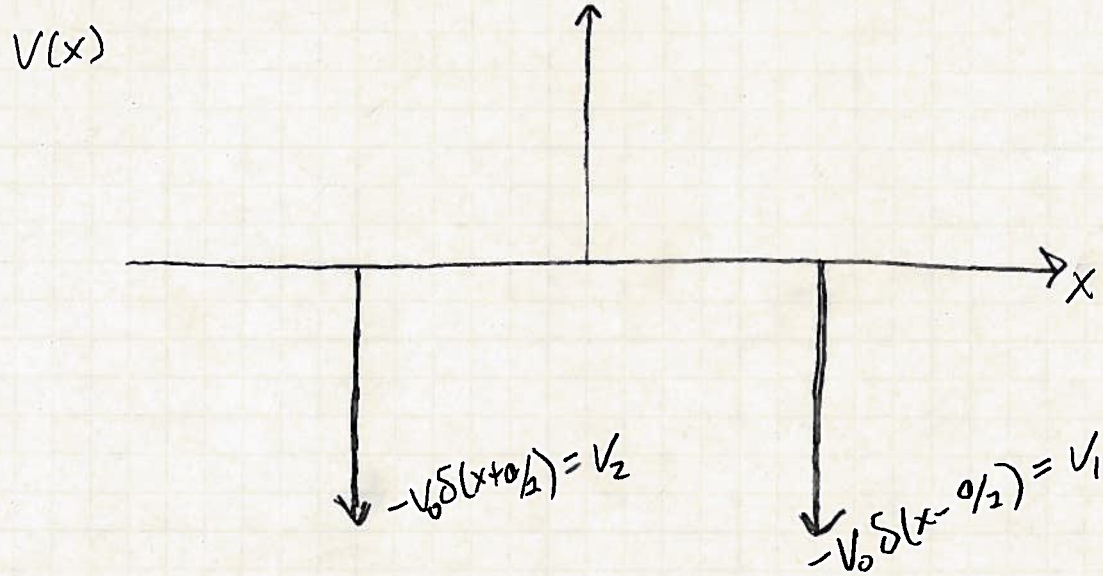
Bonding and antibonding Orbitals



$$f_1 = \sqrt{\alpha}\, e^{-\alpha|x-a/2|} \qquad \alpha \equiv \frac{mV_0}{\hbar^2}$$

$$f_2 = \sqrt{\alpha}\, e^{-\alpha|x+a/2|} \qquad \varepsilon = -\frac{mV_0^2}{2\hbar^2}$$

$$\hat{H} = \hat{T} + \hat{V} = \hat{T} + \hat{V}_1 + \hat{V}_2$$

with $V_1(x) = -V_0\,\delta(x-a/2)$

$V_2(x) = -V_0\,\delta(x+a/2)$

$$\langle f_1|\hat{H}|f_1\rangle = \langle f_1|\hat{T}+\hat{V}_1|f_1\rangle + \langle f_1|\hat{V}_2|f_1\rangle$$

$$= -\varepsilon \quad - V_0\int_{-\infty}^{\infty} dx\, |f_1(x)|^2\,\delta(x+a/2)$$

$$= -\varepsilon - V_0|f_1(x=-a/2)|^2$$

$$\boxed{H_{11} = \varepsilon - V_0\,\alpha\, e^{-2\alpha a}}$$

By symmetry $\boxed{H_{11} = H_{22}}$

$$H_{12} = \langle f_1 | \hat{T} | f_2 \rangle + \underbrace{\langle f_1 | \hat{V}_1 | f_2 \rangle + \langle f_1 | \hat{V}_2 | f_2 \rangle}$$

↳ By symmetry, these two have got to be the same → only need to do integral once

Now

$$\langle f_1 | \hat{T} | f_2 \rangle = \int_{-\infty}^{\infty} dx \, f_1(x) \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} f_2(x)$$

Now we have the slight problem that $\frac{d^2 f_2}{dx^2}$ is infinite at $x = -a/2$, so we have to deal w/ this singularity. Away from this singularity

$$\frac{d^2 f_2(x)}{dx^2} = \begin{cases} \alpha^{5/2} e^{-\alpha(x + a/2)} & x > -a/2 \\ \alpha^{5/2} e^{+\alpha(x + a/2)} & x < -a/2 \end{cases}$$

So

$$\langle f_1 | \hat{T} | f_2 \rangle = \frac{-\hbar^2}{2m} \int_{-\infty}^{-\frac{a}{2} - \varepsilon} dx \, \alpha^{1/2} e^{+\alpha(x - a/2)} \alpha^{5/2} e^{\alpha(x + a/2)} \rightarrow I_1$$

$$+ \frac{-\hbar^2}{2m} \int_{-a/2 + \varepsilon}^{a/2} dx \, \alpha^{1/2} e^{+\alpha(x - a/2)} \alpha^{5/2} e^{-\alpha(x + a/2)} \rightarrow I_2$$

$$+ \frac{-\hbar^2}{2m} \int_{a/2}^{\infty} dx \, \alpha^{1/2} e^{-\alpha(x - a/2)} \alpha^{5/2} e^{-\alpha(x + a/2)} \rightarrow I_3$$

$$- \frac{\hbar^2}{2m} \int_{-a/2 - \varepsilon}^{-a/2 + \varepsilon} dx \, f_1(x) \frac{d^2 f_2(x)}{dx^2} \rightarrow I_4$$

All of these integrals are straightforward → take lim $\varepsilon \to 0$, pull out $\alpha^{-3}\left(\frac{-\hbar^2}{2m}\right)$

$$I_1 = \int_{-\infty}^{-a/2} dx\, e^{2\alpha x}$$

$$= \frac{1}{2\alpha} e^{2\alpha x}\Big|_{-\infty}^{-a/2} = \frac{1}{2\alpha} e^{-2\alpha a/2} = \boxed{\frac{1}{2\alpha} e^{-\alpha a} = I_1}$$

$$I_2 = \int_{-a/2}^{a/2} dx\, e^{-2\alpha a/2}$$

$$\boxed{I_2 = e^{-\alpha a}\, a}$$

$$I_3 = \int_{a/2}^{\infty} dx\, e^{-2\alpha x} = -\frac{1}{2\alpha} e^{-2\alpha x}\Big|_{a/2}^{\infty}$$

$$\boxed{I_3 = \frac{1}{2\alpha} e^{-\alpha a}} \to \text{same as } I_1 \checkmark$$

$$I_4 = \lim_{\varepsilon \to 0} \int_{-a/2-\varepsilon}^{-a/2+\varepsilon} dx\, f_1(x) \frac{d^2 f_2(x)}{dx}$$

$$= \lim_{\varepsilon \to 0} f_1(-a/2) \int_{-a/2-\varepsilon}^{-a/2+\varepsilon} dx\, \frac{d^2 f_2(x)}{dx^2}$$

$$= f_1(-a/2) \lim_{\varepsilon \to 0} \int_{-\varepsilon}^{\varepsilon} dx\, \frac{d^2 \psi_1}{dx^2} = f_1(-a/2)\left(-\frac{2m V_0}{\hbar^2}\right)\psi_1(0)$$

$$= \sqrt{\alpha}\, e^{-\alpha a}(-2\alpha)\sqrt{\alpha}$$

$$= -2\alpha^2 e^{-\alpha a}$$

Combining

$$\langle f_1|\hat{T}|f_2\rangle = -\frac{\hbar^2}{2m}\alpha^3\left(\frac{1}{2\alpha}e^{-\alpha a} + 0\,e^{-\alpha a} + \frac{1}{2\alpha}e^{-\alpha a}\right)$$

$$-\frac{\hbar^2}{2m}\left(-2\alpha^2 e^{-\alpha a}\right)$$

$$= \frac{\hbar^2}{2m}\left(2\alpha^2 - \alpha^2 - \alpha^3 a\right)e^{-\alpha a}$$

$$\boxed{T_{12} = \frac{\hbar^2}{2m}\left(\alpha^2 - \alpha^3 a\right)e^{-\alpha a} = T_{21}}$$

since $\hat{T}$ is Hermitian

$$V_{12} = \int_{-\infty}^{\infty} dx\, f_1(x) f_2(x)\left[-V_0\delta(x-a/2) - V_0\delta(x+a/2)\right]$$

$$= -V_0 f_1(x-a/2) f_2(x-a/2) - V_0 f_1(x+a/2) f_2(x+a/2)$$

$$= -V_0\sqrt{\alpha}\,e^{-\alpha a}\sqrt{\alpha} \quad - V_0\sqrt{\alpha}\sqrt{\alpha}\,e^{-\alpha a}$$

$$V_{12} = -2V_0\alpha e^{-\alpha a} = V_{21}$$

So $\boxed{H_{12} = H_{21} = \left[\frac{\hbar^2}{2m}\left(\alpha^2 - \alpha^3 a\right) - 2V_0\alpha\right]e^{-\alpha a}}$

So the Hamiltonian Matrix is

$$H = \begin{bmatrix} \varepsilon - V_0 \alpha e^{-2\alpha a} & \left[\frac{\hbar^2}{2m}(\alpha^2 - \alpha^3 a) - 2V_0\alpha\right] e^{-2\alpha a} \\ \left(\frac{\hbar^2}{2m}(\alpha^2 - \alpha^3 a) - 2V_0\alpha\right) e^{-\alpha a} & \varepsilon - V_0 \alpha e^{-2\alpha a} \end{bmatrix}$$

$$= \begin{bmatrix} \varepsilon - h_1(a) & h_2(a) \\ h_2(a) & \varepsilon - h_1(a) \end{bmatrix}$$

Now for the S matrix, f_1 and f_2 are normalized so $S_{11} = \langle f_1 | f_1 \rangle$ and $S_{22} = \langle f_2 | f_2 \rangle$ are both one.

$$S_{12} = \langle f_1 | f_2 \rangle = \int_{-\infty}^{\infty} dx\, f_1(x)\, f_2(x)$$

$$= \int_{-\infty}^{-a/2} dx\, \alpha\, e^{+\alpha(x+a/2)}\, e^{+\alpha(x-a/2)}$$

$$+ \int_{-a/2}^{a/2} dx\, \alpha\, e^{-\alpha(x+a/2)}\, e^{+\alpha(x-a/2)}$$

$$+ \int_{a/2}^{\infty} dx\, \alpha\, e^{-\alpha(x+a/2)}\, e^{-\alpha(x-a/2)}$$

$$S_{12} = \frac{1}{2} e^{-\alpha a} + \alpha a e^{-\alpha a} + \frac{1}{2} e^{-\alpha a}$$

$$= (\alpha a + 1) e^{-\alpha a} \equiv S_1(a)$$

So

$$\mathbb{S} = \begin{bmatrix} 1 & S(a) \\ S(a) & 1 \end{bmatrix}$$

So now the task is to solve

$$(\mathbf{H} - \mathbf{S}E)\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

or $$S^{-1} H \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

The matrix $S^{-1}H$ depends on α...

see MATLAB code.

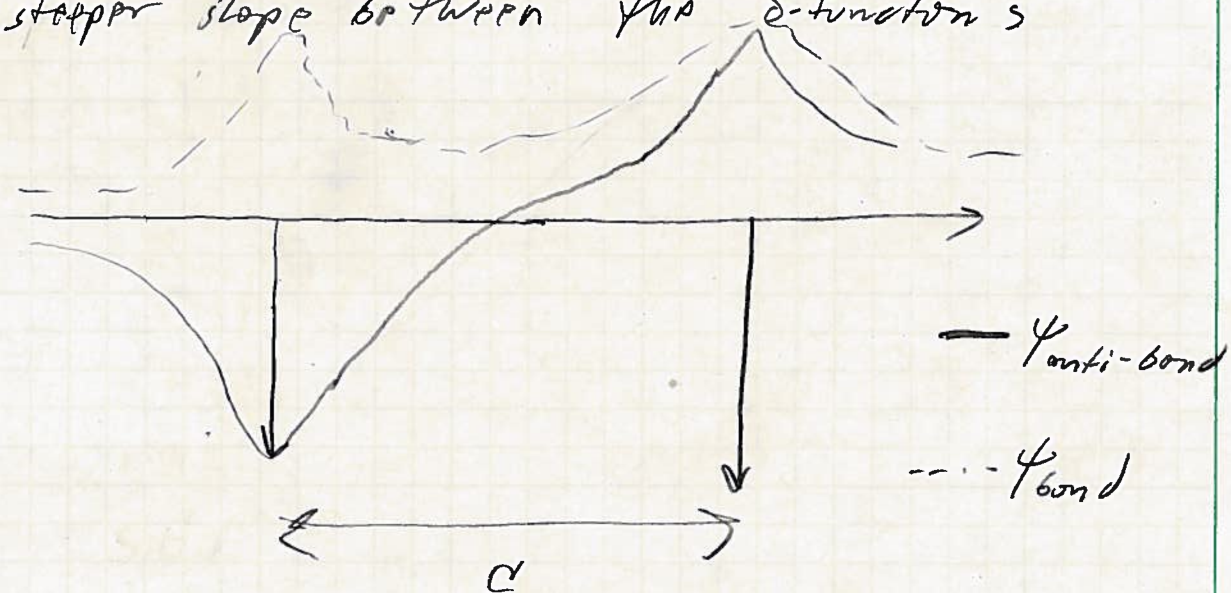
for soln and plot

By symmetry the only reasonable eigenvectors are

$$\underset{\sim}{\psi}_{bond} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \underset{\sim}{\psi}_{anti\text{-}bond} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Any other eigenvectors (orbital combinations) would favor one side of the molecule more than the other.

As the δ-functions get closer together the antibonding orbital has a steeper and steeper slope between the δ-functions



while the bonding orbital remains smooth. The kinetic energy of the bonding orbital gets very high for the antibonding orbital and is not compensated for by the lower potential energy.

The MATLAB plot shows the energy for the bonding and antibonding orbitals as a fcn of a.