1 Exercise 1 - Diatomic molecule

a. Calculate energies

Solution: The Schrödinger equation for this system reads

$$\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle, \tag{1}$$

where $\left|\Psi\right\rangle = c_1\left|1\right\rangle + c_2\left|2\right\rangle$. Now, to obtain the two equations we are looking for we need to compute the products $\langle 1|\hat{H}|\Psi\rangle$ and $\langle 2|\hat{H}|\Psi\rangle$, so let's do that.

$$\begin{aligned}
\left\langle 1\right|\hat{H}\left(c_1\left|1\right\rangle + c_2\left|2\right\rangle\right) &= \left\langle 1\right|E\left(c_1\left|1\right\rangle + c_2\left|2\right\rangle\right), \\
c_1\cancelto{E_0}{\langle 1|\hat{H}|1\rangle} + c_2\cancelto{\beta}{\langle 1|\hat{H}|2\rangle} &= c_1E\cancelto{1}{\langle 1|1\rangle} + c_2E\cancelto{S}{\langle 1|2\rangle}, \\
c_1(E_0 - E) + c_2(\beta - ES) &= 0.
\end{aligned} \tag{2}$$

The second equation is

$$\begin{aligned}
\left\langle 2\right|\hat{H}\left(c_1\left|1\right\rangle + c_2\left|2\right\rangle\right) &= \left\langle 2\right|E\left(c_1\left|1\right\rangle + c_2\left|2\right\rangle\right), \\
c_1\cancelto{\beta}{\langle 2|\hat{H}|1\rangle} + c_2\cancelto{E_0}{\langle 2|\hat{H}|2\rangle} &= c_1E\cancelto{S}{\langle 2|1\rangle} + c_2E\cancelto{1}{\langle 2|2\rangle}, \\
c_1(\beta - ES) + c_2(E_0 - E) &= 0.
\end{aligned} \tag{3}$$

Therefore the system composed by eq. 2 and eq. 3 has the following matrix

$$\begin{bmatrix} E_0 - E & \beta - ES \\ \beta - ES & E_0 - E \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}. \tag{4}$$

Such system has a non-trivial solution if

$$\begin{vmatrix} E_0 - E & \beta - ES \\ \beta - ES & E_0 - E \end{vmatrix} = 0. \tag{5}$$

Then, let's calculate it

$$\begin{aligned}
0 &= (E_0 - E)^2 - (\beta - ES)^2, \\
&= E_0^2 - 2E_0E + E^2 - (\beta^2 - 2\beta ES + E^2S^2), \\
&= E_0^2 - 2E_0E + E^2 - \beta^2 + 2\beta ES - E^2S^2, \\
&= E^2(1 - S^2) + E(2(\beta S - E_0)) + E_0^2 - \beta^2.
\end{aligned} \tag{6}$$

We can solve eq. 6 with the quadratic formula or plug it in wolfram alpha and save time. After doing that we will obtain the two solutions

$$\boxed{E_- = \frac{E_0 - \beta}{1 - S},} \tag{7}$$

$$\boxed{E_+ = \frac{E_0 + \beta}{1 + S}.} \tag{8}$$

If we plug eq. 8 into eq. 2 and assume $S + 1 \neq 0$ we get

$$\begin{aligned}
0 &= c_1\left(E_0 - \frac{E_0 + \beta}{S + 1}\right) + c_2\left(\beta - \frac{E_0 + \beta}{S + 1}S\right) \\
&= c_1(E_0(S + 1) - (E_0 + \beta)) + c_2(\beta(S + 1) - (E_0 + \beta)S), \\
&= c_1(E_0S + \cancel{E_0} - \cancel{E_0} - \beta)) + c_2(\cancel{\beta S} + \beta - E_0S - \cancel{\beta S}), \\
&= c_1(E_0S - \beta)) + c_2(\beta - E_0S), \\
&= c_1(E_0S - \beta)) - c_2(-\beta + E_0S), \\
&= (c_1 - c_2)(E_0S - \beta).
\end{aligned} \tag{9}$$

So if $(E_0 S - \beta) \neq 0$ then $c_1 = c_2$ solves eq. 9. Now if we use that to normalize Ψ we will find the analytical value

$$\begin{aligned}
1 &= \langle \Psi \mid \Psi \rangle, \\
&= (c_1 \langle 1| + c_1 \langle 2|)(c_1 |1\rangle + c_1 |2\rangle), \\
&= c_1^2(\langle 1| + \langle 2|)(|1\rangle + |2\rangle), \\
&= c_1^2(\cancelto{1}{\langle 1|1\rangle} + 2\cancelto{S}{\langle 1|2\rangle} + \cancelto{1}{\langle 2|2\rangle}), \\
&= c_1^2 2(1+S).
\end{aligned} \tag{10}$$

Therefore

$$c_1 = \frac{1}{\sqrt{2(1+S)}}, \tag{11}$$

when we take E_+, and the corresponding wavefunction is

$$\boxed{|\Psi_+\rangle = \frac{|1\rangle + |2\rangle}{\sqrt{2(1+S)}}.} \tag{12}$$

To derive the remaining wavefunction we can insert eq. 7 into eq. 3, assuming that $1 - S \neq 0$ we can perform this calculations

$$\begin{aligned}
0 &= c_1(\beta - \frac{E_0 - \beta}{1-S} S) + c_2(E_0 - \frac{E_0 - \beta}{1-S}), \\
&= c_1(\beta - \cancel{\beta S} - E_0 S + \cancel{\beta S}) + c_2(\cancel{E_0} - E_0 S - \cancel{E_0} + \beta), \\
&= c_1(\beta - E_0 S) + c_2(-E_0 S + \beta), \\
&= (c_1 + c_2)(\beta - E_0 S)
\end{aligned} \tag{13}$$

The solution to eq. 13 if $\beta - E_0 S \neq 0$ is $c_2 = -c_1$, we can then again normalize the wavefunction

$$\begin{aligned}
1 &= \langle \Psi \mid \Psi \rangle, \\
&= (c_1 \langle 1| - c_1 \langle 2|)(c_1 |1\rangle - c_1 |2\rangle), \\
&= c_1^2(\langle 1| - \langle 2|)(|1\rangle - |2\rangle), \\
&= c_1^2(\cancelto{1}{\langle 1|1\rangle} - 2\cancelto{S}{\langle 1|2\rangle} + \cancelto{1}{\langle 2|2\rangle}), \\
&= c_1^2 2(1-S).
\end{aligned} \tag{14}$$

Then

$$c_1 = \frac{1}{\sqrt{2(1-S)}}, \tag{15}$$

and we can finally write the normalized wavefunction

$$\boxed{|\Psi_-\rangle = \frac{|1\rangle + |2\rangle}{\sqrt{2(1-S)}}.} \tag{16}$$

To determine which one corresponds to the bonding and which one to the antibonding we need to remember that $\beta < 0$ and S is usually small hence we have $E_+ < E_-$, so **the bonding state corresponds to $|\Psi_+\rangle$ and the antibonding to $|\Psi_-\rangle$.**

Compared to the solution obtained in class condidering the overlap to be zero, we get an additional $1 + S$ or $1 - S$ factor on the energies, as well as in the normalization.

2 Exercise 2 - Heteronuclear diatomic molecule

a. Heteronuclear Diatomic Molecule

Solution: Now we are going to consider a heteronuclear diatomic molecule with two atoms A and B, and wavefunction

$$|\Psi\rangle = c_A |A\rangle + c_B |B\rangle . \tag{17}$$

using eqs. 1, and 17, we can do the following

$$\begin{aligned} \langle A| \hat{H} (c_A |A\rangle + c_B |B\rangle) &= \langle A| E (c_A |A\rangle + c_B |B\rangle), \\ c_A \cancelto{E_A}{\langle A|\hat{H}|A\rangle} + c_B \cancelto{\beta}{\langle A|\hat{H}|B\rangle} &= c_A E \cancelto{1}{\langle A|A\rangle} + c_B E \cancelto{0}{\langle A|B\rangle}, \\ c_A(E_A - E) + c_B\beta &= 0. \end{aligned} \tag{18}$$

the same with $\langle B|$

$$\begin{aligned} \langle B| \hat{H} (c_A |A\rangle + c_B |B\rangle) &= \langle B| E (c_A |A\rangle + c_B |B\rangle), \\ c_A \cancelto{\beta}{\langle B|\hat{H}|A\rangle} + c_B \cancelto{E_B}{\langle B|\hat{H}|B\rangle} &= c_A E \cancelto{0}{\langle B|A\rangle} + c_B E \cancelto{1}{\langle B|B\rangle}, \\ c_A\beta + c_B(E_B - E) &= 0. \end{aligned} \tag{19}$$

So now the system to solve is

$$\begin{bmatrix} E_A - E & \beta \\ \beta & E_B - E \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}. \tag{20}$$

The system has solution if

$$\begin{vmatrix} E_A - E & \beta \\ \beta & E_B - E \end{vmatrix} = 0, \tag{21}$$

and this means

$$\begin{aligned} 0 &= (E_A - E)(E_B - E) - \beta^2, \\ &= E_A E_B - E E_B - E E_A + E^2 - \beta^2, \\ &= E^2 + E(-1)(E_A + E_B) + (E_A E_B - \beta^2). \end{aligned} \tag{22}$$

The solution to eq. 22 is

$$\begin{aligned} E_\pm &= \frac{E_B + E_A \pm \sqrt{(E_A + E_B)^2 - 4(E_A E_B - \beta^2)}}{2}, \\ &= \frac{E_B + E_A \pm \sqrt{E_A^2 + E_B^2 + 2E_A E_B - 4E_A E_B + 4\beta^2)}}{2}, \\ &= \frac{E_B + E_A \pm \sqrt{(E_A - E_B)^2 + 4\beta^2)}}{2}, \\ &= \frac{E_B + E_A}{2} \pm \sqrt{\left(\frac{E_A - E_B}{2}\right)^2 + \beta^2}, \\ &= \boxed{\frac{E_B + E_A}{2} \pm \sqrt{\Delta^2 + \beta^2},} \end{aligned} \tag{23}$$

where in the last term we used

$$\Delta = \frac{E_A - E_B}{2}. \tag{24}$$

Now that we know this, obtaining the coefficients is really easy. Let's take for example eq. 18 and isolate c_B

$$c_A(E_A - E) + c_B\beta = 0,$$

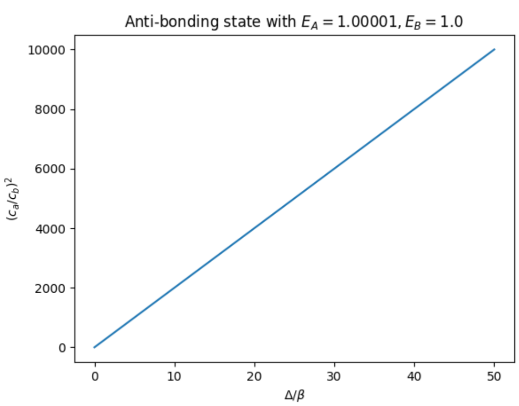
$$\Rightarrow \boxed{c_B = -\frac{c_A(E_A - E)}{\beta}}. \tag{25}$$

Now we must remember that the normalization on this case when $\langle A|B\rangle = 0$ imposes $c_A^2 + c_B^2 = 1$, hence

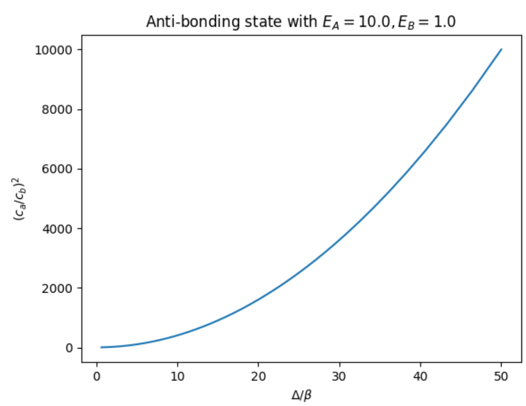
$$\begin{aligned} 1 &= c_A^2 + c_B^2, \\ &= c_A^2 + c_A^2\left(\frac{E_A - E}{\beta}\right)^2, \\ &= c_A^2\left(1 + \left(\frac{E_A - E}{\beta}\right)^2\right). \end{aligned}$$

$$\Rightarrow \boxed{c_A} \boxed{= \frac{1}{\sqrt{1 + \left(\frac{E_A - E}{\beta}\right)^2}}}. \tag{26}$$

Now we just need to plug the energy of the bonding state (E_-) or the anti-bonding state (E_+), in order to get the coefficients we are looking for.



a)



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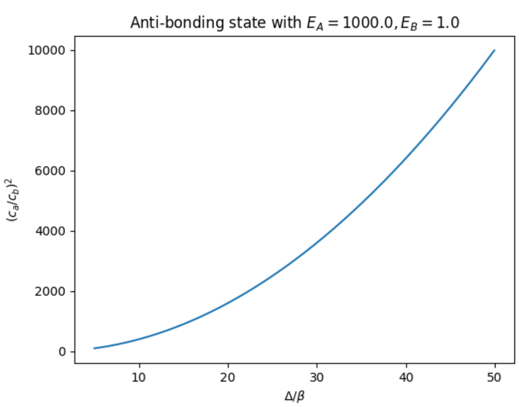

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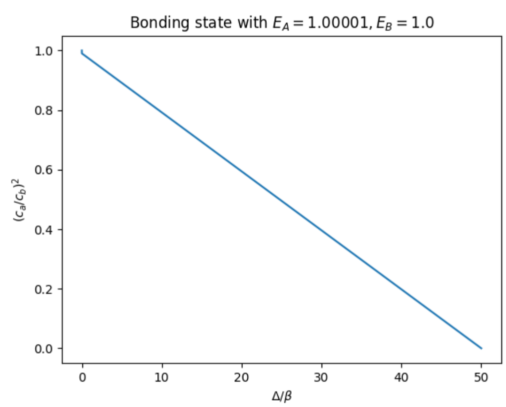

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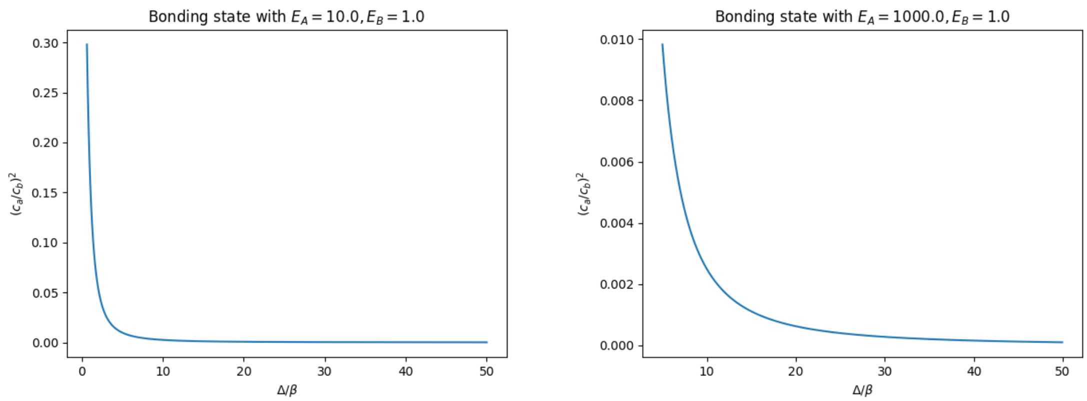

e) f)

Figure 1: $(c_a/c_b)^2$ plotted for the anti-bonding (a,b,c) and the bonding states (d,e,f)

As we can see in Fig. 1 as Δ/β increases, the ratio $(c_a/c_b)^2$ increases for the anti-bonding state, and decreases for the bonding state. Therefore, most of the charge would be concentrated at molecule A for the anti-bonding state, and at molecule B for the bonding state. Also as the energy difference between the two molecules goes to zero the curves tend to straight lines, but the order of magnitude of $(c_a/c_b)^2$ is the same.

3 Exercise 3 - Tight-binding chain in 1D

a. Radii

Solution: d