

1 Exercise 1 - Diatomic molecule

a. Calculate energies

Solution: The Schrödinger equation for this system reads

$$\hat{H} |\Psi\rangle = E |\Psi\rangle, \quad (1)$$

where $|\Psi\rangle = c_1 |1\rangle + c_2 |2\rangle$. 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.

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

The second equation is

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

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

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

Such system has a non-trivial solution if

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

Then, let's calculate it

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

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

$$E_- = \frac{E_0 - \beta}{1 - S}, \quad (7)$$

$$E_+ = \frac{E_0 + \beta}{1 + S}. \quad (8)$$

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

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

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

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

Therefore

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

when we take E_+ , and the corresponding wavefunction is

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

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

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

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

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

Then

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

and we can finally write the normalized wavefunction

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

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 considering 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

$$|\Psi\rangle = c_A |A\rangle + c_B |B\rangle. \quad (17)$$

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

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

the same with $\langle B |$

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

So now the system to solve is

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

The system has solution if

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

and this means

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

The solution to eq. 22 is

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

where in the last term we used

$$\Delta = \frac{E_A - E_B}{2}. \quad (24)$$

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

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

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

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

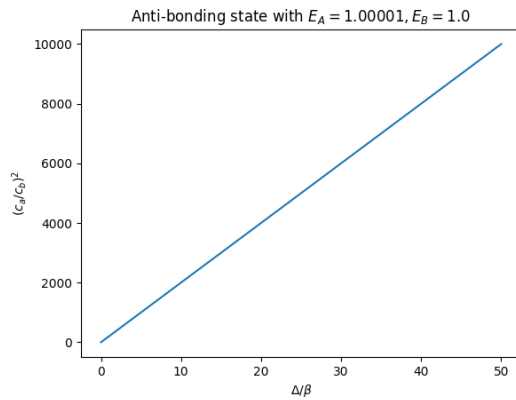
$$1 = c_A^2 + c_B^2,$$

$$= c_A^2 + c_A^2 \left(\frac{E_A - E}{\beta} \right)^2,$$

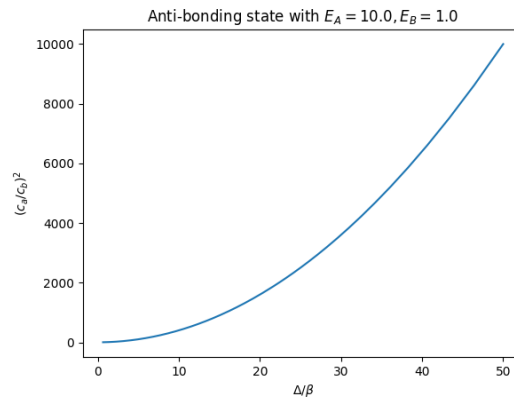
$$= c_A^2 \left(1 + \left(\frac{E_A - E}{\beta} \right)^2 \right).$$

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

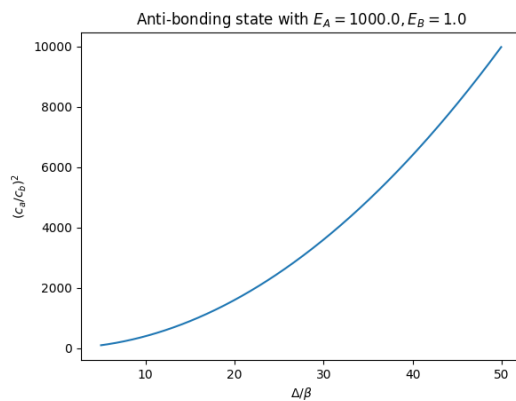
Now we just need to plug the energy of the bonding state (E_-) or the anti-bonding state (E_+), in order to get the coefficients we are looking for.



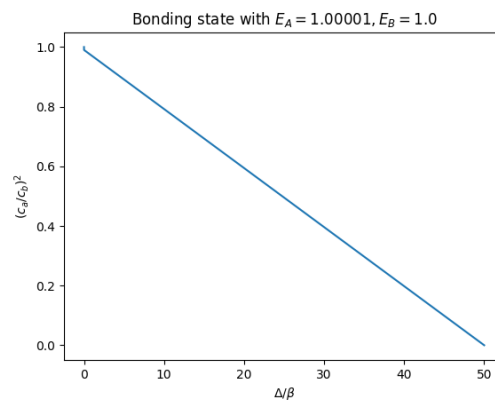
a)



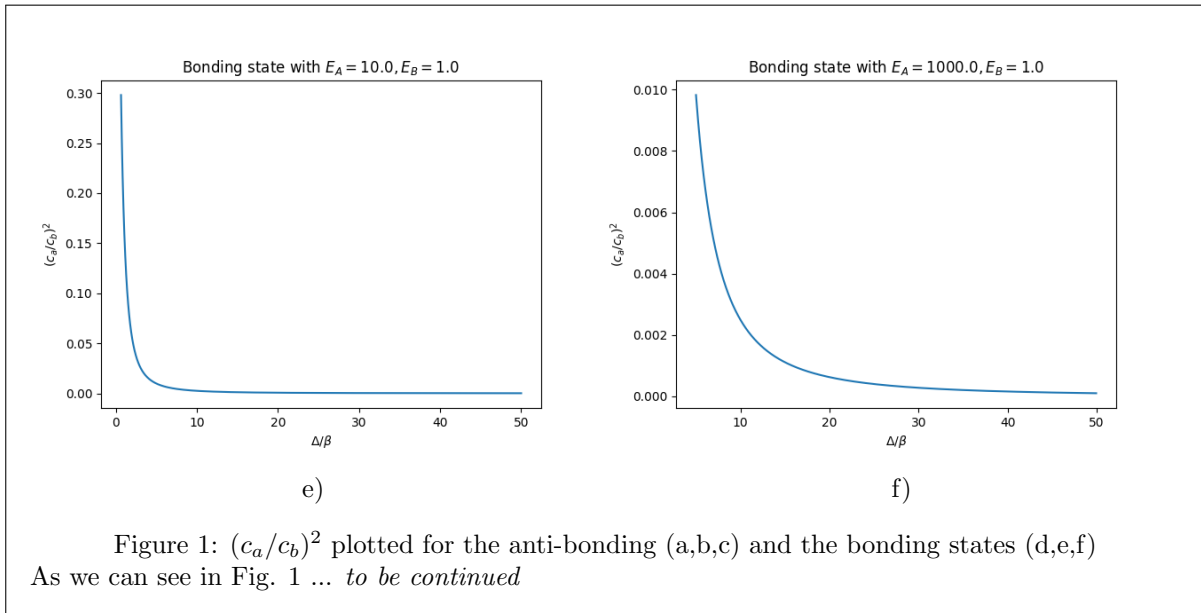
b)



c)



d)



3 Exercise 3 - Tight-binding chain in 1D

a. Radii

Solution: d