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 $\left\langle 1\right|\hat{H}\left|\Psi\right\rangle$ and $\left\langle 2\right|\hat{H}\left|\Psi\right\rangle$, so let's do that.

$$\left\langle 1\right|\hat{H}\left(c_1\left|1\right\rangle + c_2\left|2\right\rangle\right) = \left\langle 1\right|E\left(c_1\left|1\right\rangle + c_2\left|2\right\rangle\right),$$

$$c_1\underbrace{\left\langle 1|\hat{H}|1\right\rangle}_{E_0} + c_2\underbrace{\left\langle 1|\hat{H}|2\right\rangle}_{\beta} = c_1 E\underbrace{\left\langle 1|1\right\rangle}_{1} + c_2 E\underbrace{\left\langle 1|2\right\rangle}_{S},$$

$$c_1(E_0 - E) + c_2(\beta - ES) = 0. \tag{2}$$

The second equation is

$$\left\langle 2\right|\hat{H}\left(c_1\left|1\right\rangle + c_2\left|2\right\rangle\right) = \left\langle 2\right|E\left(c_1\left|1\right\rangle + c_2\left|2\right\rangle\right),$$

$$c_1\underbrace{\left\langle 2|\hat{H}|1\right\rangle}_{\beta} + c_2\underbrace{\left\langle 2|\hat{H}|2\right\rangle}_{E_0} = c_1 E\underbrace{\left\langle 2|1\right\rangle}_{S} + c_2 E\underbrace{\left\langle 2|2\right\rangle}_{1},$$

$$c_1(\beta - ES) + c_2(E_0 - E) = 0. \tag{3}$$

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

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

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

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

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

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

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

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

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

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

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 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

$$\langle A| \hat{H} (c_A |A\rangle + c_B |B\rangle) = \langle A| E (c_A |A\rangle + c_B |B\rangle),$$

$$c_A \underbrace{\langle A|\hat{H}|A\rangle}_{E_A} + c_B \underbrace{\langle A|\hat{H}|B\rangle}_{\beta} = c_A E \underbrace{\langle A|A\rangle}_{1} + c_B E \underbrace{\langle A|B\rangle}_{0},$$

$$c_A(E_A - E) + c_B\beta = 0. \tag{18}$$

the same with $\langle B|$

$$\langle B| \hat{H} (c_A |A\rangle + c_B |B\rangle) = \langle B| E (c_A |A\rangle + c_B |B\rangle),$$

$$c_A \underbrace{\langle B|\hat{H}|A\rangle}_{\beta} + c_B \underbrace{\langle B|\hat{H}|B\rangle}_{E_B} = c_A E \underbrace{\langle B|A\rangle}_{0} + c_B E \underbrace{\langle B|B\rangle}_{1},$$

$$c_A\beta + c_B(E_B - E) = 0. \tag{19}$$

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

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

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

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

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

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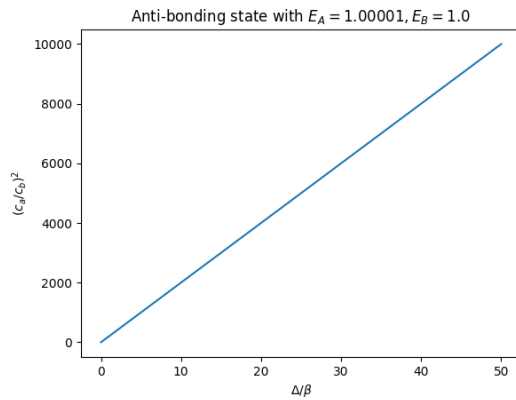
$$1 = c_A^2 + c_B^2,$$
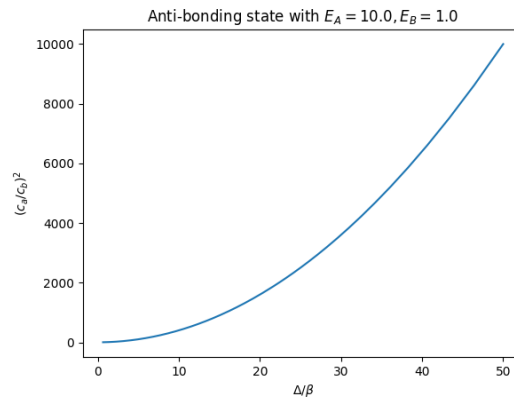
$$= c_A^2 + c_A^2 \left(\frac{E_A - E}{\beta}\right)^2,$$

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

$$\Rightarrow c_A = \frac{1}{\sqrt{1 + \left(\frac{E_A - E}{\beta}\right)^2}}. \tag{26}$$
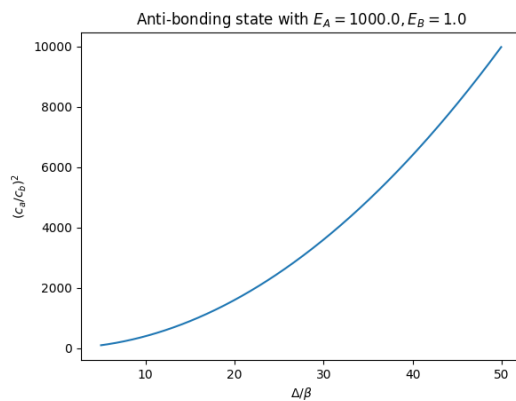
Now we just need to plug the energy of the bonding state (E_-) or the anti-bonding state (E_+), in order to get the coefficients we are looking for.
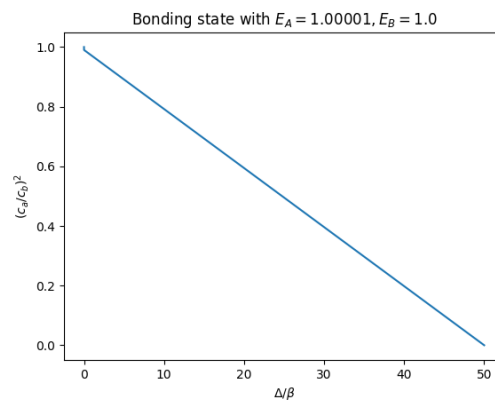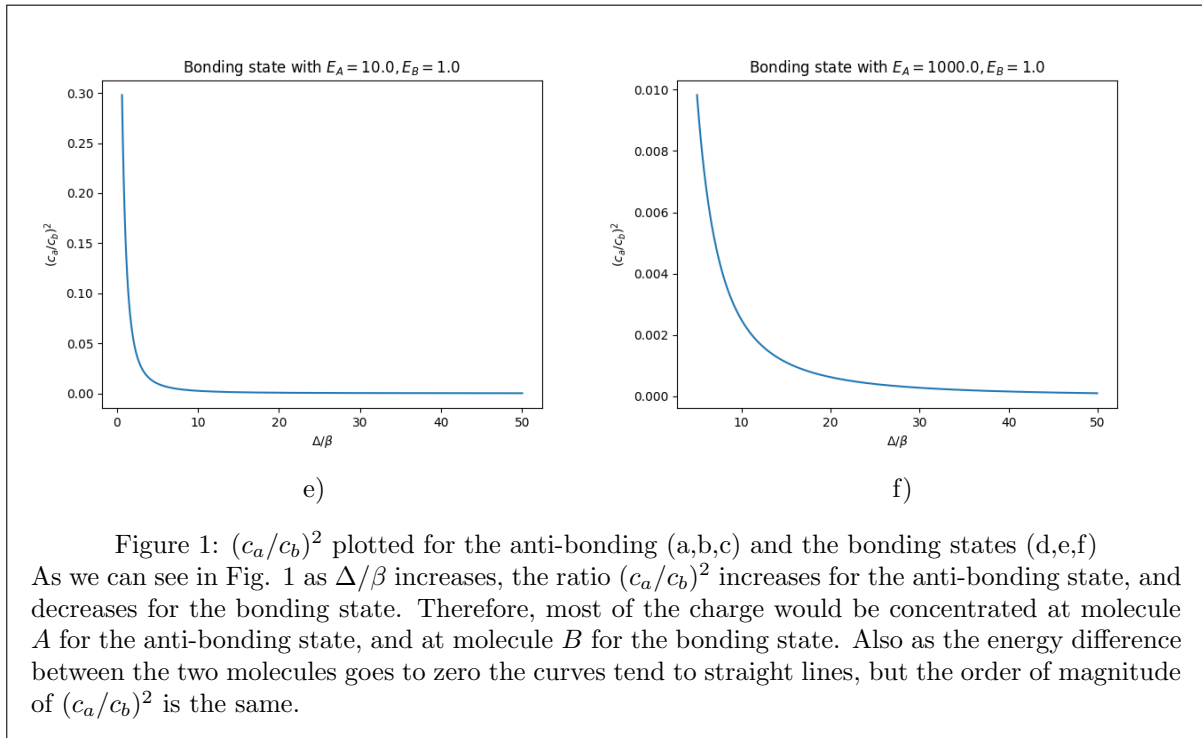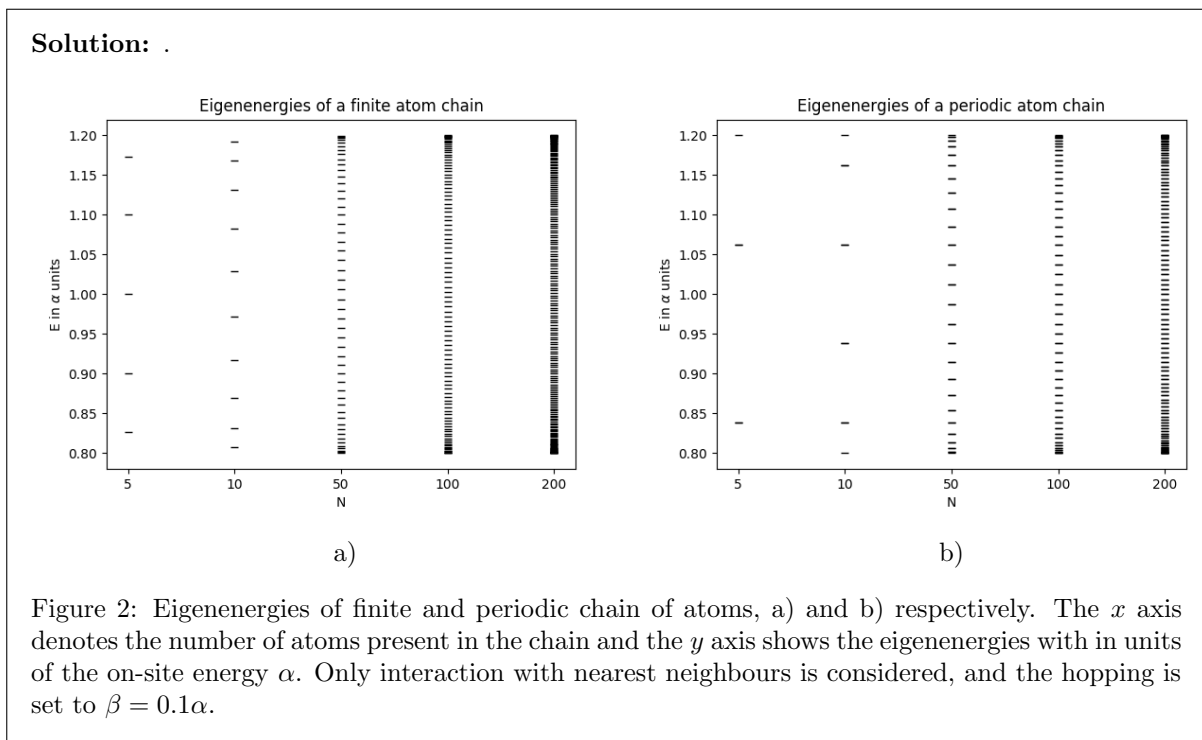

a)

b)

c)

d)

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. Eigenenergies and Spectrum

Solution: .

Figure 2: Eigenenergies of finite and periodic chain of atoms, a) and b) respectively. The x axis denotes the number of atoms present in the chain and the y axis shows the eigenenergies with in units of the on-site energy α. Only interaction with nearest neighbours is considered, and the hopping is set to $\beta = 0.1\alpha$.

As in the lecture, we can see that as the number of atoms in the chain (N) increases the spectrum widens. Also we can see in both cases that when N is too large the width of the spectrum is approximately 0.4, this totally makes sense, since we expect the full width to be 4β when $N \to \infty$ The spectrum of the finite chain is given by

$$E = \alpha + 2\beta \cos\left(\pi m/(N+1)\right), \quad m \in 1, \ldots, N \tag{27}$$

And as we can see in fig. 2 the numericall results fit fairly well.

a)   b)
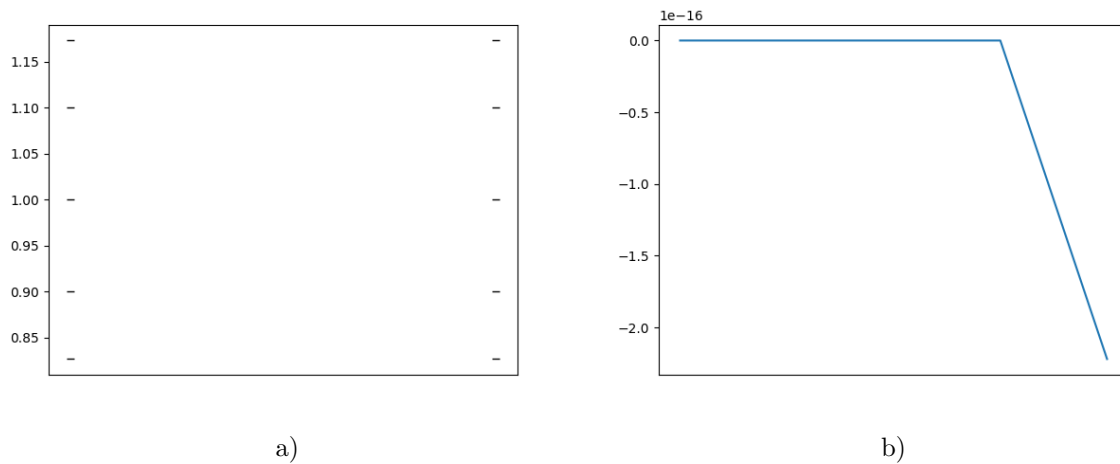
Figure 3: a) On the left column the spectrum obtained numerically is shown, on the right the one obtained using eq. 27. b) The difference between the anallytical and the numerical spectrum is plotted. Both plots for the case when $N = 5$, the remaining N values yield similar results.

b. Analysis of the periodic chain

Solution: When we add periodic boundary conditions we can see that some degeneracies arise. Also we can see that no matter what N we have, we always have an energy of $1.2 = \alpha + 2\beta$, which is to be expected since the spectrum now is given by

$$E = \alpha + 2\beta \cos\left(2\pi m/N\right), \quad m \in 0, 1, \ldots, N-1, \tag{28}$$

and $E = \alpha + 2\beta$ corresponds to the case when $m = 0$, which we always have. So, this is the reason why we can always reach that energy in the periodic chain as oposed to the finite chain. The degeneracies are explained by eq, 28 and the fact that the cosine is a periodic function. And finally, again as $N \to \infty$ the width of the spectrum tends to 4β. As we can see on fig. 2, the anallytical and numerical results for the spectrum fit also sufficiently well. Let's remember that 10^{-16} is the order of the machine error, so we can say that in both cases our approximations yielded sensible and trustable results.

a)   b)

Figure 4: Periodic chain case. a) On the left column the spectrum obtained numerically is shown, on the right the one obtained using eq. 28. b) The difference between the anallytical and the numerical spectrum is plotted. Both plots for the case when $N = 5$, the remaining N values yield similar results.