1 Exercise 1 - Diatomic molecule

a. Calculate energies

Solution: The Schrödinger equation for this system reads

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

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.

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

The second equation is

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

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 $(E_0S - \beta) \neq 0$ 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

$$\begin{aligned}
0 &= c_1(\beta - \frac{E_0 - \beta}{1 - S}S) + c_2(E_0 - \frac{E_0 - \beta}{1 - S}), \\
&= c_1(\beta - \cancel{\beta S} - E_0S + \cancel{\beta S}) + c_2(\cancel{E_0} - E_0S - \cancel{E_0} + \beta), \\
&= c_1(\beta - E_0S) + c_2(-E_0S + \beta), \\
&= (c_1 + c_2)(\beta - E_0S)
\end{aligned} \tag{13}$$

The solution to eq. 13 if $\beta - E_0S \neq 0$ 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. Radii

Solution: d

3 Exercise 3 - Tight-binding chain in 1D

a. Radii

Solution: d