Lecture #4 - Homo- & heteronuclear diatomic molecule: Sutton Ch. 2 pp 25-31

\[
\langle n\ell m_\ell | n\ell m_\ell \rangle \\
\sum_i |i\rangle \langle i| = 1 \\
\beta = \langle 1| \hat{H} |2\rangle
\]
$\text{H}_2$: a homonuclear diatomic molecule
2 H atoms, 1s orbitals only

$\sigma^*$ antibonding molecular orbital

$\sigma$ bonding molecular orbital

1s atomic orbital

Energy
Goal: find molecular orbitals, $|\Psi\rangle$ and their energies, $E$

$$|\Psi\rangle = \langle 1,1s | \Psi \rangle |1,1s\rangle + \langle 2,1s | \Psi \rangle |2,1s\rangle$$

$$|\Psi\rangle = c_1 |1,1s\rangle + c_2 |2,1s\rangle$$

We know these atomic orbitals, and their energies. These are the basis kets.

Assume orthogonal (not quite true, but OK) $\langle 1,1s | 2,1s \rangle = 0$
Overlap of atomic orbitals on different atoms

A large overlap integral requires spatial overlap, but spatially overlapping orbitals can still have zero overlap if the signs are appropriately arranged. e.g. $2s$ is orthogonal to $2p$ on the same atom.
We want to find molecular orbitals, and their energies, $E$

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

$$|\Psi\rangle = c_1 |1,1s\rangle + c_2 |2,1s\rangle$$

$$\hat{H} \left[ c_1 |1,1s\rangle + c_2 |2,1s\rangle \right] = E \left[ c_1 |1,1s\rangle + c_2 |2,1s\rangle \right]$$

**On-site matrix element**

$H_{11} = E_0$ (assume known)

**Hopping matrix element**

$H_{12} = \beta$ (assume known)

**Project onto basis ket #1**

$$E \left[ \begin{array}{c} c_1 \langle 1,1s | \hat{H} |1,1s\rangle + c_2 \langle 1,1s | \hat{H} |2,1s\rangle \\ \end{array} \right] = E \left[ \begin{array}{c} c_1 \langle 1,1s | 1,1s\rangle + c_2 \langle 1,1s | 2,1s\rangle \\ \end{array} \right]$$
On-site energy: 
\[ \langle 1 | \hat{H} | 1 \rangle = \langle 1 | -\frac{\hbar^2}{2m} \nabla^2 + V_1(r) + V_2(r) | 1 \rangle \]

\[ E_0 = E_{1,\text{atomic}} + \langle 1 | V_2(r) | 1 \rangle \]

On-site energy is approximately the atomic energy, but small correction due to other potential. WF 1 is small where \( V_2 \) is large and vice versa (note: e-e interactions neglected).

\[ \langle x | 1 \rangle | 1 \rangle, \quad 2 \rangle \langle x | 2 \rangle \]

\[ \begin{array}{c}
    0 \\
    V_1 \\
    V_2 \\
    V_0 \\
\end{array} \]

\[ \begin{array}{c}
    1a \\
    2a \\
    3a \\
\end{array} \]
Hopping energy:

\[ \langle 1 | \hat{H} | 2 \rangle = \langle 1 | -\frac{\hbar^2}{2m} \nabla^2 + V_1(r) + V_2(r) | 2 \rangle \]

\[ \beta = E_{1,atomic} \langle 1 | 2 \rangle + \langle 1 | V_2(r) | 2 \rangle \]

\[ \beta = \langle 1 | V_2(r) | 2 \rangle \]

Hopping energy is integral of individual potential and both atomic wave functions. Could have additional contribution if there is n-n overlap.

\[ \langle x | 1 \rangle \quad | 1 \rangle \quad \begin{array}{c} \text{peak} \\ \text{at \ } 1a \end{array} \quad 2a \quad \begin{array}{c} \text{peak} \\ \text{at \ } 2a \end{array} \quad \langle x | 2 \rangle \]

\[ V_0 \quad V_1 \quad 1a \quad 2a \quad 3a \quad V_2 \]
We want to find molecular orbitals, and their energies, $E$

\[ c_1 E_0 + c_2 \beta = E c_1 \]
\[ c_1 \beta + c_2 E_0 = E c_2 \]

Project onto basis kets

\[
\begin{vmatrix}
E_0 - E & \beta \\
\beta & E_0 - E
\end{vmatrix} = 0
\]

Linear algebra $\Rightarrow$ quadratic eqn

\[ E_a = E_0 - \beta \]
\[ E_b = E_0 + \beta \]

\[ \beta = \langle 1s|V_2(r)|2s \rangle < 0 \]

For overlapping $s$ orbitals, $\beta$ is negative. This is because $s$ orbitals are +ve everywhere and $V_2 < 0$ (attractive potential)
We want to find molecular orbitals, and their energies, $E$

\[
\begin{align*}
    c_1 E_0 + c_2 \beta &= E c_1 \\
    c_1 \beta + c_2 E_0 &= E c_2
\end{align*}
\]

Now we can find the $c$'s for each of $E_b$ and $E_a$, and hence the corresponding $\Psi_b$ and $\Psi_a$.

\[
\begin{align*}
    \Psi_a &= \frac{1}{\sqrt{2}} \left( |1,1s\rangle - |2,1s\rangle \right) \\
    \Psi_b &= \frac{1}{\sqrt{2}} \left( |1,1s\rangle + |2,1s\rangle \right)
\end{align*}
\]
H$_2$ molecule

constructive combination

electron density between nuclei

destructive combination

electron density outside of nuclei

nucleus of the hydrogen atom

phase of the orbital

node

http://wps.prenhall.com
H$_2$ molecule

Bonding is a quantum mechanical phenomenon that results from the interference of quantum waves!

To view bonding as the "sharing" of electrons, we can show (Sutton p33-31) that an electron oscillates from atom #1 to atom #2 at a frequency $2\beta/h$. How does it overcome the large ionization potential? It tunnels! Again a quantum mechanical phenomenon.
\[ \Psi_a = \frac{1}{\sqrt{2}} \left( |1, p\rangle + |2, p\rangle \right) \]

\[ \Psi_b = \frac{1}{\sqrt{2}} \left( |1, p\rangle - |2, p\rangle \right) \]

Why is the –ve sign associated with the bonding orbital in this example?
π bonding with \( p \)-orbitals

\( \pi \) bonding molecular orbital

\( \pi^* \) antibonding molecular orbital

2\( p \) atomic orbital

Energy
MO diagram for $p$-orbitals
• H₂ molecule has 2 atoms and the 2 molecular orbitals are (relatively) close in energy, one higher and one lower than the energy of the atomic orbital.

• The hopping term represents tunneling of electrons across the potential barrier between atoms (see Sutton). The faster the tunneling, the stronger the interaction, and the bigger the splitting.

• The orbitals are bonding (electron density between nuclei tending to draw nuclei together), or antibonding (electron density on opposite sides of nuclei, causing nuclear repulsion).
Heteronuclear diatomic molecule

\[ |B, sp\rangle \quad |A, s\rangle \]

\[ \langle B | \hat{H} | B \rangle = E_B \quad \langle A | \hat{H} | A \rangle = E_A \]

On-site integrals

\[ \langle A | \hat{H} | B \rangle = \langle B | \hat{H} | A \rangle = \beta \]

Off-site integral

\[ \hat{H} |\Psi\rangle = E |\Psi\rangle \]

General form of MO

\[ |\Psi\rangle = c_A |A\rangle + c_B |B\rangle \]

Schrödinger eigenvalue equation
Want to find these molecular orbitals and their energies, $E$

$$c_A E_A + c_B \beta = E c_A$$

$$c_A \beta + c_B E_B = E c_B$$

Project onto basis kets

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

Linear algebra $\Rightarrow$ quadratic eqn

$$E_a = \varepsilon + \left(\Delta^2 + \beta^2\right)^{1/2}$$

$$E_b = \varepsilon - \left(\Delta^2 + \beta^2\right)^{1/2}$$
Want to find these molecular orbitals, and their energies, $E$

\[
c_A E_A + c_B \beta = E c_A
\]
\[
c_A \beta + c_B E_B = E c_B
\]

Now we can find the $c$'s for each of $E_b$ and $E_a$, and hence the corresponding $\Psi_b$ and $\Psi_a$.

\[
\frac{C_{A,a}^2}{C_{B,a}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 - 2(\Delta / \beta)(1 + (\Delta / \beta)^2)^{1/2}}
\]
\[
\frac{C_{A,b}^2}{C_{B,b}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 + 2(\Delta / \beta)(1 + (\Delta / \beta)^2)^{1/2}}
\]
\[
\frac{c_{A,a}^2}{c_{B,a}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 - 2(\Delta / \beta)(1+(\Delta / \beta)^2)^{1/2}}
\]

\[
\frac{c_{A,b}^2}{c_{B,b}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 + 2(\Delta / \beta)(1+(\Delta / \beta)^2)^{1/2}}
\]
Electronegativity

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Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.
This commonly shown picture is actually inaccurate. It shows 1s-2p hybridization. One always sees 2s-2p hybridization. 2s electron distribution is different from 1s!
HF and HCl

Overlap of the bonding $sp^3$ hybrid orbital of F and Cl with H in HF and HCl.
Overlap of the 1s orbital of hydrogen is better with the smaller $2sp^3$ hybrid orbital of fluorine than with the larger $3sp^3$ hybrid orbital of chlorine, resulting in a shorter, stronger bond in HF than in HCl.