**Lecture 13: Diatomic orbitals**

- Hydrogen molecule ion (H$_2^+$)
- Overlap and exchange integrals
- Bonding/Anti-bonding orbitals
- Molecular orbitals
- Chapter 24 of Haken & Wolf
  Chapter 11 of Atkins

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**Schrödinger equation for hydrogen molecule ion**

- Simplest example of a chemical bond is the hydrogen molecule ion (H$_2^+$).
- Consists of two protons and a single electron.
- If nuclei are distant, electron is localised on one nucleus. Wavefunctions are then those of atomic hydrogen.

- $\phi_a$ is the hydrogen atom wavefunction of electron belonging to nucleus $a$. Must therefore satisfy

\[
\left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi \varepsilon_0 r_a} \right\} \phi_a(r_a) = E_a^0(r_a) \phi_a(r_a) \quad (1)
\]

and correspondingly for other wavefunction, $\phi_b$. The energies are therefore

$$E_a^0 = E_b^0 = E^0$$


**Schrödinger equation for hydrogen molecule ion**

- If atoms are brought into close proximity, electron localised on \( b \) will now experience an attractive Coulomb force of nucleus \( a \).

- Must therefore modify Schrödinger equation to include Coulomb potentials of both nuclei:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a} - \frac{e^2}{4\pi\varepsilon_0 r_b} \right] \psi = E \psi \quad (2)
\]

where \( \psi = c_a \phi_a + c_b \phi_b \)

- To find the coefficients \( c_a \) and \( c_b \), substitute into Eqn. 2:

\[
\begin{align*}
H_a &= \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a} \right] c_a \phi_a + \frac{e^2}{4\pi\varepsilon_0 r_a} c_a \phi_a = E(c_a \phi_a + c_b \phi_b) \\
H_b &= \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_b} \right] c_b \phi_b + \frac{e^2}{4\pi\varepsilon_0 r_b} c_b \phi_b = E(c_a \phi_a + c_b \phi_b)
\end{align*}
\]

**Solving the Schrödinger equation**

- Can simplify last equation using Eqn. 1 and the corresponding equation for \( H_a \) and \( H_b \):

\[
\begin{align*}
H_a &= \frac{e^2}{4\pi\varepsilon_0 r_a} c_a \phi_a + \frac{e^2}{4\pi\varepsilon_0 r_a} c_a \phi_a = E(c_a \phi_a + c_b \phi_b) \\
H_b &= \frac{e^2}{4\pi\varepsilon_0 r_b} c_b \phi_b + \frac{e^2}{4\pi\varepsilon_0 r_b} c_b \phi_b = E(c_a \phi_a + c_b \phi_b)
\end{align*}
\]

- By writing \( E_a^0 \phi_a \) in place of \( H_a \phi_a \) gives

\[
\begin{align*}
E_a^0 c_a \phi_a + E_b^0 c_b \phi_b = E(c_a \phi_a + c_b \phi_b)
\end{align*}
\]

- Rearranging,

\[
\begin{align*}
E_a^0 c_a \phi_a + E_b^0 c_b \phi_b = E(c_a \phi_a + c_b \phi_b)
\end{align*}
\]

- As \( E_a^0 = E_b^0 \) by symmetry, we can set \( E_a^0 - E = E_b^0 - E = -\Delta E \),

\[
\begin{align*}
-\Delta E \frac{e^2}{4\pi\varepsilon_0 r_a} c_a \phi_a + -\Delta E \frac{e^2}{4\pi\varepsilon_0 r_b} c_b \phi_b = 0
\end{align*}
\]
**Overlap and exchange integrals**

- $\phi_a$ and $\phi_b$ depend on position, while $c_a$ and $c_b$ do not. Now we know that for orthogonal wavefunctions
  \[ \int \phi_a^* \phi_a dV = \int \phi_b^* \phi_b dV = 1 \quad \text{Normalisation integral} \]

but $\phi_a$ and $\phi_b$ are not orthogonal, so
  \[ \int \phi_a^* \phi_b dV = S(r_{ab}) \quad \text{Overlap integral} \]

- If we now multiply Eqn. 3 by $\phi_a^*$ and integrate the results, we obtain
  \[ \int \phi_a^*(r_a) \left( -\frac{e^2}{4\pi\varepsilon_0 r_b} \right) \phi_a(r_a) dV = C(r_{ab}) \quad (4) \]
  \[ \int \phi_a^*(r_a) \left( -\frac{e^2}{4\pi\varepsilon_0 r_a} \right) \phi_b(r_a) dV = D(r_{ab}) \quad (5) \]

- As $-e|\phi_a|^2$ is the charge density of the electron $\Rightarrow$ Eqn. 4 is the Coulomb interaction energy between electron charge density and nuclear charge $e$ of nucleus $b$.

- The $-e\phi_a \phi_b$ in Eqn. 5 means that electron is partly in state $a$ and partly in state $b \Rightarrow$ an exchange between states occurs. Eqn. 5 therefore called an exchange integral.

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**Overlap and exchange integrals**

- Eqn. 4 can be visualised via figure at right.
  - Represents the Coulomb interaction energy of an electron density cloud in the Coulomb field on the nucleus.

- Eqn. 5 can be visualised via figure at right.
  - Non-vanishing contributions are only possible when the wavefunctions overlap.

- See Chapter 24 of Haken & Wolf for further details.
Orbital energies

- If we multiply Eqn 3 by $\phi^*_a$ and integrate we get
  \[
  \int \phi_a^* \left(-\Delta E - \frac{e^2}{4\pi\epsilon_0 r_a^3} \right) \phi_a + \left(-\Delta E - \frac{e^2}{4\pi\epsilon_0 r_b^3} \right) \phi_b \, dV
  \]

- Collecting terms gives,
  \[(-\Delta E + C)c_a + (-\Delta E \cdot S + D)c_b = 0 \quad (6)\]

- Similarly,
  \[
  \int \phi_a^* \left(-\Delta E - \frac{e^2}{4\pi\epsilon_0 r_a^3} \right) \phi_a + \left(-\Delta E - \frac{e^2}{4\pi\epsilon_0 r_b^3} \right) \phi_b \, dV
  \]

  \[\Rightarrow (-\Delta E \cdot S + D)c_a + (-\Delta E + C)c_b = 0 \quad (7)\]

- Eqns. 6 and 7 can be solved for $c_a$ and $c_b$ via the matrix equation:
  \[
  \begin{pmatrix}
  -\Delta E + C & -\Delta E \cdot S + D \\
  -\Delta E \cdot S + D & -\Delta E + C
  \end{pmatrix}
  \begin{pmatrix}
  c_a \\
  c_b
  \end{pmatrix}
  = 0
  \]

- Non-trivial solutions exist when determinant vanishes:
  \[
  \left|\begin{array}{cc}
  -\Delta E + C & -\Delta E \cdot S + D \\
  -\Delta E \cdot S + D & -\Delta E + C
  \end{array}\right| = 0
  \]

- Therefore \((-\Delta E + C)^2 - (-\Delta E \cdot S + D)^2 = 0\)

  \[\Rightarrow C - \Delta E = \pm (D - \Delta E \cdot S)\]

- This gives two values for $\Delta E$:
  \[\Delta E_a = \frac{C - D}{1 - S} \quad \text{and} \quad \Delta E_b = \frac{C + D}{1 + S}\]

- As $C$ and $D$ are negative, $\Delta E_b < \Delta E_a$

- $\Delta E_b$ correspond to bonding molecular orbital energies. $\Delta E_a$ to anti-bonding MOs.

- $H_2^+$ atomic and molecular orbital energies are shown at right.
**Bonding and anti-bonding orbitals**

- Substituting for $\Delta E_a$ into Eqn. 6 $\Rightarrow c_b = -c_a = -c$. The total wavefunction is thus
  
  $\psi_n = c(\phi_a - \phi_b)$  \hspace{1cm} \textit{Anti-bonding orbital}

- Similarly for $\Delta E_b \Rightarrow c_a = c_b = c$, which gives
  
  $\psi_n = c(\phi_a + \phi_b)$  \hspace{1cm} \textit{Bonding orbital}

- For symmetric case (top right), occupation probability for $\psi$ is positive. Not the case for an asymmetric wavefunctions (bottom right).

- Energy splits depending on whether dealing with a bonding or an anti-bonding wavefunction.

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**Bonding and anti-bonding orbitals**

- The energy $E$ of the hydrogen molecular ion can finally be written
  
  $E = E^0 + \Delta E = E^0 + \frac{C \pm D}{1 \pm S}$

- ‘+’ correspond to anti-bonding orbital energies, ‘-’ to bonding.

- Energy curves below are plotted to show their dependence on $r_{ab}$

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Molecular orbitals

Decreased negative charge between the nuclei leads to decreased attractions between the negative charge from the electrons and the positively charged nuclei. This makes the sigma 1s antibonding molecular orbital higher potential energy than the separate 1s atomic orbitals.

Increased negative charge between the nuclei leads to increased attractions between the negative charge from the electrons and the positively charged nuclei. This makes the sigma 1s bonding molecular orbital lower potential energy than the separate 1s atomic orbitals.

Molecular orbitals

There is less overlap between parallel p orbitals than between two p orbitals overlapping end-on.
Molecular orbitals

- Energies of bonding and anti-bonding molecular orbitals for first row diatomic molecules.

- Two electrons in H₂ occupy bonding molecular orbital, with anti-parallel spins. If irradiated by UV light, molecule may absorb energy and promote one electron into its anti-bonding orbital.