

### 3 The Way Forward - Assumptions and Approximations

#### Simplification 1

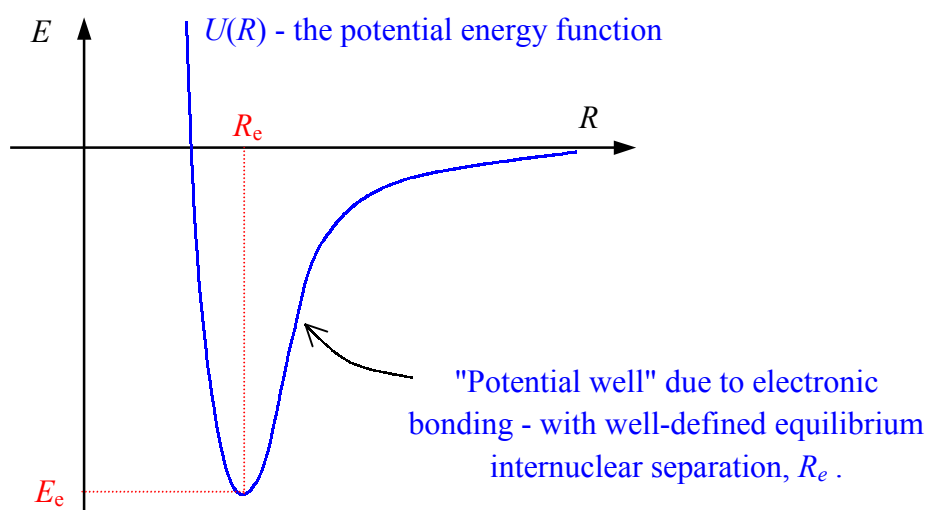
The electrons move much faster than the nuclei (since they are much lighter) - we will therefore treat the nuclear and electronic motion entirely independently.

..... this is the **Born-Oppenheimer approximation**.

The approach is:

- Freeze the molecule with a fixed internuclear separation ( $R_{AB}$ , hereafter called  $R$ ); then carry out calculations to obtain the total energy,  $U$ , and wavefunctions for that  $R$  value.
- Repeat for different values of  $R$ , to obtain the complete *potential energy function*,  $U(R)$ .

This gives results of the following form:



The total energy of the free ("unfrozen") bound-molecule is then given by:

$$E_{\text{total}} = E_e + E_{\text{vrt}}$$

Electronic energy (incl. total energy of electrons in molecular environment and internuclear repulsion)

Vibrational, rotational and translational energy of the molecules

To actually determine the electronic energy we still have to solve a Schrödinger equation, but this first approximation means that it is now a much simpler equation.

For a particular value of  $R$  (the internuclear separation), the equation is:

$$\hat{H}_e \Psi_e(\underline{r}_1, \underline{r}_2) = U(R) \Psi_e(\underline{r}_1, \underline{r}_2)$$

or

$$\hat{H}_e \Psi_e(\underline{r}_1, \underline{r}_2) = E_e \Psi_e(\underline{r}_1, \underline{r}_2) \quad \text{at } R = R_e$$

where:

$\hat{H}_e$  is the electronic Hamiltonian, i.e. the full Hamiltonian,  $\hat{H}$ , but without the nuclear KE terms.

$\Psi_e(\underline{r}_1, \underline{r}_2)$  is the *electronic wavefunction* for the molecule (which is a function of the vectorial positions of the two electrons)

Unfortunately, the Schrödinger equation is still impossible to solve because the interelectronic repulsion term (opposite) depends upon the positions of both electrons (since  $r_{12} = |\underline{r}_1 - \underline{r}_2|$ ).

$$V_{12} = \left( \frac{e^2}{4\pi\epsilon_0 r_{12}} \right)$$

## Simplification 2

..... is known as the **independent electron model** or **orbital approximation**.

**Consider each electron to move in some sort of "average potential" which incorporates the interactions with the two nuclei and an "averaged interaction" with the other electron.**

The electronic Hamiltonian can then be separated into two parts:

$$\hat{H}_e = \hat{H}_1 + \hat{H}_2$$

where:

$\hat{H}_1$  is dependent only upon the properties of electron (1) and upon  $R$ .

$\hat{H}_2$  is dependent only upon the properties of electron (2) and upon  $R$ .

This is a major step forward since we can now (see explanation and caveat in box overleaf) look for solutions of the form:

$$\Psi_e(\underline{r}_1, \underline{r}_2) = \psi_a(1) \cdot \psi_b(2)$$

Molecular orbital "a" -  
containing electron 1

Molecular orbital "b" -  
containing electron 2

where

$$\hat{H}_1 \psi_a = \epsilon_a \psi_a$$

and  $\epsilon_a$  is the energy of orbital "a"

$$\hat{H}_2 \psi_b = \epsilon_b \psi_b$$

and  $\epsilon_b$  is the energy of orbital "b"

and the total electronic energy (at the equilibrium bond length) is given by:

$$E_e = \epsilon_a + \epsilon_b$$

i.e. by the sum of the energies of the individual occupied molecular orbitals.

### *Consequences of the Orbital Approximation*

$$\begin{aligned} \hat{H}_e \Psi_e &= (\hat{H}_1 + \hat{H}_2)(\psi_a(1) \cdot \psi_b(2)) \\ &= \hat{H}_1(\psi_a(1) \cdot \psi_b(2)) + \hat{H}_2(\psi_a(1) \cdot \psi_b(2)) \\ &= (\hat{H}_1 \psi_a(1)) \cdot \psi_b(2) + (\hat{H}_2 \psi_b(2)) \cdot \psi_a(1) \end{aligned}$$

(since  $\hat{H}_1$  acts only upon the wavefunction for electron 1, i.e. on  $\psi_a(1)$ , etc.)

$$\begin{aligned} \Rightarrow \hat{H}_e \Psi_e &= \epsilon_a \psi_a(1) \psi_b(2) + \epsilon_b \psi_b(2) \psi_a(1) \\ &= (\epsilon_a + \epsilon_b) \psi_a(1) \psi_b(2) \end{aligned}$$

i.e.  $\hat{H}_e \Psi_e = E_e \Psi_e$  where  $E_e = \epsilon_a + \epsilon_b$

In actual fact a wavefunction of the form  $\Psi_e(r_1, r_2) = \psi_a(1) \cdot \psi_b(2)$  is unacceptable since:

- it permits the two electrons to be distinguished
- the wavefunction is not antisymmetric upon exchange of the two electrons

The wavefunction can however be modified to meet these criteria

$$\Psi_e(r_1, r_2) = \psi_a(1) \cdot \psi_b(2) - \psi_a(2) \cdot \psi_b(1)$$

without compromising the additional simplicity afforded by the orbital approximation.

### **Simplification 3**

So all we now need to do is to solve the one-electron Schrödinger equation:

$$\hat{H}_1 \psi_a = \epsilon_a \psi_a \quad [1]$$

Effective one-electron  
Hamiltonian

One-electron wavefunction,  
a *molecular orbital*.

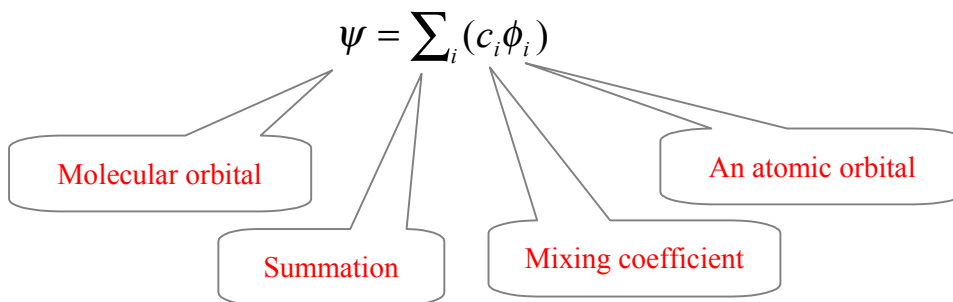
The solutions are the molecular orbital wavefunctions,  $\{\psi_a\}$ , and molecular orbital energies,  $\{\epsilon_a\}$ .

To actually do this we make one final approximation which

..... is the **linear combination of atomic orbitals (LCAO) approximation** .

This supposes that we can construct molecular orbitals from linear superpositions of atomic orbitals centred on individual atoms.

i.e.



..... this is an idea with which you should already be partly familiar. In its simplest form a molecular orbital may be constructed from a summation of one orbital on one atom, with a second orbital on a different atom.

Example : Hydrogen ( H<sub>2</sub> )

Each hydrogen atom has a single valence orbital, this being the 1s orbital. Two molecular orbitals may be formed by the constructive and destructive overlap of these two atomic orbitals.

1s ± 1s

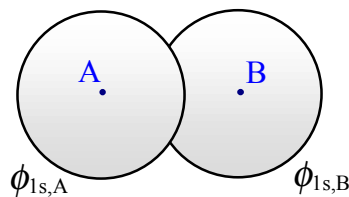
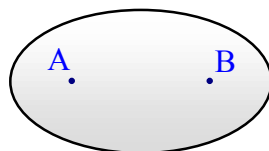


Diagram showing the superposition of the two 1s atomic orbitals



1s σ  
(1σ<sub>g</sub>)

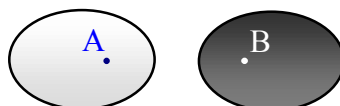


Bonding molecular orbital

$$\psi_+ = c_+ \phi_{1s,A} + c_+ \phi_{1s,B} = c_+ (\phi_{1s,A} + \phi_{1s,B})$$

or

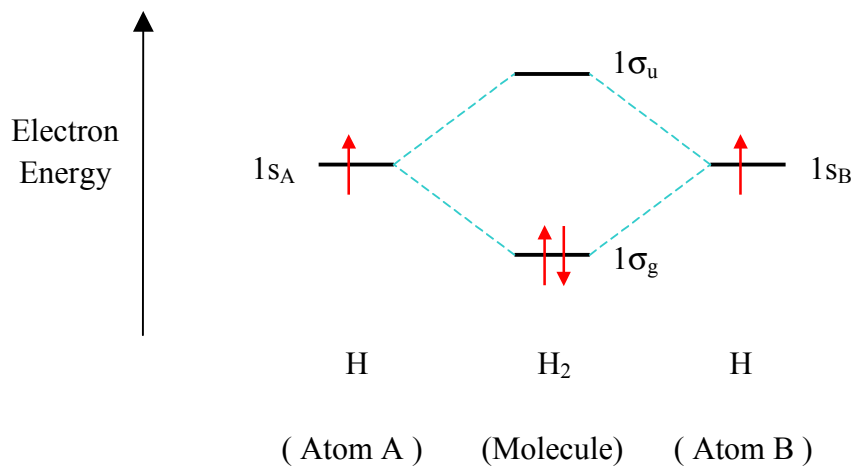
1s σ\*  
(1σ<sub>u</sub>)



Antibonding molecular orbital

$$\psi_- = c_- \phi_{1s,A} - c_- \phi_{1s,B} = c_- (\phi_{1s,A} - \phi_{1s,B})$$

This interaction of atomic orbitals, which gives rise to the molecular orbitals, may also be represented in the form of an orbital (electron) energy diagram which shows the relative energies of the orbitals. In the specific case of hydrogen each of the isolated atoms has one electron in its 1s orbital and when the atoms combine to form H<sub>2</sub> the two electrons may be accommodated (with opposite spins) in the bonding molecular orbital, as illustrated below.



Note that in this instance two atomic orbitals give rise to two molecular orbitals - we shall see later that this is a general characteristic, i.e. linear combinations of  $n$  atomic orbitals give rise to  $n$  molecular orbitals.

However this pictorial approach fails to answer some important questions

1. what are the values of the mixing coefficients ?
2. what are the exact energies of the molecular orbitals ?

**Important : Change of Notation**

.... from hereon, we will switch to using numerical labels for the atomic orbitals and their associated coefficients, e.g.

$$\psi = c_1\phi_1 + c_2\phi_2$$

where  $\phi_i$  simply represents a specific atomic orbital on a specific atom ( $i$ ).