

## 4 LCAO and the Variational Principle

LCAO does not give exact solutions to the one-electron Schrödinger equation [1], only approximate solutions. How do we make these approximate solutions as good as possible ?

### The Variational Principle

For a particular wavefunction, the estimate (expectation value) of the orbital energy ( $E$  - previously referred to as  $\epsilon$ ) is given by :

$$E = \frac{\int \psi^* \hat{H} \psi . d\tau}{\int \psi^* \psi . d\tau} \quad [2]$$

where:

$\psi$  - molecular orbital wavefunction (expressed as LCAO)

$\psi^*$  - complex conjugate of  $\psi$  ( $\psi^* = \psi$  if the wavefunction is entirely real).

$\hat{H}$  - effective one-electron Hamiltonian

$d\tau$  - integral over all space

The variational principle states that the value of  $E$  given by equation [2] is always greater than the true energy for the exact solution, from which it follows that the best approximate solution (i.e. the best values for the coefficients in the LCAO construction) can be obtained by minimising the value of the energy,  $E$ , given by this equation.

### Procedure for Implementing the Principle

1. Decide which atomic orbitals might contribute to the MO (symmetry considerations are of immense value at this point) and construct the summation for  $\psi$

i.e. 
$$\psi = c_1\phi_1 + c_2\phi_2 + \dots$$

2. Obtain an expression for  $E$  where

$$E = \frac{\int \psi^* \hat{H} \psi . d\tau}{\int \psi^* \psi . d\tau}$$

If  $\psi$  is entirely "real" (i.e. has no imaginary components) then  $\psi^* = \psi$ , and

$$E = \frac{\int \psi \hat{H} \psi . d\tau}{\int \psi^2 . d\tau}$$

3. Find the values of  $c_1, c_2, \dots$  that minimize the value of  $E$ ; once you have obtained these coefficients then

$$\text{Wavefunction, } \psi = \sum_i (c_i \phi_i), \quad \text{Orbital energy, } \epsilon = E_{min}$$

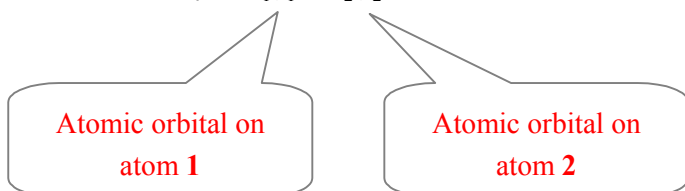
## Overlap of Two Atomic Orbitals

When just two orbitals are permitted to interact then the general expression for the molecular orbital expressed as a linear combination of atomic orbitals

$$\psi = \sum_i (c_i \phi_i)$$

simplifies to

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

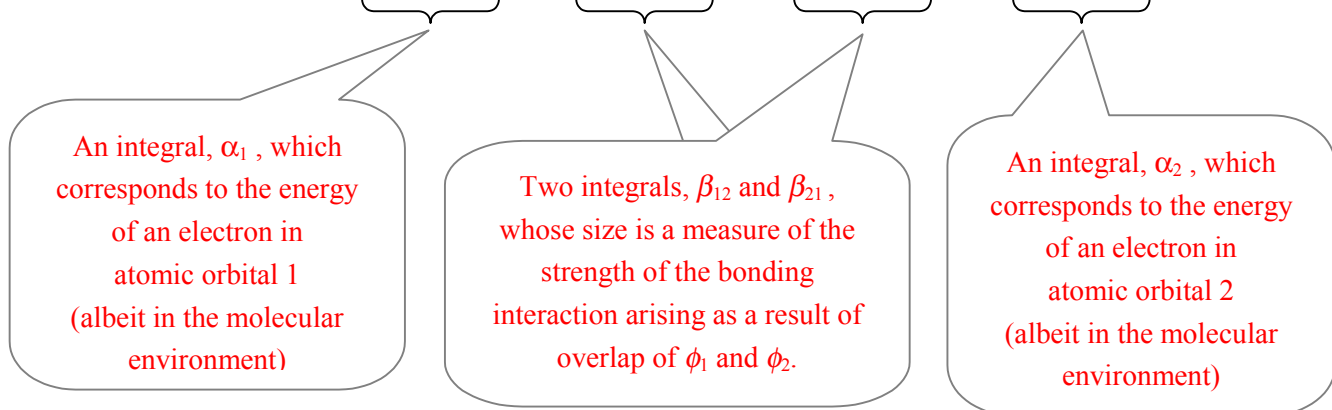


The expression for  $E$  now becomes :

$$E = \frac{\int \psi \hat{H} \psi . d\tau}{\int \psi^2 . d\tau} = \frac{\int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2) . d\tau}{\int (c_1 \phi_1 + c_2 \phi_2)^2 . d\tau} \quad [3]$$

(a) Consider first the top line of the fraction.

$$\begin{aligned} \int \psi \hat{H} \psi . d\tau &= \int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2) . d\tau \\ &= c_1^2 \int \phi_1 \hat{H} \phi_1 . d\tau + c_1 c_2 \int \phi_1 \hat{H} \phi_2 . d\tau + c_1 c_2 \int \phi_2 \hat{H} \phi_1 . d\tau + c_2^2 \int \phi_2 \hat{H} \phi_2 . d\tau \end{aligned}$$



i.e.

$$\int \psi \hat{H} \psi . d\tau = c_1^2 \alpha_1 + c_1 c_2 \beta_{12} + c_1 c_2 \beta_{21} + c_2^2 \alpha_2$$

As long as the  $\phi_i$  functions are entirely real, then  $\beta_{12} = \beta_{21}$  (since  $\hat{H}$  is an Hermitian operator) and this simplifies to ...

$$\int \psi \hat{H} \psi .d\tau = c_1^2 \alpha_1 + 2c_1 c_2 \beta_{12} + c_2^2 \alpha_2$$

(b) Now consider the bottom line of the fraction.

$$\int \psi^2 .d\tau = \int (c_1 \phi_1 + c_2 \phi_2)(c_1 \phi_1 + c_2 \phi_2) .d\tau$$

$$= c_1^2 \int \phi_1^2 .d\tau + c_1 c_2 \int \phi_1 \phi_2 .d\tau + c_1 c_2 \int \phi_2 \phi_1 .d\tau + c_2^2 \int \phi_2^2 .d\tau$$

= 1 ; since the atomic orbitals are "normalized"

Two equal integrals; the integral is known as the "overlap integral" and denoted  $S$  (it is positive)

= 1 ; since the atomic orbitals are "normalized"

i.e.

$$\int \psi^2 .d\tau = c_1^2 + c_2^2 + 2c_1 c_2 S$$

Substitution of the expressions for the integrals into eqn. [3] therefore gives:

$$E = \frac{c_1^2 \alpha_1 + 2c_1 c_2 \beta_{12} + c_2^2 \alpha_2}{c_1^2 + c_2^2 + 2c_1 c_2 S} \quad [4]$$

We now need to find the values of  $c_1, c_2$  that minimize the value of  $E$  .

### Summary of Terminology

$\alpha_i$  is known as the *Coulomb integral* : it is equal to the energy of an electron in the corresponding atomic orbital,  $i$  , albeit with the atom in the molecular environment - it is negative.

$\beta_{ij}$  is known as the *resonance integral* : it is a measure of the strength of the bonding interaction as a result of the overlap of orbitals  $i$  and  $j$  - it is negative for constructive overlap of orbitals.

$S$  is known as the *overlap integral* : is a measure of the effectiveness of overlap of the orbitals (its magnitude is always significantly less than one, i.e.  $S \ll 1$  ).

Why is  $S$  known as the "overlap integral" ?

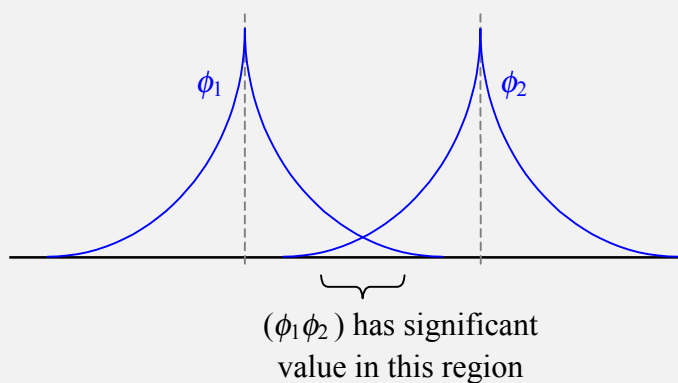
..... consider the case of two 1s orbitals.

$$S = \int \phi_1 \phi_2 \cdot d\tau$$

1s orbital centred on nucleus 1      1s orbital centred on nucleus 2      Integral over all space

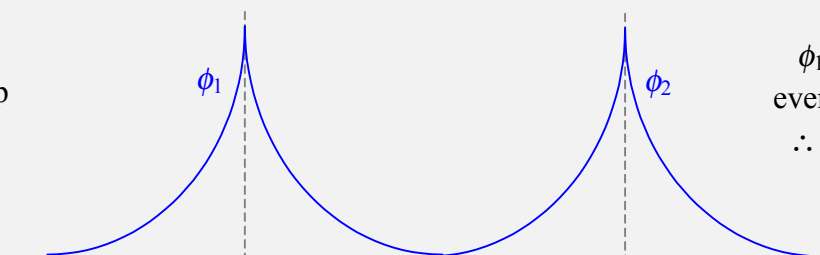
Consider the value of the product  $\phi_1\phi_2$  along a line passing through the two nuclei

Orbitals overlap



$\phi_1\phi_2$  has finite value in the region of overlap  
 $\therefore S \neq 0$

Orbitals do "not" overlap



$\phi_1\phi_2 \approx 0$  everywhere  
 $\therefore S \approx 0$

The magnitude of  $S$  is thus a measure of the efficiency of orbital overlap and depends upon both the internuclear separation and the spatial extent of the orbitals.

## The Secular Equations and Secular Determinant

Rearrangement of eqn. [4] yields

$$E(c_1^2 + c_2^2 + 2c_1c_2S) = c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2$$

To minimize  $E$  with respect to  $c_1$  and  $c_2$  we need to set both  $\frac{\partial E}{\partial c_1} = 0$  and  $\frac{\partial E}{\partial c_2} = 0$

(See Appendix 1 for details)

Differentiation with respect to  $c_1$  and setting the derivative equal to zero gives

$$\Rightarrow \underline{c_1(\alpha_1 - E) + c_2(\beta_{12} - ES) = 0} \quad [5]$$

Differentiation with respect to  $c_2$  and setting the derivative equal to zero gives

$$\Rightarrow \underline{c_1(\beta_{12} - ES) + c_2(\alpha_2 - E) = 0} \quad [6]$$

Equations [5] and [6] are simultaneous equations in  $c_1$  and  $c_2$ , known as the "*secular equations*". These equations need to be solved to obtain the appropriate values for  $c_1$  and  $c_2$ .

For non-trivial solutions (i.e. solutions other than  $c_1 = c_2 = 0$ ) we require (see Appendix 2) that the corresponding "*secular determinant*" be equal to zero:

i.e.

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} - ES \\ \beta_{12} - ES & \alpha_2 - E \end{vmatrix} = 0 \quad [7]$$

Solving this equation will tell us for what values of  $E$  we can get non-trivial solutions.

### Case 1 : Overlap of Two Identical Orbitals

This is the simplest possible case - the classic example would be  $H_2$ , but the approach is also a reasonable approximation for the bonding in any homonuclear diatomic molecule,  $X_2$ , and can also be applied to certain types of localised, two-centre bonding in more complex molecules.

Since  $\phi_1$  and  $\phi_2$  are the same type of orbital (e.g. both hydrogen 1s orbitals) :

$$\alpha_1 = \alpha_2 = \alpha$$

and for simplicity let the resonance integral  $\beta_{12}$  simply be represented by  $\beta$ .

The secular determinant now simplifies to :

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \quad [8]$$

### 1.1 The Simplest Solution

It is now possible to make a further simplification .... namely that  $S \ll 1$  (i.e. the *overlap integral* is very small, or, if you prefer,  $S \approx 0$ ) - this is the **neglect of overlap approximation** (and, as we shall see later, also one of the Hückel approximations) and the result is that the determinant simplifies to

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad [9]$$

Expanding the determinant (see Appendix 2) gives :

$$(\alpha - E)^2 - \beta^2 = 0$$

$$\Rightarrow (\alpha - E)^2 = \beta^2$$

$$\Rightarrow (E - \alpha) = \pm\beta$$

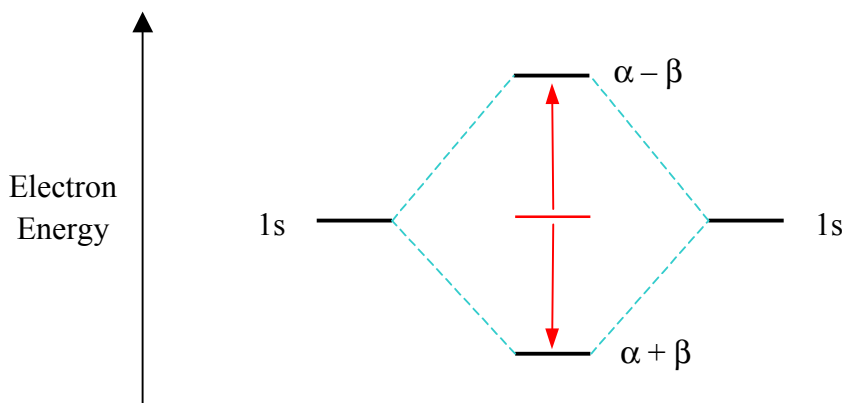
i.e.

$$E_+ = (\alpha + \beta)$$

or

$$E_- = (\alpha - \beta)$$

Given that  $\beta$  is negative (see 4.3), then it is clear that  $E_+$  is lower in energy than  $E_-$  and therefore that  $E_+$  corresponds to the energy of the bonding molecular orbital.



At this level of approximation the bonding and antibonding molecular orbitals are symmetrically distributed above and below the original atomic orbitals on the orbital energy diagram.

< Lecture - examples of homonuclear diatomics ( $H_2$ ,  $He_2$ ,  $Li_2$ ,  $O_2$ ), ethylene ( $C_2H_4$ ) >

## 1.2 The More Realistic Solution

If we are not prepared to neglect the orbital overlap then expanding the determinant of eqtn. [8] gives the following equation:

$$\begin{aligned}(\alpha - E)^2 - (\beta - ES)^2 &= 0 \\ \Rightarrow (\alpha - E)^2 &= (\beta - ES)^2 \\ \Rightarrow (\alpha - E) &= \sqrt{(\beta - ES)^2} = -(\beta - ES) \text{ or } +(\beta - ES) \\ \Rightarrow (E - \alpha) &= \pm(\beta - ES) \\ \Rightarrow E(1 \pm S) &= \alpha \pm \beta\end{aligned}$$

So, the energy of the bonding molecular orbital is given by

$$E_+ = \frac{(\alpha + \beta)}{(1 + S)}$$

whilst the energy of the antibonding molecular orbital is given by

$$E_- = \frac{(\alpha - \beta)}{(1 - S)}$$

Once again, given that  $\beta$  is negative (see 4.3), then it is clear that  $E_+$  is still lower in energy than  $E_-$  and therefore that  $E_+$  corresponds to the energy of the bonding molecular orbital.

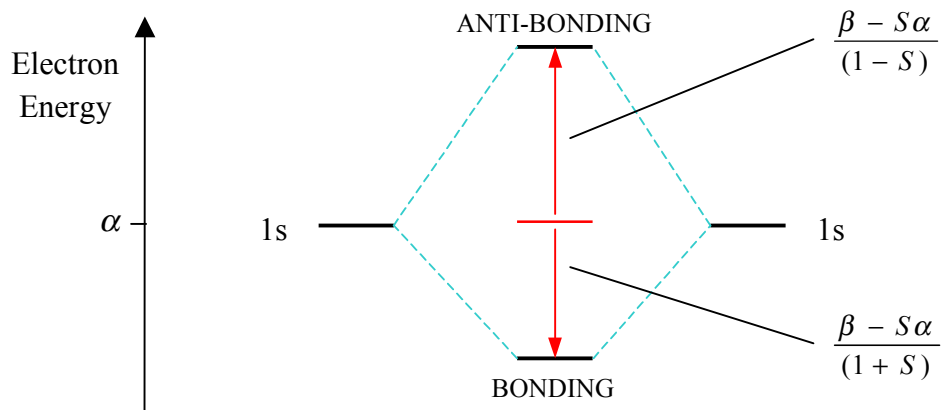
The expressions for the orbital energies may be reformulated as follows to better illustrate the values relative to the energy of the constituent atomic orbitals:

$$\begin{aligned}E_+ &= \frac{(\alpha + \beta)}{(1 + S)} = \alpha + \frac{(\beta - S\alpha)}{(1 + S)} \\ E_- &= \frac{(\alpha - \beta)}{(1 - S)} = \alpha - \frac{(\beta - S\alpha)}{(1 - S)}\end{aligned}$$

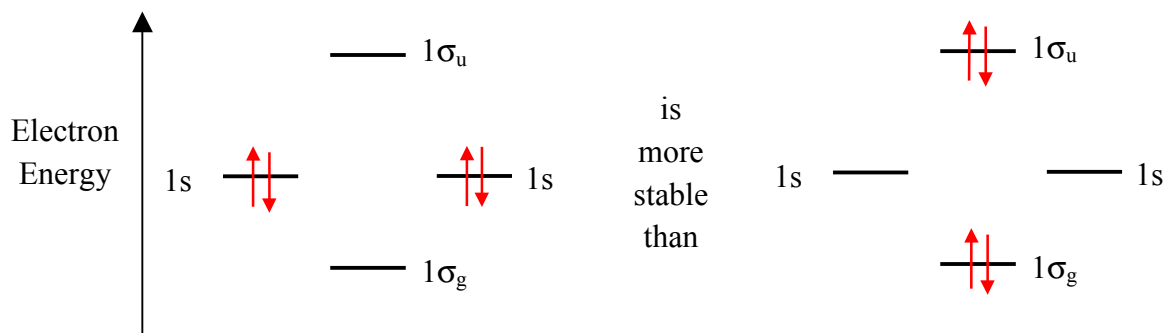
Since  $S > 0$ ,  $(1 + S) > (1 - S)$  and hence the above equations for  $E_+$  and  $E_-$  demonstrate that

..... *the antibonding orbital is more strongly antibonding than the bonding orbital is bonding.*

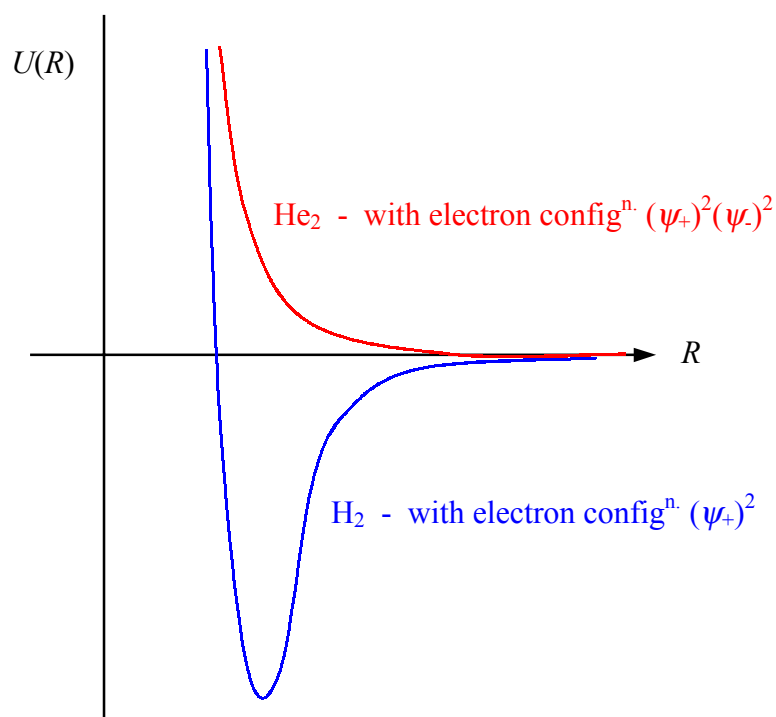
We may again represent this situation diagrammatically using an orbital energy diagram, noting that the bonding and antibonding molecular orbitals are now **asymmetrically** distributed about the original atomic orbitals on the orbital energy diagram.



One consequence of the asymmetry is that  $\text{He}_2$ , for example, is not a stable molecule, i.e.



This is reflected in the comparison of the potential energy curves for hydrogen and helium



## Case 2 : Overlap of Two Dissimilar Orbitals.

An example of this type would be the bonding in a heteronuclear diatomic molecule such as CO.

For the sake of simplicity we will neglect overlap (i.e. assume, as we have done before, that  $S \approx 0$ ) in which case the secular determinant of eqn. [7] simplifies to:

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{12} & \alpha_2 - E \end{vmatrix} = 0$$

Expanding the determinant (see Appendix 2), again replacing  $\beta_{12}$  by  $\beta$  for ease of writing, gives :

$$(\alpha_1 - E)(\alpha_2 - E) - \beta^2 = 0$$

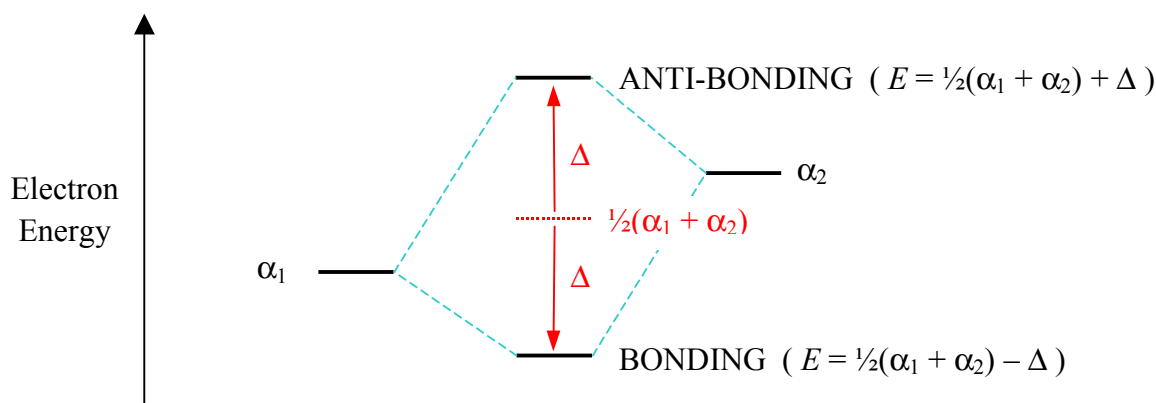
$$\Rightarrow E^2 - E(\alpha_1 + \alpha_2) + (\alpha_1\alpha_2 - \beta^2) = 0$$

This is a quadratic equation in  $E$  (comparable to  $ax^2 + bx + c = 0$ ) and applying the *general solution* for such equations gives :

$$\Rightarrow E = \frac{(\alpha_1 + \alpha_2) \pm \sqrt{(\alpha_1 + \alpha_2)^2 - 4(\alpha_1\alpha_2 - \beta^2)}}{2}$$

$$\Rightarrow E = \frac{(\alpha_1 + \alpha_2) \pm \sqrt{(\alpha_2 - \alpha_1)^2 + 4\beta^2}}{2}$$

i.e.  $E = \frac{1}{2}(\alpha_1 + \alpha_2) \pm \Delta$  where  $\Delta = \frac{1}{2}\sqrt{(\alpha_2 - \alpha_1)^2 + 4\beta^2}$  (and is positive).



< Lecture - example of formaldehyde (methanal,  $\text{H}_2\text{CO}$ ) >

## What are the Molecular Orbital Wavefunctions ?

The *Systematic Approach* to finding the wavefunctions themselves requires us to:

1. Substitute the values of  $E$  back into the secular equations to obtain two simultaneous equations for  $c_1$  and  $c_2$ .
2. Solve these simultaneous equations for  $c_1$  and  $c_2$ .

### Case 1 : Homonuclear Bonding

If we neglect overlap then the secular determinant is (see eqtn. [8] of 4.6 )

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

and the corresponding secular equations are:

$$c_1(\alpha - E) + c_2\beta = 0$$

$$c_1\beta + c_2(\alpha - E) = 0$$

For the bonding MO ,

$$E_+ = (\alpha + \beta)$$

$$\Rightarrow (\alpha - E) = -\beta$$

and substitution into the secular equations gives:

$$-c_1\beta + c_2\beta = 0 \quad \Rightarrow \quad -c_1 + c_2 = 0$$

$$c_1\beta - c_2\beta = 0 \quad \Rightarrow \quad c_1 - c_2 = 0$$

i.e.  $c_1 = c_2$

**..... the coefficients for the bonding MO of a homonuclear diatomic molecule are of the same sign and of equal magnitude.**

Using the same approach, it can easily be shown that **the coefficients for the antibonding MO of a homonuclear diatomic molecule are of equal magnitude but opposite sign.**

These results should not be a great surprise - the high symmetry of the molecule itself means that the wavefunctions must also possess a high degree of symmetry.

To get the actual value of the coefficients we need to "normalize" the molecular orbitals.

Let both coefficients of the bonding MO be denoted  $c_+$  - the wavefunction for the bonding MO may then be written:

$$\psi_+ = c_+(\phi_1 + \phi_2)$$

If a wavefunction is normalized (see Appendix 3) then the requirement on the wavefunction is that:

$$\int \psi^* \psi . d\tau = \int |\psi|^2 . d\tau = 1$$

For  $\psi_+$  therefore:

$$\Rightarrow c_+^2 \int (\phi_1 + \phi_2)^2 . d\tau = 1$$

$$\Rightarrow c_+^2 \left( \underbrace{\int \phi_1^2 . d\tau}_{=1} + 2 \underbrace{\int \phi_1 \phi_2 . d\tau}_{=S \approx 0} + \underbrace{\int \phi_2^2 . d\tau}_{=1} \right) = 1$$

$$\Rightarrow 2c_+^2 = 1 \quad \Rightarrow \quad c_+ = \frac{1}{\sqrt{2}}$$

i.e. 
$$\psi_+ = \frac{1}{\sqrt{2}}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

Similarly for the antibonding MO

$$\psi_- = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

Note : these values of the coefficients could also be obtained using the general normalisation condition of a molecular orbital (see Appendix 3) which states that when overlap is neglected

$$\sum c_i^2 = 1$$

e.g.

For  $\psi_+$  : 
$$\psi_+ = c_+\phi_1 + c_+\phi_2 \quad \text{i.e.} \quad c_1 = c_+ \quad \text{and} \quad c_2 = c_+$$

$$\sum c_i^2 = c_1^2 + c_2^2 = c_+^2 + c_+^2 = 1$$

$$\Rightarrow 2c_+^2 = 1$$

$$\Rightarrow c_+ = \frac{1}{\sqrt{2}}$$

## Case 2 : Heteronuclear Bonding

We can again proceed as in the previous case by substituting the values of  $E$  back into the secular equations, thereby obtaining two simultaneous equations for  $c_1$  and  $c_2$ .

< Lecture - specific solution for formaldehyde >

... but there is also a "general solution".

*General solution to the two-orbital problem:*

For  $\alpha_1 \leq \alpha_2$ , the general solutions for the wavefunctions (no proof will be given, and there is no need to memorize these results for the FPAM course) are:

$$\psi_- = -\sin\theta.\phi_1 + \cos\theta.\phi_2$$

$$\psi_+ = \cos\theta.\phi_1 + \sin\theta.\phi_2$$

where 
$$\tan 2\theta = \frac{\beta}{\frac{1}{2}(\alpha_1 - \alpha_2)}$$

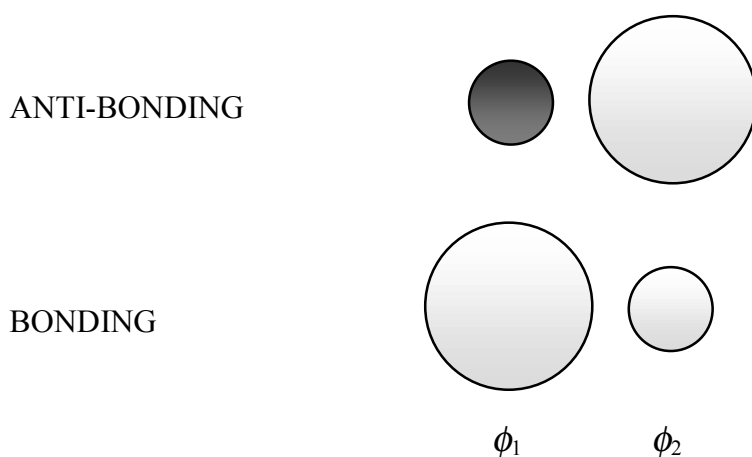
Note :  $\beta$  and  $(\alpha_1 - \alpha_2)$  are both negative, hence  $\tan 2\theta$  is positive.

$$\Rightarrow 0 < 2\theta < 90^\circ$$

$$\Rightarrow 0 < \theta < 45^\circ$$

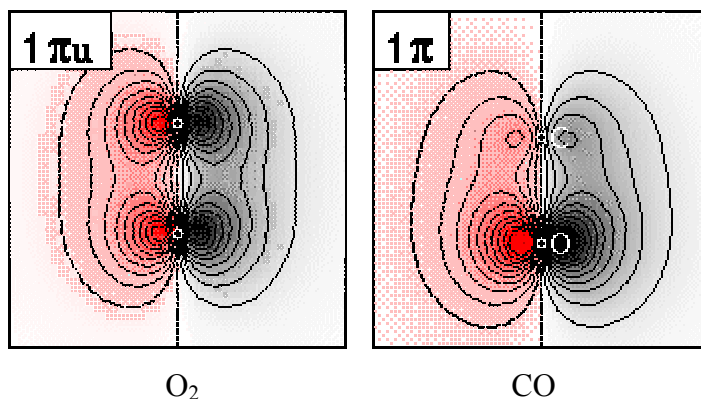
$$\Rightarrow |\cos\theta| > |\sin\theta|$$

The coefficients for the wavefunctions are therefore such that their character is as illustrated below:



i.e. the electron density in the occupied bonding MO is concentrated around the nucleus associated with the atomic orbital of lower energy (for orbitals of the same type on atoms of a particular period, this corresponds to the more electronegative nucleus and also that possessing the higher nuclear charge,  $Z$ ).

This effect can be seen in a comparison of the  $\pi$ -bonding molecular orbitals of oxygen ( $O_2$ ) and carbon monoxide (CO).



(Picture adapted from the [BALSAC Picture Gallery](#) by K. Hermann, Fritz-Haber-Institut, Berlin)

It may be noted that the coefficients of these "general solutions" automatically incorporate the *normalisation condition*.

The normalisation condition for molecular orbitals (see Appendix 3) formed by the combination of just two atomic orbitals, as in this instance, is:

$$\sum c_i^2 = 1 \quad \Rightarrow \quad c_1^2 + c_2^2 = 1$$

For the wavefunctions :  $\psi_- = -\sin\theta.\phi_1 + \cos\theta.\phi_2$   
 $\psi_+ = \cos\theta.\phi_1 + \sin\theta.\phi_2$

$$c_1^2 + c_2^2 = \sin^2\theta + \cos^2\theta$$

and since  $\sin^2\theta + \cos^2\theta = 1$  (one of the standard trigonometric relationships) it follows that,

$$c_1^2 + c_2^2 = 1$$

i.e. the wavefunctions ( $\psi_+$  and  $\psi_-$ ) given by the formulae quoted above, are already normalized.

We can also use the general solution to look at certain special (limiting) cases:

Special Case 1 : if  $|\beta| \gg \frac{1}{2}(\alpha_2 - \alpha_1)$

then

$$\Delta = \frac{1}{2} \sqrt{(\alpha_2 - \alpha_1)^2 + 4\beta^2} \approx \frac{1}{2} \sqrt{4\beta^2}$$

i.e.  $\Delta \rightarrow |\beta|$

and since  $E_{\pm} = \frac{1}{2}(\alpha_1 + \alpha_2) \mp \Delta$  (where  $\Delta$  is positive).

$$E_+ \rightarrow \frac{1}{2}(\alpha_1 + \alpha_2) + \beta$$

$$E_- \rightarrow \frac{1}{2}(\alpha_1 + \alpha_2) - \beta$$

Furthermore  $\tan 2\theta = \frac{\beta}{\frac{1}{2}(\alpha_1 - \alpha_2)} \rightarrow \infty$  since  $|\beta| \gg \frac{1}{2}(\alpha_2 - \alpha_1)$

which leads to the conclusion that

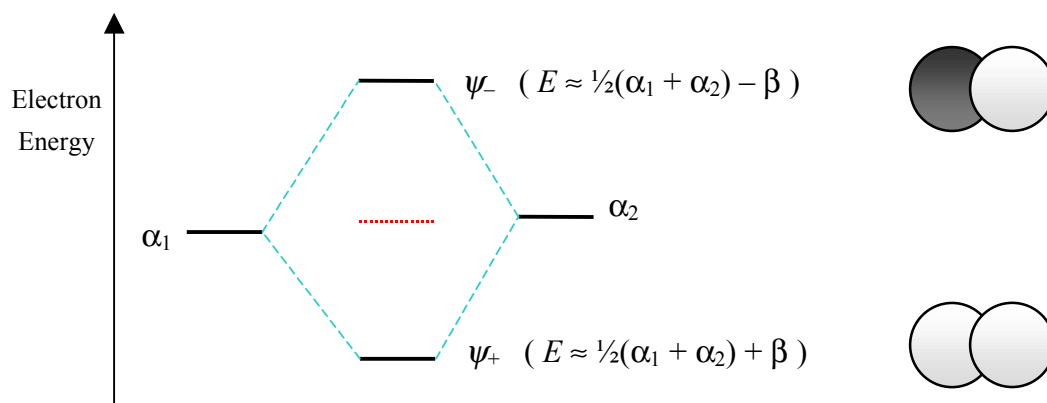
$$2\theta \rightarrow 90^\circ, \theta \rightarrow 45^\circ$$

in which case,

$$\cos\theta \rightarrow \frac{1}{\sqrt{2}} \text{ and } \sin\theta \rightarrow \frac{1}{\sqrt{2}}$$

and

$$\psi_+ \rightarrow \frac{1}{\sqrt{2}}(\phi_1 + \phi_2), \quad \psi_- \rightarrow \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$



i.e. if the interaction energy ( $\beta$ ) is much larger than the difference between the energies of the original overlapping orbitals, then we are rapidly approaching the situation which pertains when  $\alpha_1 = \alpha_2 = \alpha$  (i.e. the special case of overlap of two identical orbitals that we considered initially).

Special Case 2 : if  $|\beta| \ll \frac{1}{2}(\alpha_2 - \alpha_1)$

then

$$\Delta = \frac{1}{2}\sqrt{(\alpha_2 - \alpha_1)^2 + 4\beta^2} \approx \frac{1}{2}\sqrt{(\alpha_2 - \alpha_1)^2}$$

i.e.  $\Delta \rightarrow \frac{1}{2}(\alpha_2 - \alpha_1)$

and since  $E_{\pm} = \frac{1}{2}(\alpha_1 + \alpha_2) \mp \Delta$

$$E_+ \rightarrow \frac{1}{2}(\alpha_1 + \alpha_2) - \frac{1}{2}(\alpha_2 - \alpha_1) = \alpha_1$$

$$E_- \rightarrow \frac{1}{2}(\alpha_1 + \alpha_2) + \frac{1}{2}(\alpha_2 - \alpha_1) = \alpha_2$$

Furthermore  $\tan 2\theta = \frac{\beta}{\frac{1}{2}(\alpha_1 - \alpha_2)} \rightarrow 0$  since  $|\beta| \ll \frac{1}{2}(\alpha_2 - \alpha_1)$

which leads to the conclusion that

$$2\theta \rightarrow 0, \theta \rightarrow 0$$

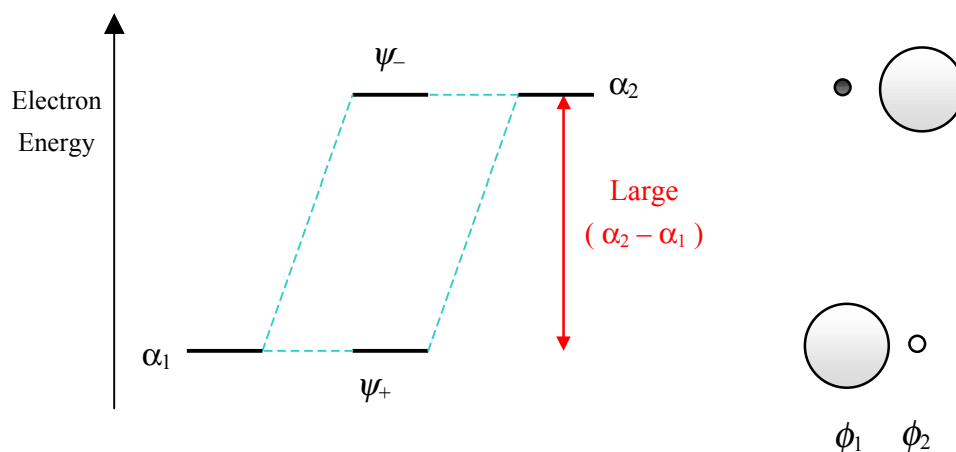
in which case,

$$\cos\theta \rightarrow 1 \text{ and } \sin\theta \rightarrow 0$$

and

$$\psi_+ \rightarrow \phi_1, \quad \psi_- \rightarrow \phi_2$$

i.e. the orbitals and their energies are almost unchanged.



### Important Conclusion

Bonding interactions arising from orbital overlap can be neglected if the energy separation of the overlapping orbitals is large compared to the interaction energy,  $\beta$ .