

7 Symmetry & Hybridisation

As the size of a molecule increases (and the number of valence atomic orbitals contributing to the bonding increases) then the solution of the secular equations can become rather difficult but consideration of *molecular symmetry can be used to greatly simplify the problem.*

To illustrate this consider a simple example - a diatomic molecule HX (where X = Li, Be, B, C, N, O, F)



The valence orbitals of the atoms concerned are: H 1s
X 2s, 2p_x, 2p_y, 2p_z

The interactions of the five valence orbitals can be described using a (5×5) secular determinant.

	1s	2s	2p _z	2p _y	2p _x	
1s	$\alpha_{1s} - E$	β_{ss}	β_{sp}	0	0	} AOs of the X-atom are orthogonal - hence they "can't interact with each other"
2s	β_{ss}	$\alpha_{2s} - E$	0	0	0	
2p _z	β_{sp}	0	$\alpha_{2p} - E$	0	0	
2p _y	0	0	0	$\alpha_{2p} - E$	0	
2p _x	0	0	0	0	$\alpha_{2p} - E$	

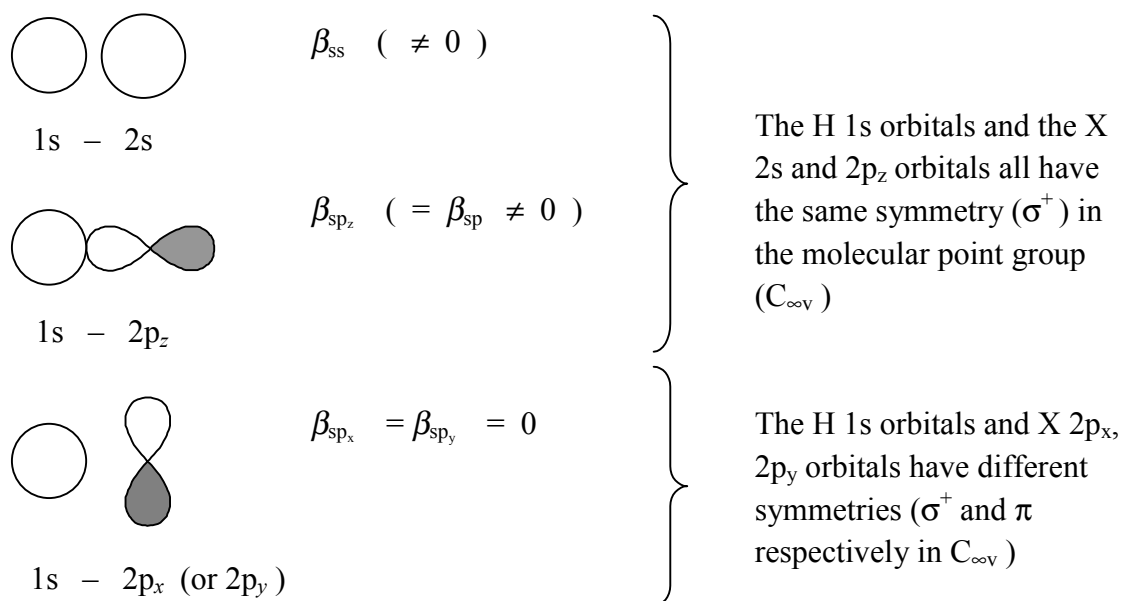
} H 1s will only give a non-zero resonance integral when it overlaps with the 2s and 2p_z orbitals of the X atom - see below.

The off-diagonal elements in the determinant may be obtained by noting that:

- (i) Integrals involving two different orbitals of the X atom are exactly zero, since the atomic orbitals are orthogonal to one another.
- (ii) The resonance integrals due to the interactions of the H 1s orbital with the orbitals of the X atom are only non-zero if the orbitals have the "same symmetry" (that is, the same symmetry within the point group of the molecule).

Conversely, if the two overlapping orbitals are of different symmetries then any constructive overlap of the orbitals is always exactly counterbalanced by an equal amount of destructive overlap and the net interaction is always exactly zero.

..... these two contrasting situations are illustrated below.



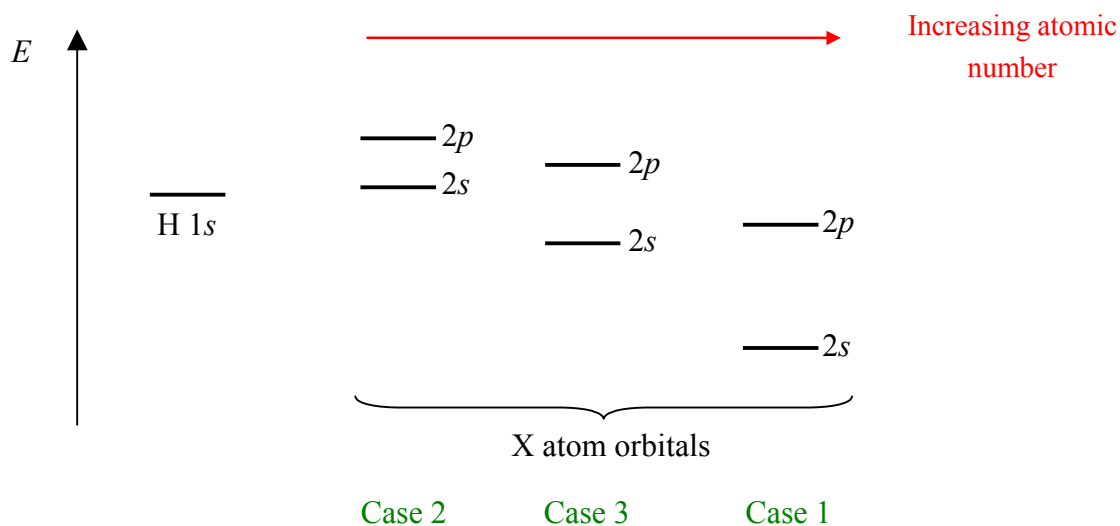
Consequently, in this case, rows 4 and 5 have no (non-zero) off-diagonal elements, because the 2p_x and 2p_y orbitals are of different symmetry to the H 1s orbital. The (5×5) secular determinant can therefore be simplified to two trivial (1×1) determinants and a (3×3) determinant.

$$\left| \begin{array}{ccc} (5 \times 5) \\ \end{array} \right| = 0 \quad \left\{ \begin{array}{l} |\alpha_{2p} - E| = 0 \quad \Rightarrow \quad E = \alpha_{2p_x} \\ |\alpha_{2p} - E| = 0 \quad \Rightarrow \quad E = \alpha_{2p_y} \\ \left| \begin{array}{ccc} \alpha_{1s} - E & \beta_{ss} & \beta_{sp} \\ \beta_{ss} & \alpha_{2s} - E & 0 \\ \beta_{sp} & 0 & \alpha_{2p} - E \end{array} \right| = 0 \end{array} \right.$$

We can conclude that in this molecule, the 2p_x and 2p_y orbitals of the X atom are non-bonding, and more generally that *it is only necessary to consider interactions between orbitals possessing the same symmetry in the molecular environment.*

Solution of the (3×3) Determinant

Strictly any solution necessarily involves both the 2s and 2p_z orbitals of the X atom - however, the extent to which each is involved depends upon the energies of the orbitals relative to that of the 1s orbital of the H atom, and this varies significantly across the periodic table.



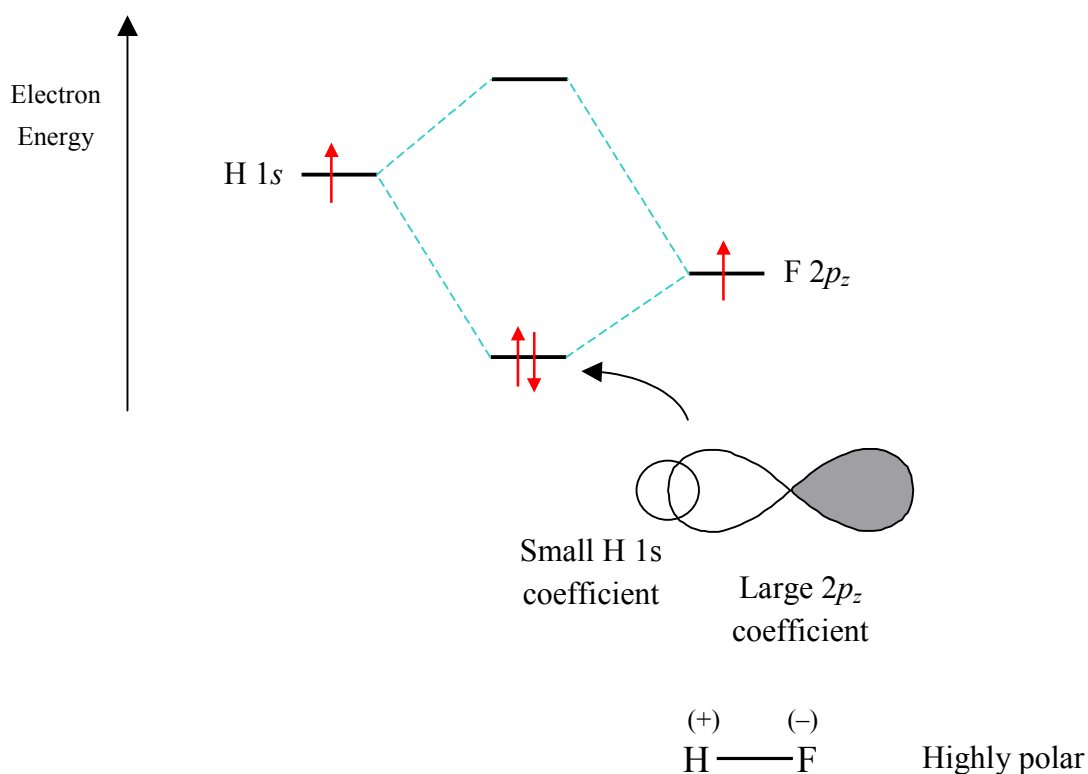
The above diagram illustrates how the relative orbital energies might vary for different X atoms; we now need to remember (see 4.15) that

There is only a significant bonding interaction between two orbitals if the energy separation, $|\alpha_2 - \alpha_1|$ is not large compared to the interaction energy, as represented by the resonance integral, β_{12} .

We can therefore identify three "limiting" cases:

Case 1 : the main interaction is $H\ 1s - X\ 2p_z$... and if we completely neglect any interaction with $X\ 2s$ then the problem simplifies to a (2×2) determinant.

e.g. HF



Case 2 : the main interaction is H $1s - X 2s$... and if we completely neglect any interaction with X $2p_z$ then the problem again simplifies to a (2x2) determinant - this limiting case is most closely approached for LiH .

Case 3 : .. is the intermediate case.

To illustrate what sort of solutions might be obtained in this case we can consider a "model" system (obtained by making some drastic simplifying assumptions) - let us suppose that:

$$\begin{aligned}\alpha_{2s} &= \alpha_{1s} + \frac{1}{2}\beta \\ \alpha_{2p} &= \alpha_{1s} - \frac{1}{2}\beta\end{aligned}$$

and $\beta_{ss} = \beta_{sp}$ (and, for simplicity, just call this β)

Then,

$$\begin{vmatrix} \alpha_{1s} - E & \beta_{ss} & \beta_{sp} \\ \beta_{ss} & \alpha_{2s} - E & 0 \\ \beta_{sp} & 0 & \alpha_{2p} - E \end{vmatrix} = 0$$

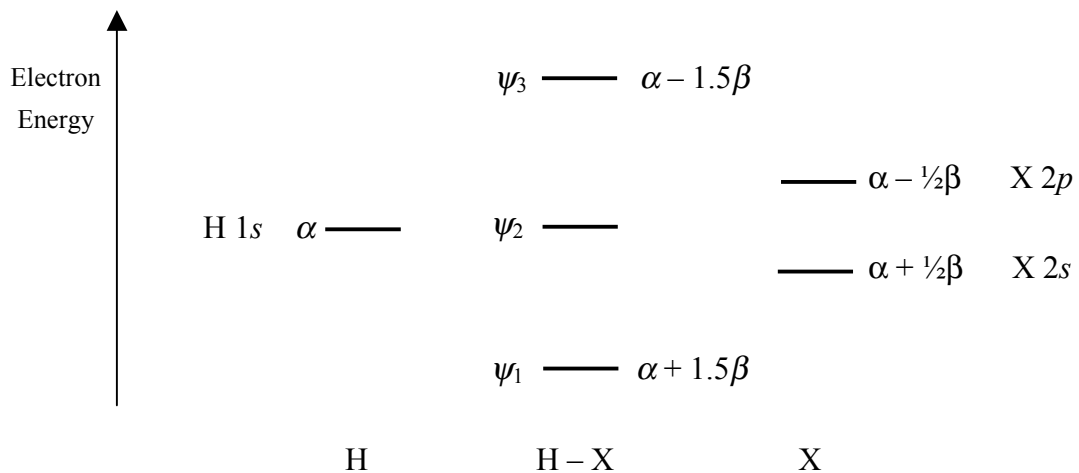
simplifies to

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & (\alpha + \frac{1}{2}\beta) - E & 0 \\ \beta & 0 & (\alpha - \frac{1}{2}\beta) - E \end{vmatrix} = 0$$

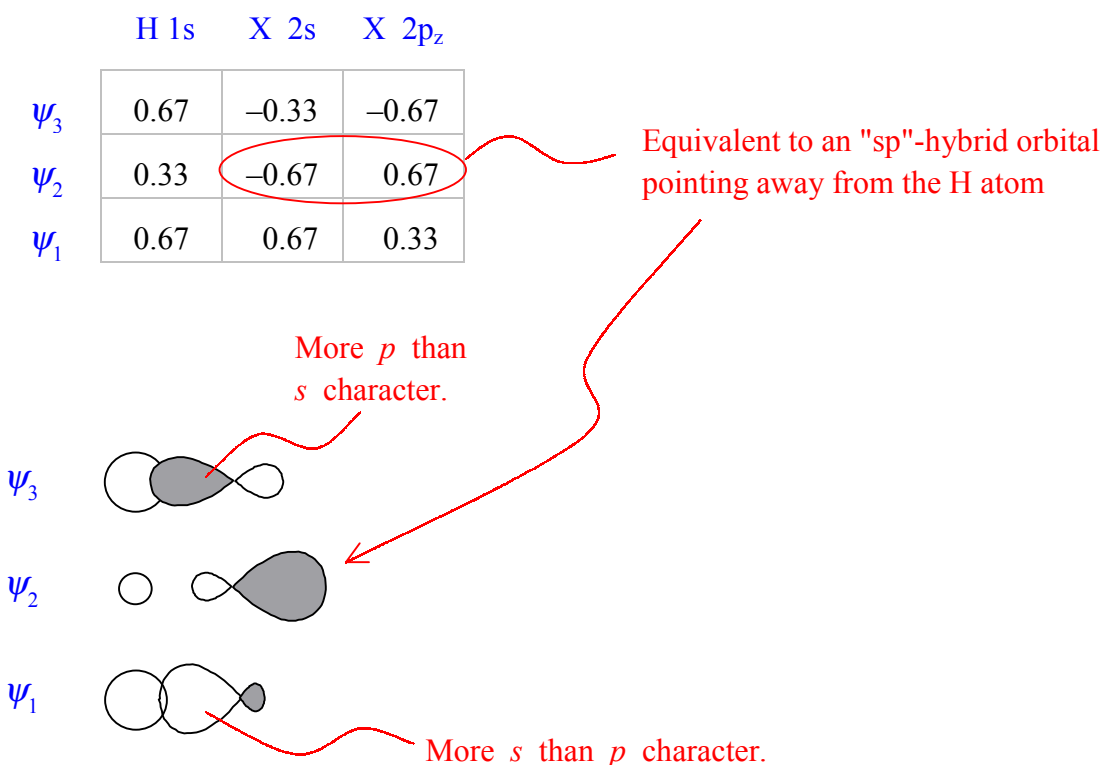
where α is the value for α_{1s} .

$$\Rightarrow \begin{vmatrix} x & 1 & 1 \\ 1 & (x + \frac{1}{2}) & 0 \\ 1 & 0 & (x - \frac{1}{2}) \end{vmatrix} = 0$$

To which the solutions are ...



Now consider the MO coefficients



Note that similar, but not identical, MO energies and orbital coefficients would be predicted using a valence bond approach (as illustrated below) in which we first "hybridise" the 2s and 2p_z orbitals of the X atom to give two sp hybrid orbitals and then let the one pointing towards the H atom interact with the H 1s orbital whilst the other is considered to undergo no interaction with the H 1s orbital and may thus be labelled a *non-bonding* orbital,

