## **Molecular Orbital Theory**

In molecular orbital theory covalent bonds are the result of atoms combining atomic orbitals to form new molecular orbitals. Since atomic orbitals are wavefunctions they have wave character which means that when two atomic orbitals (wavefunctions) combine, they do so both *constructively* (in-phase) and *destructively* (out-of-phase).



Perhaps it is easier to see what is happening on a molecular orbital energy level diagram:





Bond order is a measure of the stabilisation resulting from the formation of the molecule

- bond order = no. of filled bonding orbitals no. of filled antibonding orbitals
- $H_2 = 1 0 = 1$  which is the same as predicted by the Lewis model (one pair of electrons between the two H atoms ) and valence bond theory

If the bond order is zero, the molecule will not exist **e.g. Be<sub>2</sub>** 1s<sup>2</sup> 2s<sup>2</sup>



Bond order (1-1) = 0



Generally speaking, we draw simplified MO energy level diagrams that only include the valence electrons that contribute to the bonding of the molecule.





occupation of  $1\sigma$  and  $1\sigma^*$  MO contribute nothing to bonding (1-1=0) and because of the greater bond length / distance between the nuclei in Li<sub>2</sub>, the 1s orbitals don't interact all that much

It is interesting to compare the molecular bond in  $H_2$  with  $Li_2$ . The 2s orbitals are more diffuse than 1s so there is less overlap between them and as a result, less electron density between the two lithium nuclei than between the two hydrogen nuclei. The Li-Li bond is weaker.

This is reflected in the bond dissociation enthalpies:  $H_{2(g)} = + 436 \text{ kJ mol}^{-1}$  $\text{Li}_{2(g)} = + 105 \text{ kJ mol}^{-1}$ 

**E.g. F<sub>2</sub>** 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>

We now need to think about how p-orbitals combine to form molecular orbitals.



The z-axis is defined as running along the F-F bond so a  $p_z$  orbital from each fluorine atom will have the correct direction to be able to combine to form  $\sigma$  bonding and  $\sigma^*$  antibonding molecular orbitals.

In-phase combination of  $p_z$  orbitals



 $\sigma^*$  antibonding molecular orbital

The  $p_x$  and  $p_y$  atomic orbitals are perpendicular to the F-F axis so the  $p_x$  orbitals on each fluorine atom (and, separately, the two  $p_y$  orbitals) combine to form  $\Pi$  bonding and  $\Pi^*$  antibonding molecular orbitals.



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- the  $\Pi$  bonding MO formed from the combination of  $p_x$  atomic orbitals has the same energy as the  $\Pi$  bonding MO formed from the combination of  $p_y$  atomic orbitals (they are said to be degenerate). The same goes for the two  $\Pi^*$  antibonding MO
- the interactions between the two  $p_x$  atomic orbitals or between the two  $p_y$  atomic orbitals is less effective (than the interaction between the two  $p_z$  atomic orbitals) because they are not pointing directly at each other this means that ...

1.  $\Pi$  orbitals are not as stabilised or as unstabilised as  $\sigma$  orbitals, as compared to the original atomic orbitals

2.  $\square$ -overlap is more distance sensitive than  $\sigma$  overlap so the greater the distance between the two nuclei, the weaker the bond - we notice this, for example, in the elements of Period 2 which more commonly form double and triple bonds (N=N) than elements in other Periods (P-P)

 $\bullet$  the  $p_x$  orbital on one atom cannot combine with the  $p_y$  orbital on the other atom as they don't have the same symmetry



Bond order (4-3) = 1; there is a single bond in  $F_2$ 

