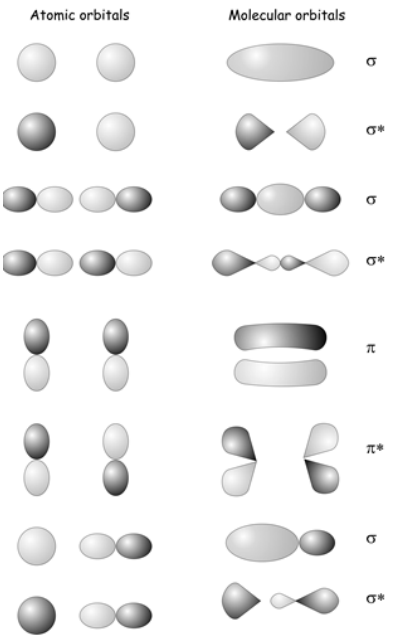
1.18: Bonding in Diatomics



You will already be familiar with the idea of constructing molecular orbitals from linear combinations of atomic orbitals from previous courses covering bonding in diatomic molecules. By considering the symmetries of s and p orbitals on two atoms, we can form **bonding** and **antibonding** combinations labeled as having either σ or π symmetry depending on whether they resemble s or p orbitals when viewed along the bond axis (see diagram below). In all of the cases shown, only atomic orbitals that have the same symmetry when viewed along the bond axis z can form a chemical bond e.g. two s orbitals, two p_z orbitals , or an s and a p_z can form a bond, but a p_z and a p_x or an s and a p_x or a p_y cannot. It turns out that the rule that determines whether or not two atomic orbitals can bond is that *they must belong to the same symmetry species within the point group of the molecule*.

We can prove this mathematically for two atomic orbitals ϕ_i and ϕ_j by looking at the overlap integral between the two orbitals.

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int \phi_i^* \phi_j d\tau \qquad (18.1) \qquad (1.18.1)$$

In order for bonding to be possible, this integral must be non-zero. The product of the two functions ϕ_1 and ϕ_2 transforms as the direct product of their symmetry species i.e. $\Gamma_{12} = \Gamma_1 \otimes \Gamma_2$. As explained above, for the overlap integral to be non-zero, Γ_{12} must contain the totally symmetric irreducible representation (A_{1g} for a homonuclear diatomic, which belongs to the point group $D_{\infty h}$). As it happens, this is only possible if ϕ_1 andϕ_2 belong to the same irreducible representation. These ideas are summarized for a diatomic in the table below.

First Atomic Orbital	Second Atomic Orbital	$\Gamma_1 \otimes \Gamma_2$	Overlap Integral	Bonding?
$s\ (A_{1g})$	$s\ (A_{1g})$	A_{1g}	Non-zero	Yes
$s\ (A_{1g})$	$p_x\ (E_{1u})$	E_{1u}	Zero	No
$s\ (A_{1g})$	$p_z\ (A_{1u})$	A_{1u}	Zero	No
$p_x\ (E_{1u})$	$p_x\ (E_{1u})$	$A_{1g} + A_{2g} + E_{2g}$	Non-zero	Yes
$p_X\ (E_{1u})$	$p_z\ (A_{1u})$	E_{1g}	Zero	No
$p_z\ (A_{1u})$	$p_z\ (A_{1u})$	A_{1g}	Non-zero	Yes

(18.2)