Review

Analogous to the atomic orbitals, wavefunctions which describe electrons in a molecule are called Molecular Orbital (MO)

MO: Polycentric 1-electron function: spreads through the molecule

One way of constructing the molecular orbitals is to add together atomic orbital wavefunctions which are located at various atoms of the molecule: Linear Combination of Atomic Orbitals (LCAO)

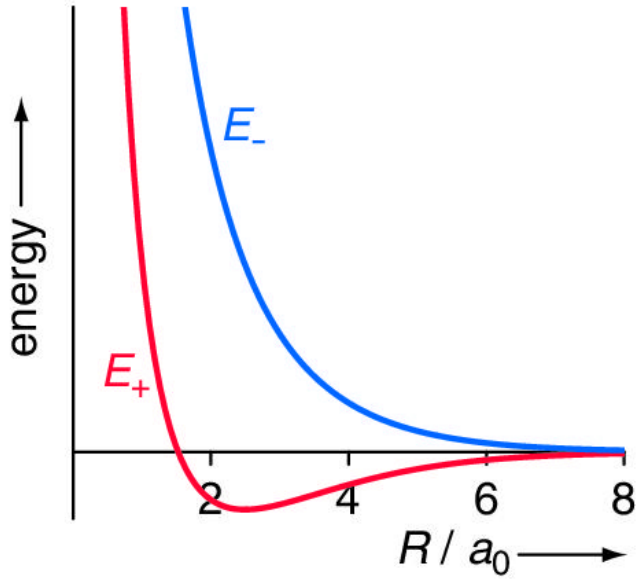
Bonding Molecular Orbital

$$\Psi_+ = c_A \Psi_A + c_B \Psi_B \qquad \text{Energy} = E_+$$

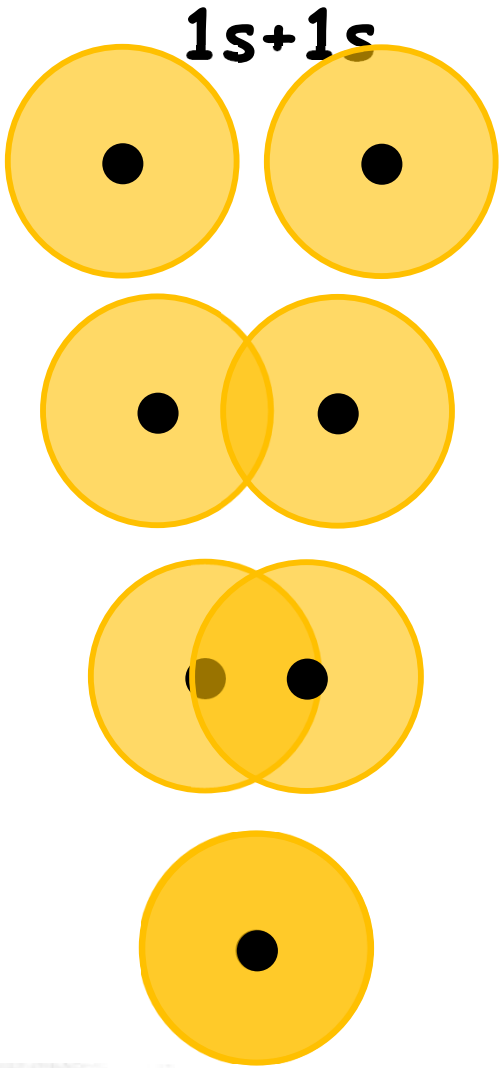
Anti-Bonding Molecular Orbital

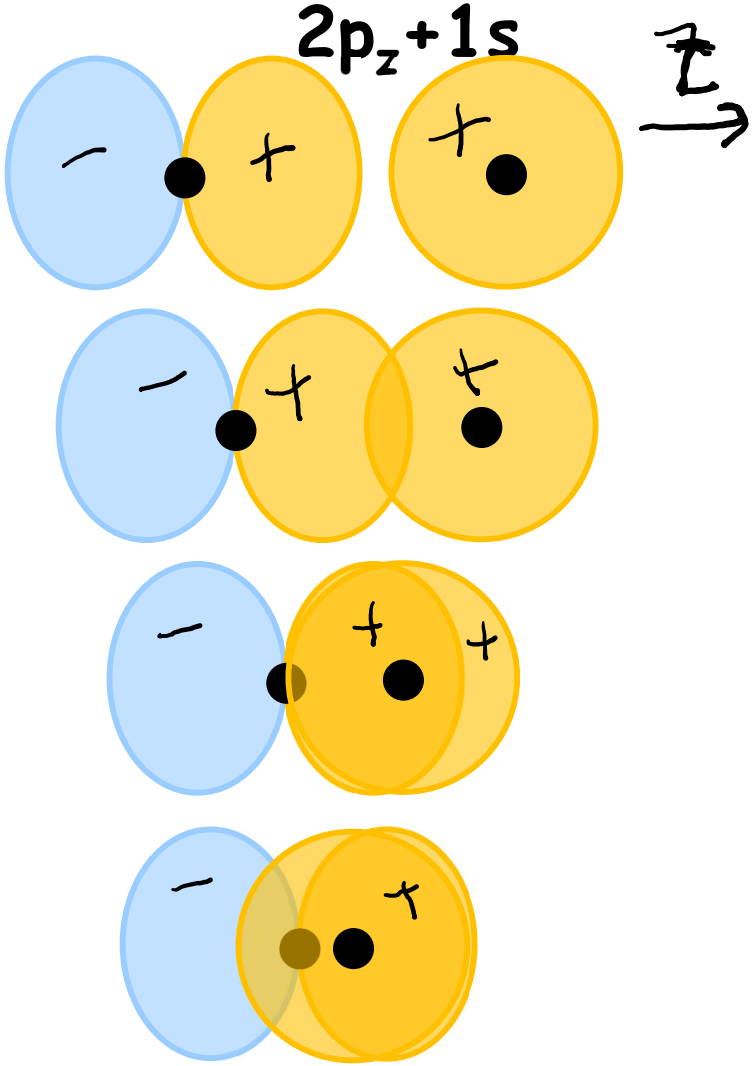
$$\Psi_- = c_A \Psi_A - c_B \Psi_B \qquad \text{Energy} = E_-$$

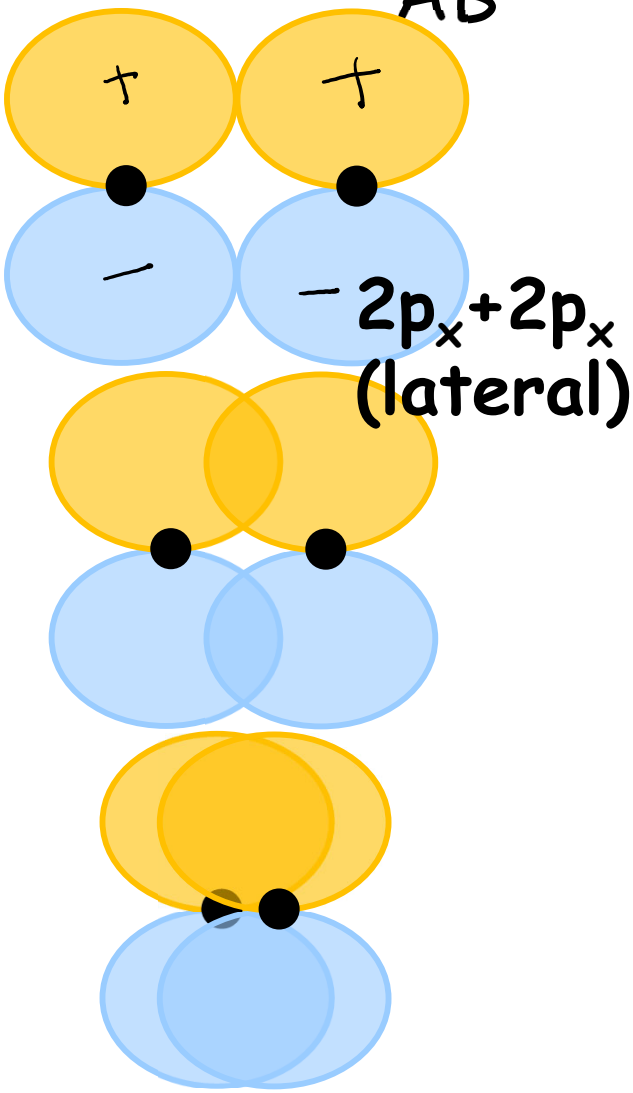
For H_2^+: $c_A = c_B = 1$

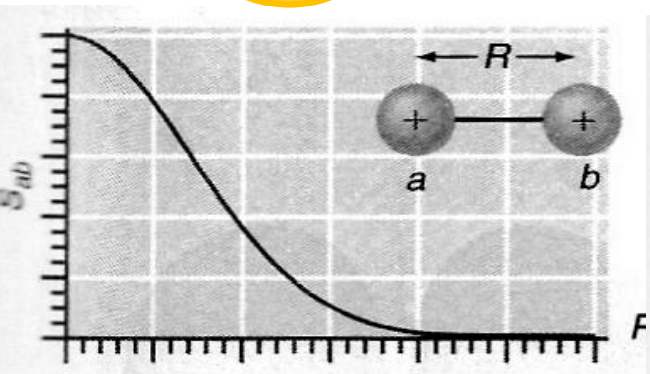


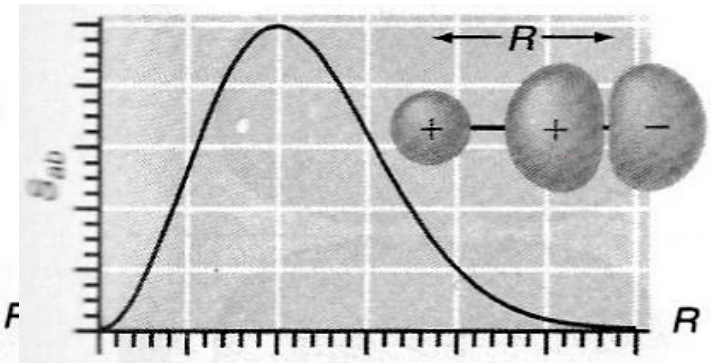
Overlap Integral depends on R_{AB}

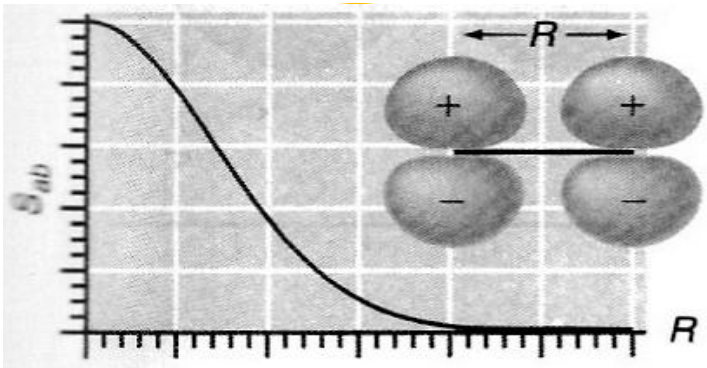






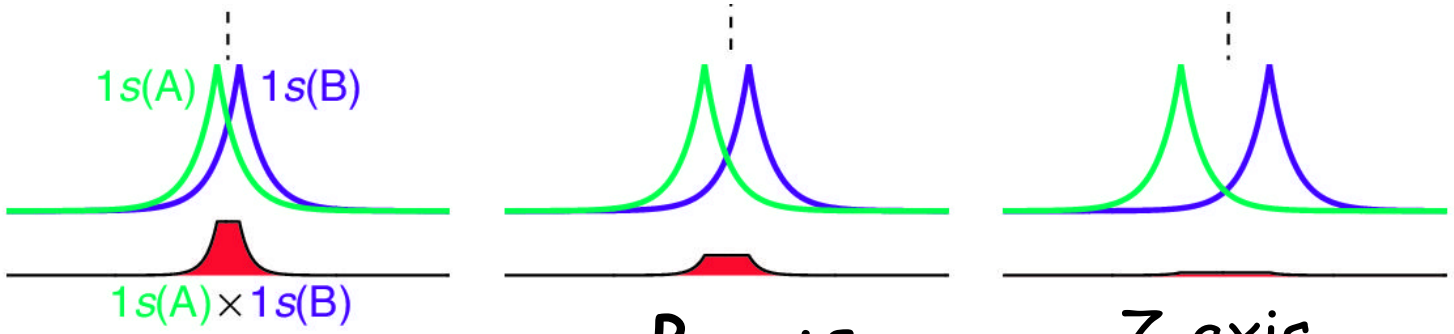






Review

$$\textit{Overlap Integral } S_{AB}(R) = \langle \psi_1 | \psi_2 \rangle = \int \psi_1 \psi_2 \, d\tau$$

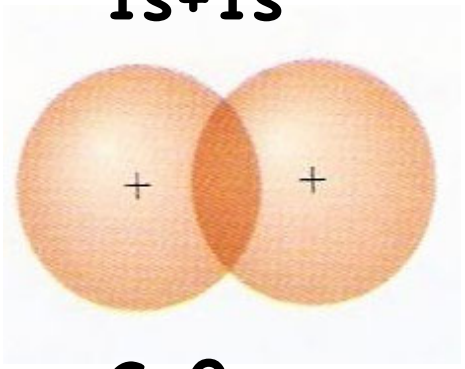


$P_{X/Y}$ +s

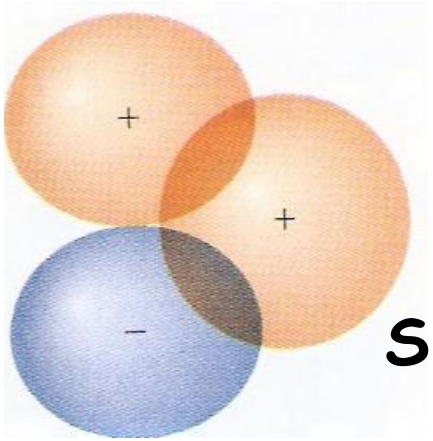
Z-axis

P_Z + s

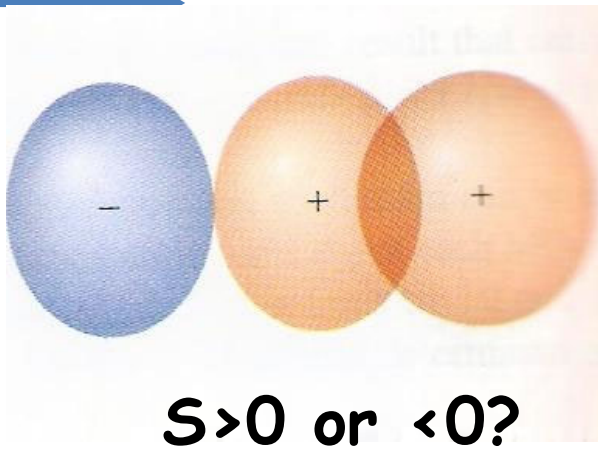
1s+1s



S>0



S=0

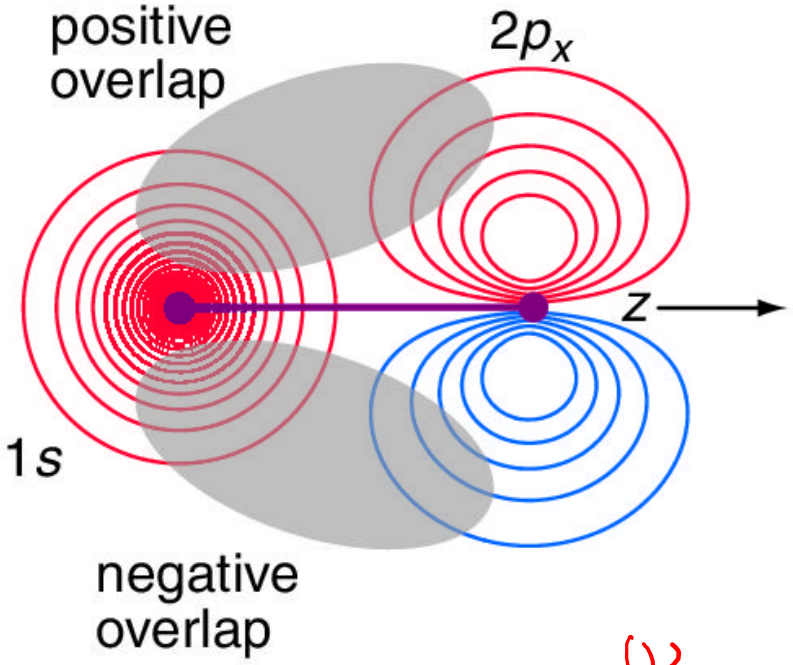


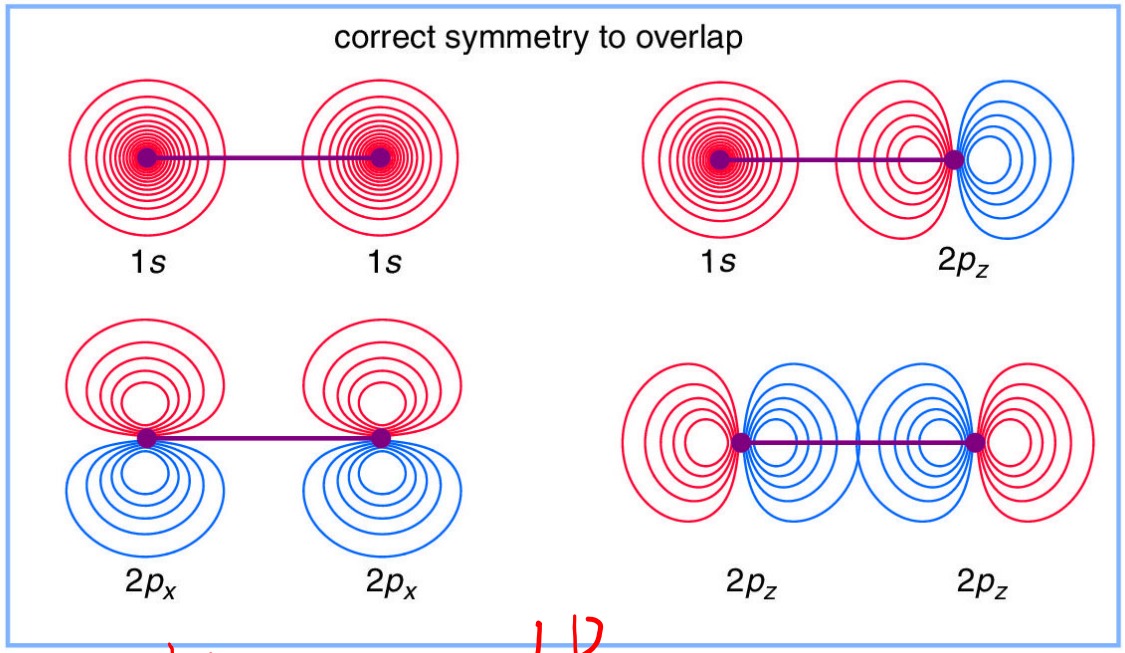
S>0 or <0?

→S is a qualitative measure of bond strength
→If S>>0; electron delocalized over molecule
→S(R) = 0 ➔ bond formation cannot occur

Overlap Integral depends on Symmetry

$P_x + s$

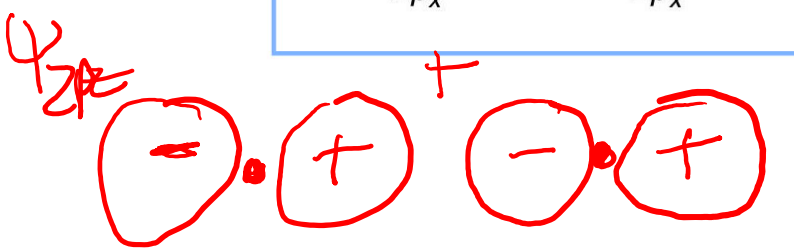


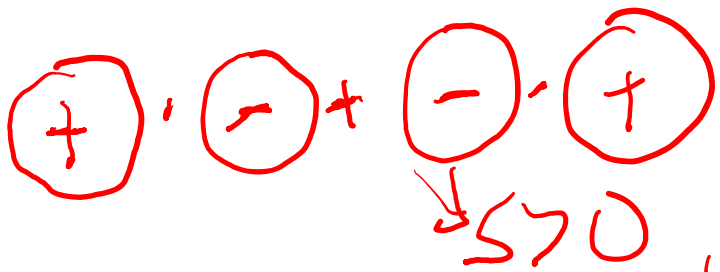


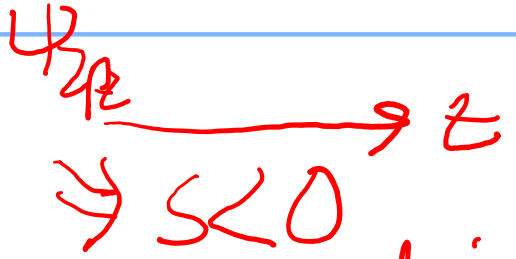
S=0

$\psi_{2pz} + \psi_{2pz}$

$-\psi_{2pz} + \psi_{2pz}$

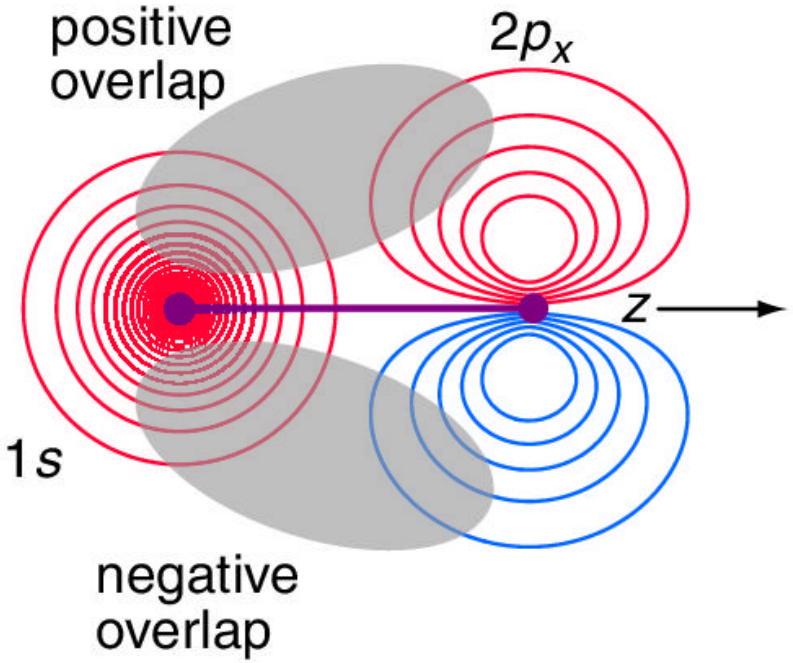


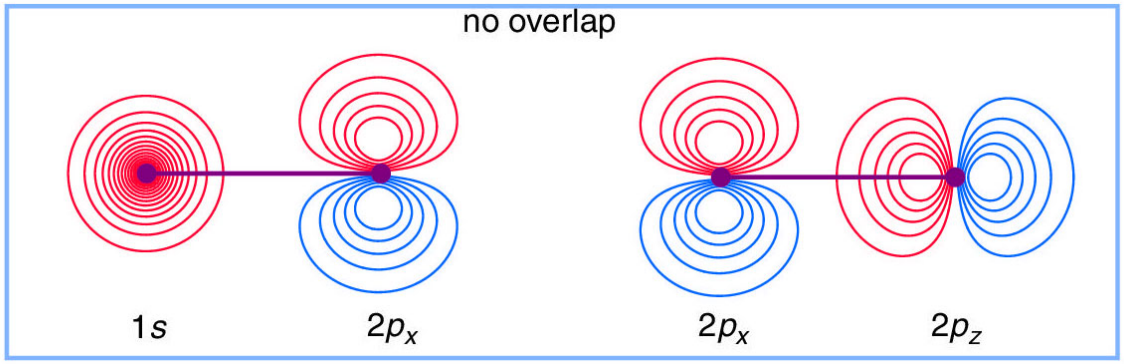




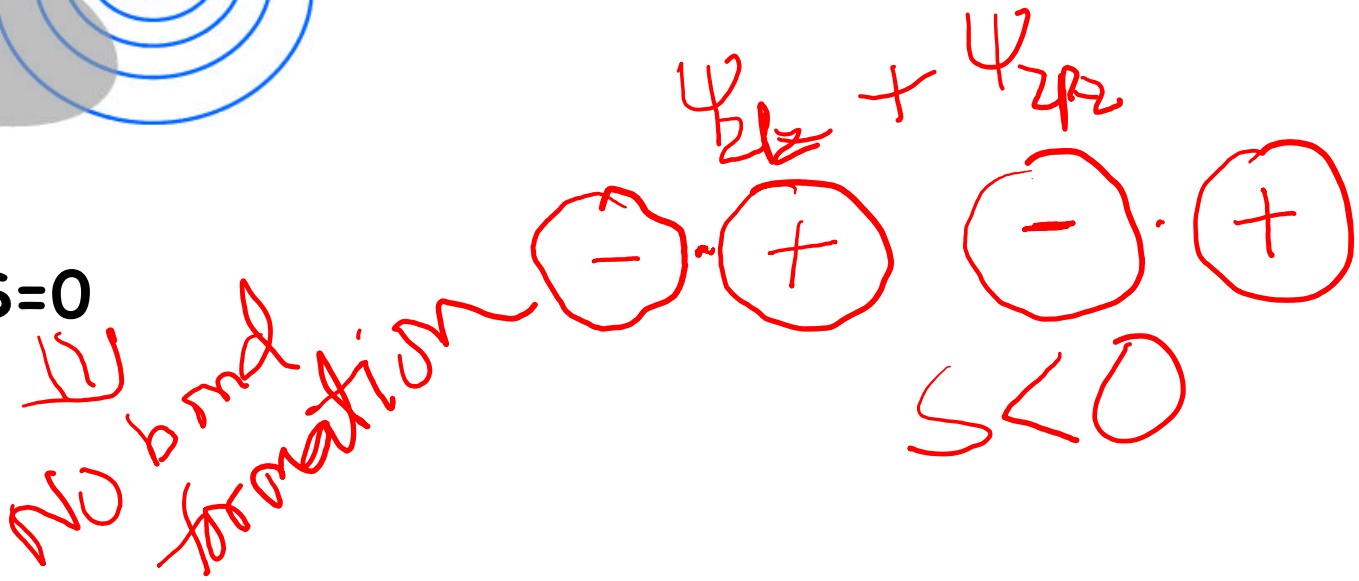
Overlap Integral depends on Symmetry

P_x + s



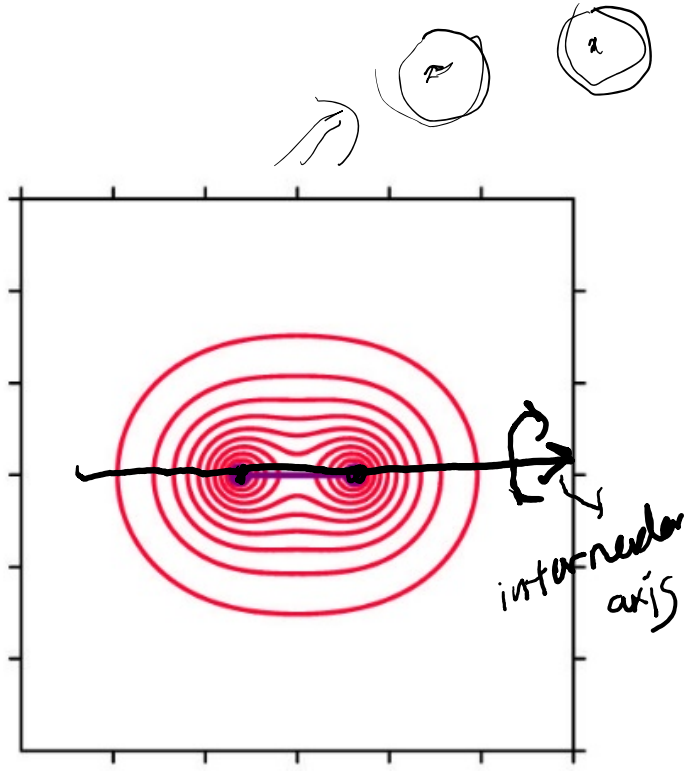


S=0

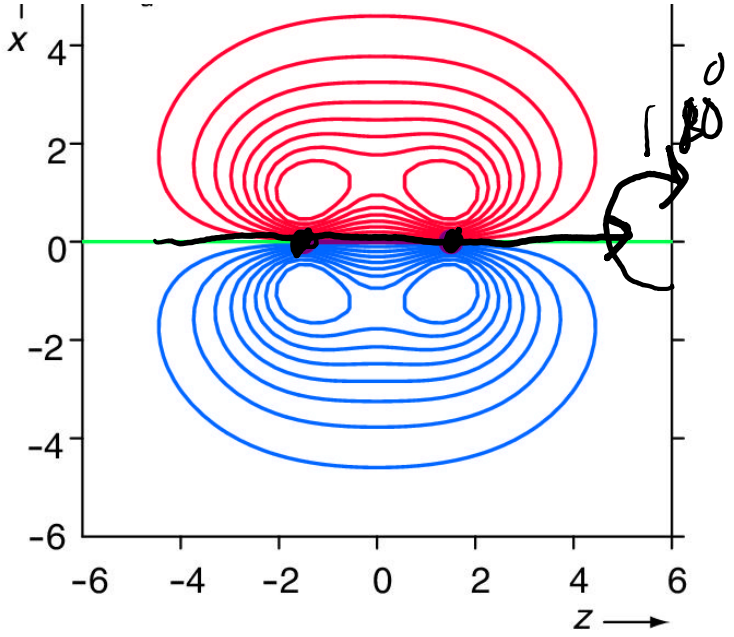


Symmetry Labels

The wavefunction of MO's which are unaffected by a rotation through any angle about the internuclear axis are labelled σ (sigma)

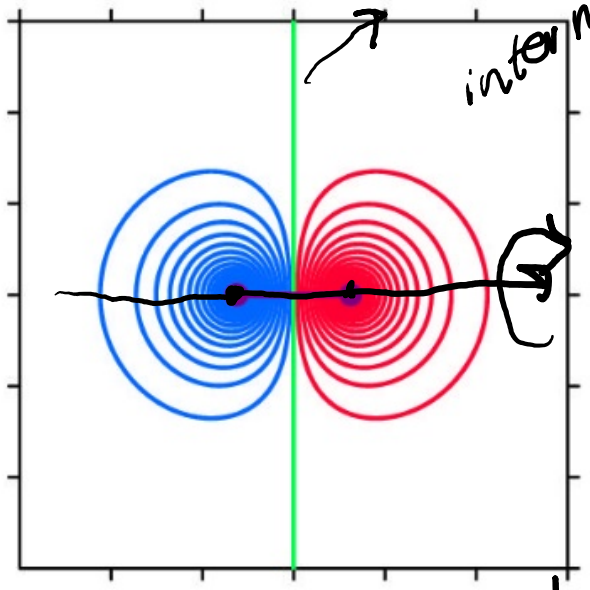


The wavefunction of MO's which changes sign through rotation by 180° about the internuclear axis are labelled π (pi)

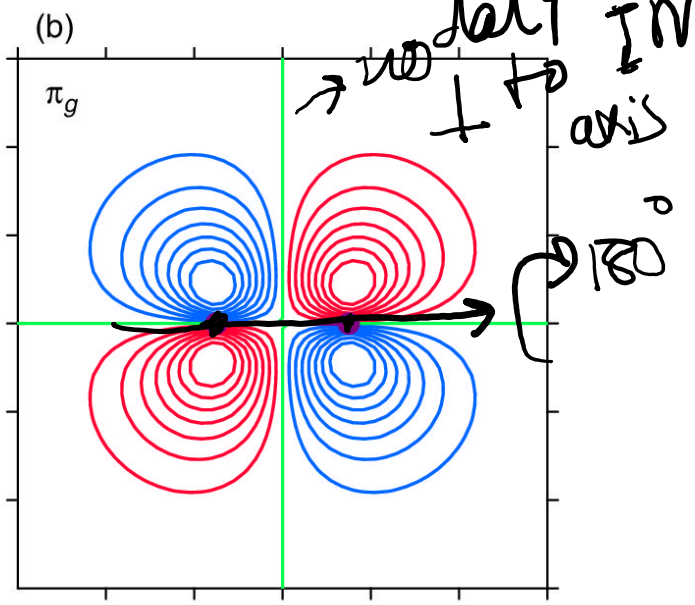


Symmetry Labels

Anti-bonding σ* (sigma)



Anti-bonding π* (pi)



Symmetry and Nomenclature of MOs

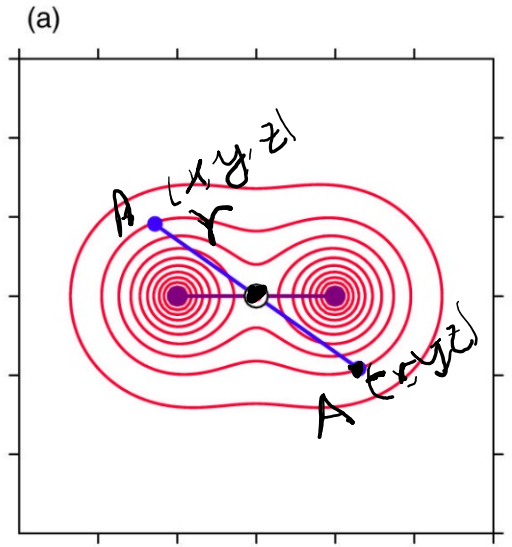
Gerade (g) (symmetric) and Ungerade (u) (antisymmetric) wrt inversion of coordinates (operation)!

$$Inversion\ Operation: \hat{I}$$

$$\hat{I} \Rightarrow (+x,+y,+z) \rightarrow (-x,-y,-z)$$

$$\hat{I}\Psi\left(\vec{r}\right) = \Psi\left(-\vec{r}\right) = +\Psi\left(\vec{r}\right): Symmetric$$

$$\hat{I}\Psi\left(\vec{r}\right) = \Psi\left(-\vec{r}\right) = -\Psi\left(\vec{r}\right): Anti-sym$$

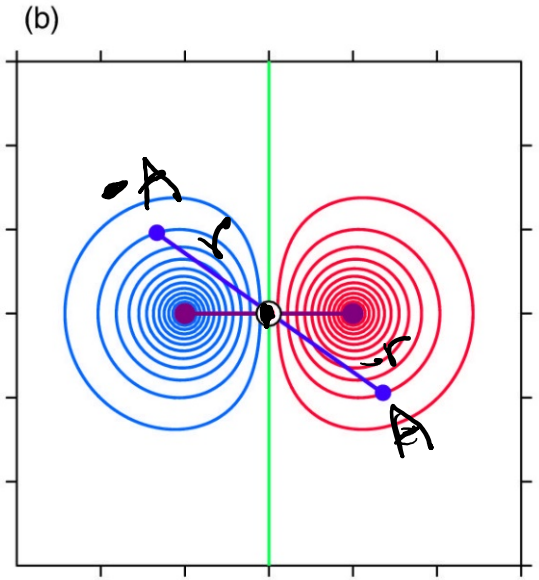


σ_g

Hydrogen molecule ion:

"b"→ Bonding using s: symmetric→σ_g

"a"→ antibonding using s: antisymmetric→ σ_u^*



σ_u^*