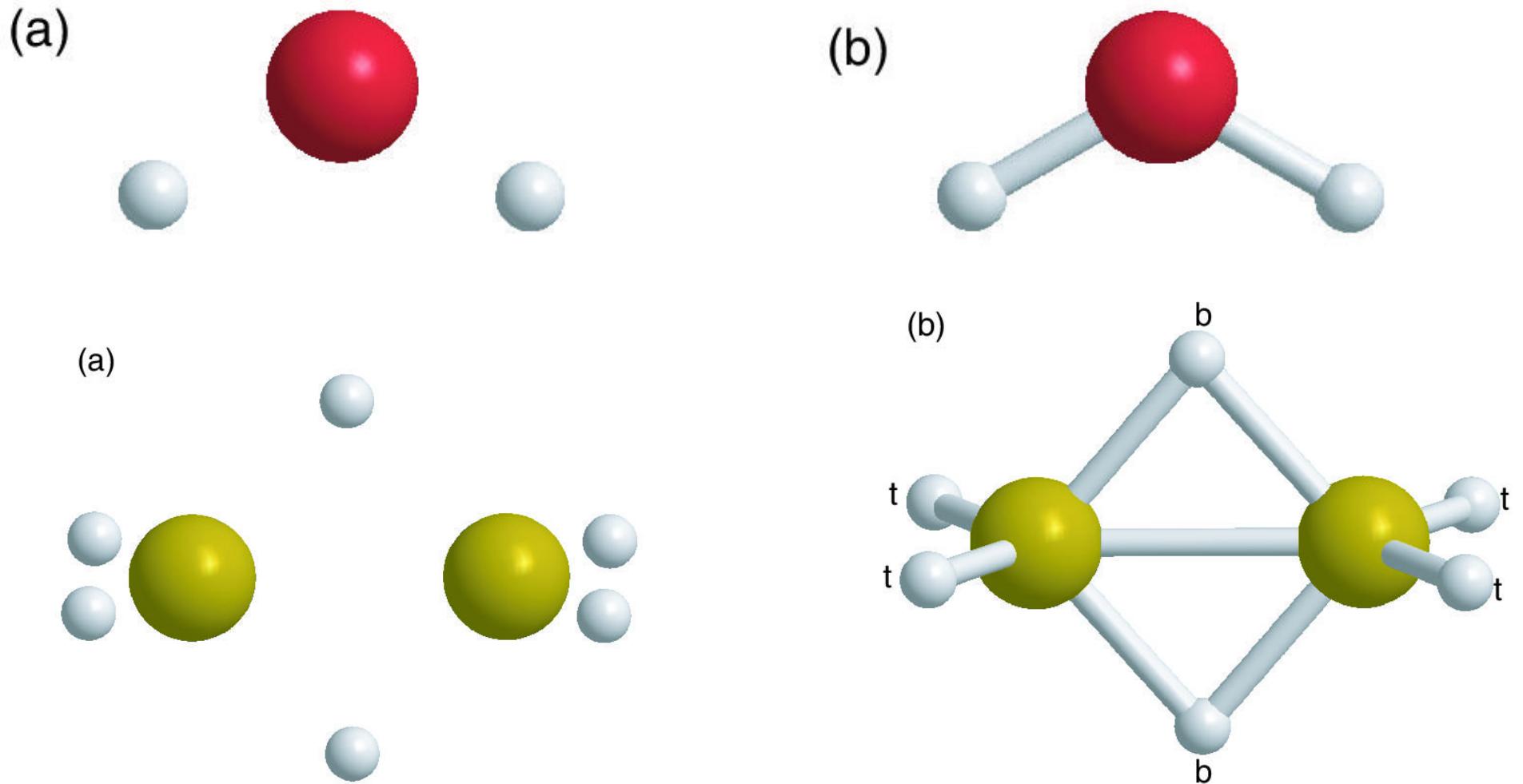


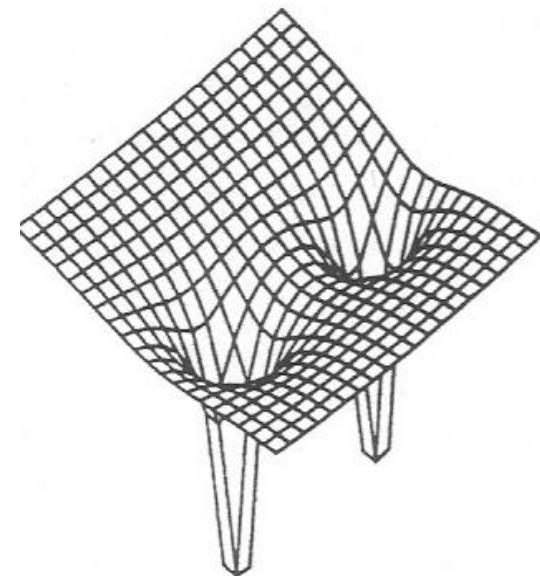
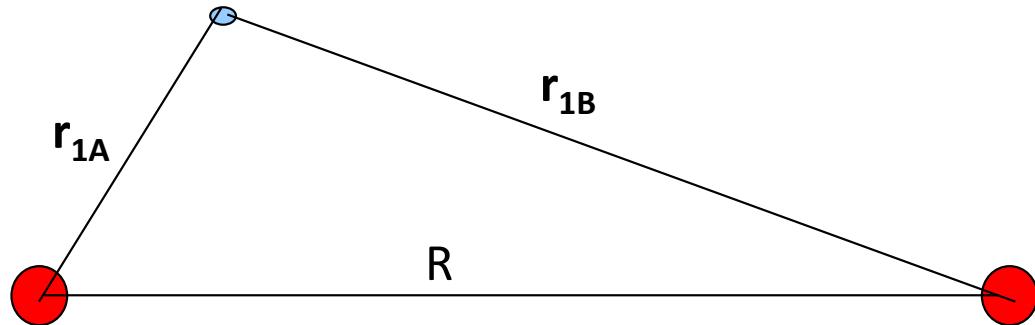
# Where are the Bonds?



B-H distances 117 pm and 132 pm; B-B distance 175 pm

# Simplest Molecule: $H_2^+$ - 1electron

2 Nuclei + 1 Electron



$H_2^+$  Molecule Ion Exists, Stable (Experimentally observed)  
Bond length  $\sim 1\text{\AA}$  ( $2a_0$ ) ; Bond Energy  $\sim 270 \text{ kJ/mole}$  ( $0.1E_H$ )

One more electron complicate matters to great extent!  
Just like many electron atoms - So, we need to build a  
Model with  $H_2^+$  and get insight into chemical bonding

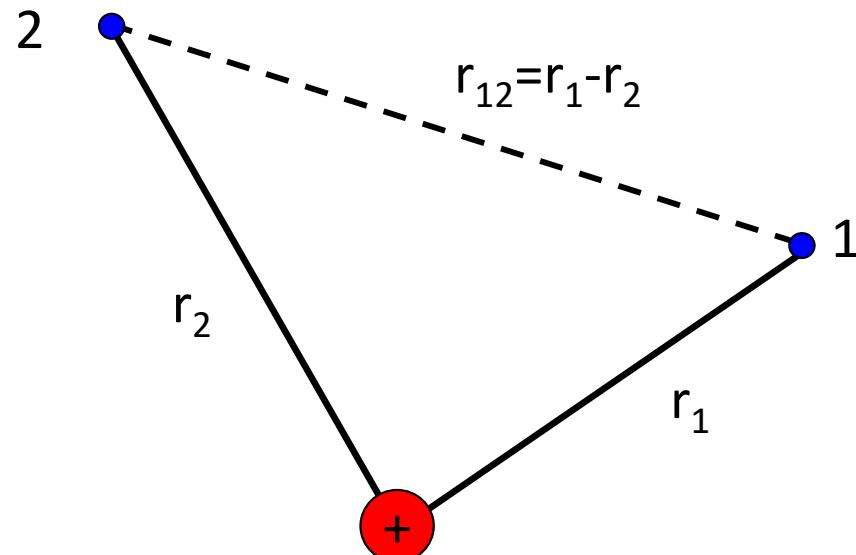
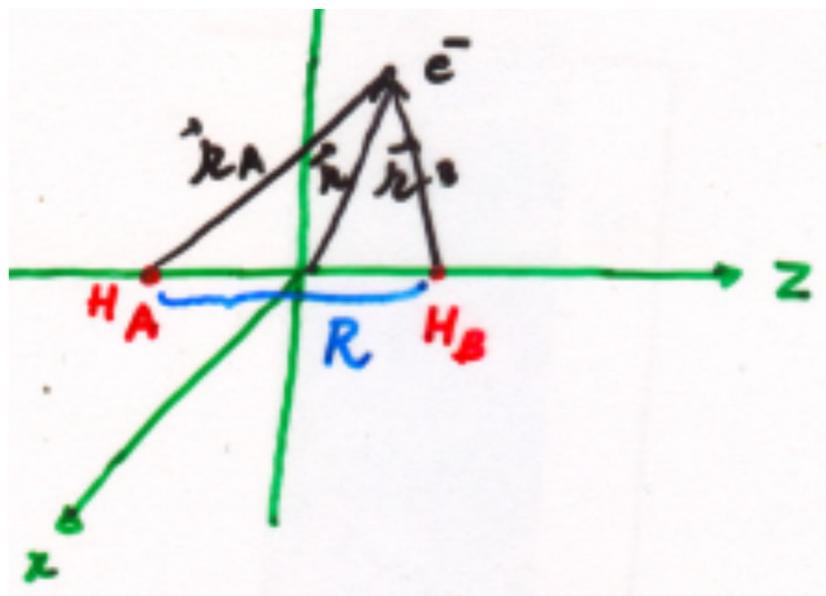
Then extend model for other multi-electronic molecules <sup>4</sup>

# Understanding Chemical Bonding

A theory is required which would teach us:

1. Why sharing leads to a lowering of energy
2. Energy of a particular bond is related to the nature of sharing
3. Why sharing might not be equal between atoms

# Simplest Molecules: $\text{H}_2^+$

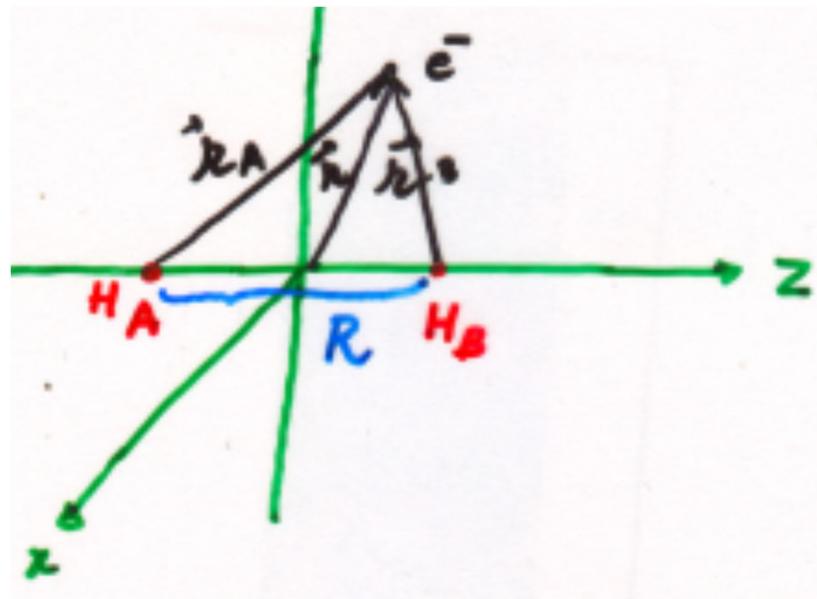


Dissociating this molecule to  $\text{H}$  and  $\text{H}^+$  requires 256 kJ/mol or 61 kcal/mol

Bond Dissociation energy

$$\text{BDE}(\text{H}_2^+) = E(\text{H}_2^+) - E(\text{H} + \text{H}^+)$$

# Simplest Molecules: $H_2^+$



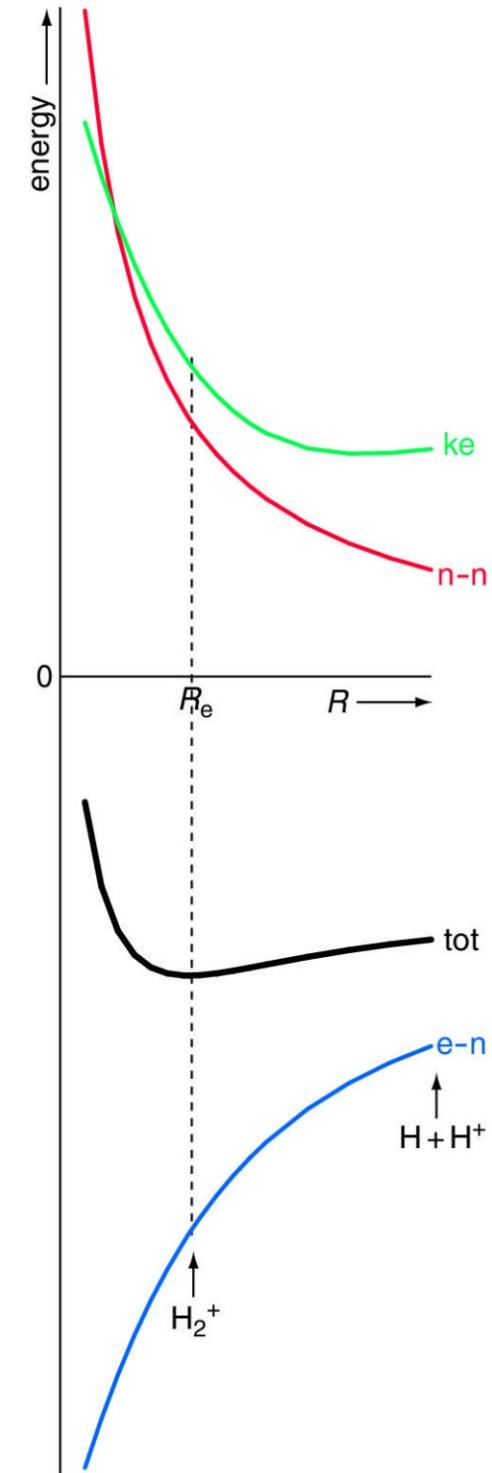
## Potential Energy

- (i) Favourable interaction of electron and nucleus which is dependent on  $R$
- (ii) Unfavourable interaction between nucleus ( $1/R$ )

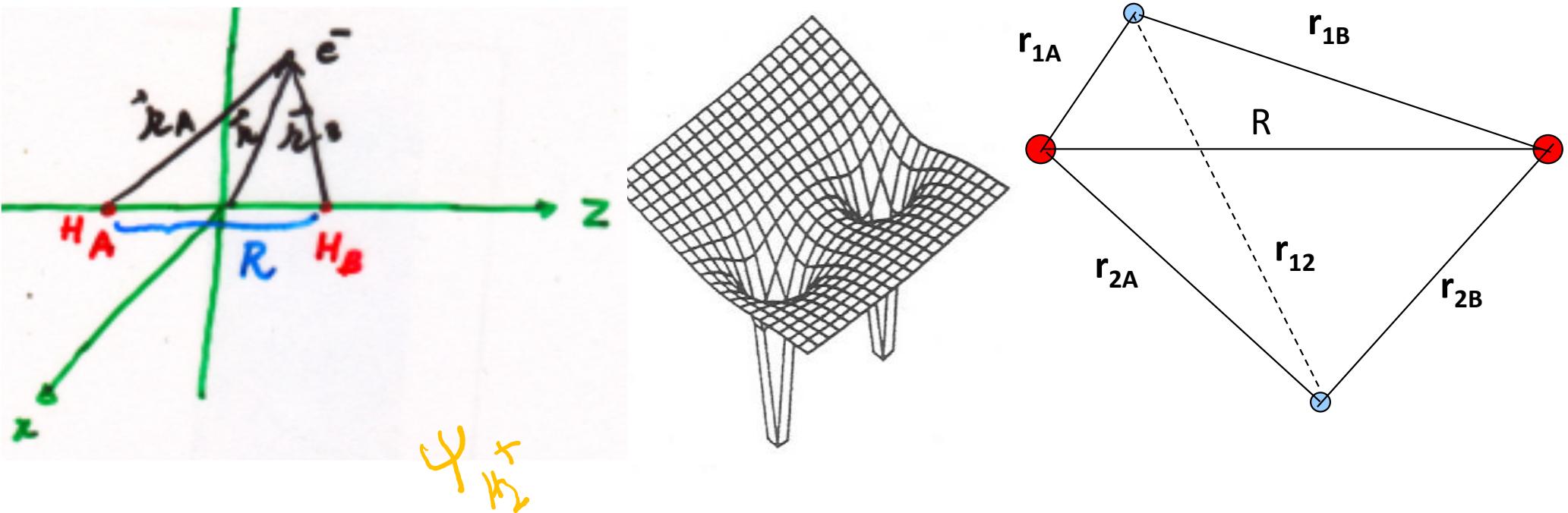
## Kinetic Energy

- (i) KE of electron associated with its motion about both nuclei

The total energy is summation of these three terms and the minimum at a particular value of  $R$  is called equilibrium separator  $R_e$



# Simplest Molecules: $H_2^+$ and $H_2$



TISE for  $H_2^+$

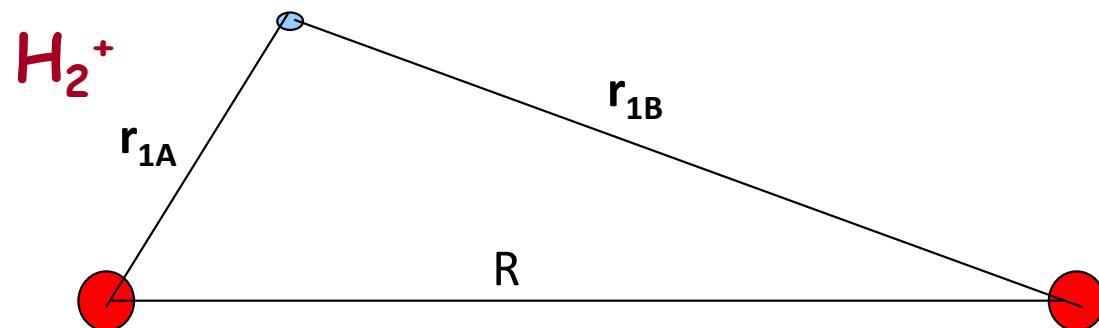
$$\hat{H}_{H_2^+}(\vec{r}, R)\Psi_{H_2^+}(\vec{r}, R) = E_{H_2^+}(\vec{r}, R)\Psi_{H_2^+}(\vec{r}, R)$$

Very difficult, but possible to solve TISE under elliptical polar coordinates at one  $R$ . Solve for energy at various  $R$

# Molecular Orbital Theory

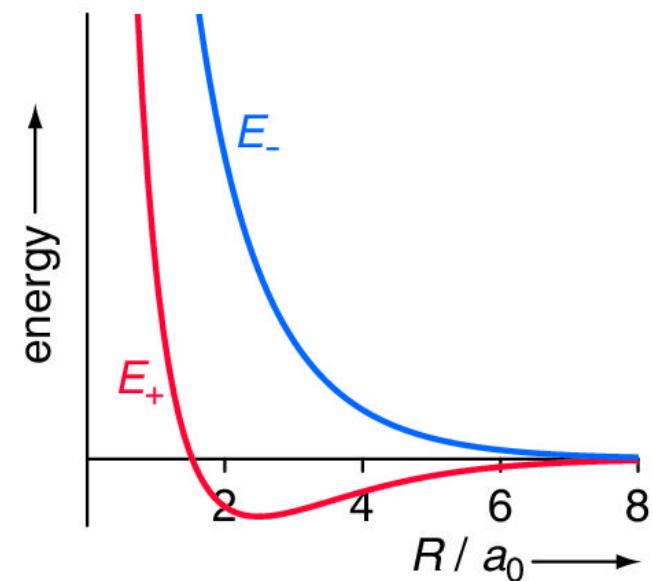
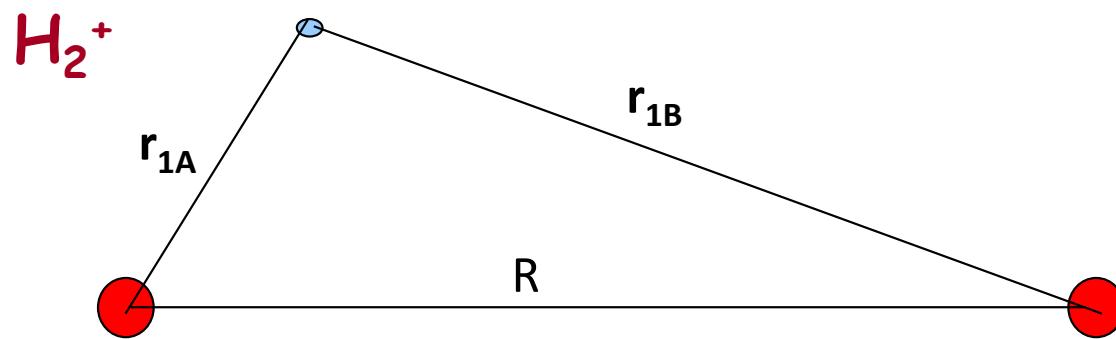
Analogous to the atomic orbitals, wavefunctions which describe electrons in a molecule are called Molecular Orbital (MO)

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)

# Molecular Orbital Theory



MO generated by Linear Combination of Atomic Orbitals (LCAO)

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

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

For  $\text{H}_2^+$ :  $c_A = c_B = 1$

Determine  $E_+$  and  $E_-$  as a function of  $R$

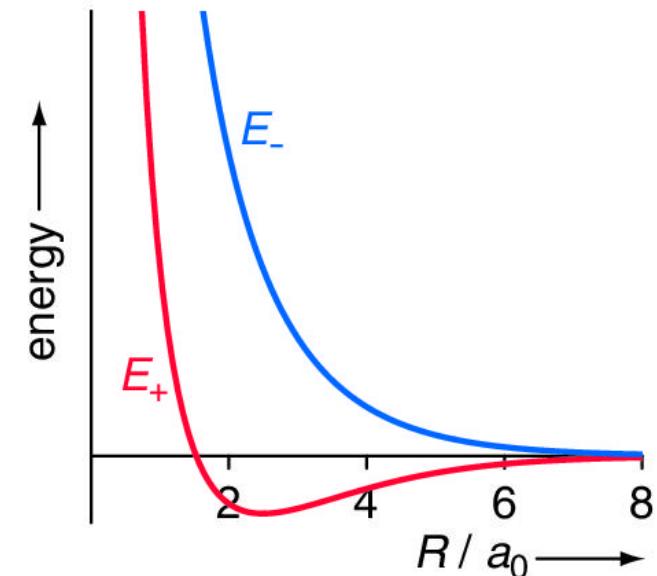
# Molecular Orbital Theory

$H_2^+$

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

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

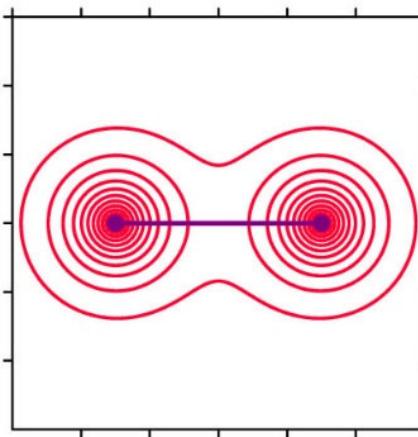
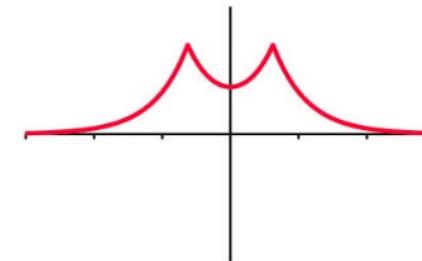
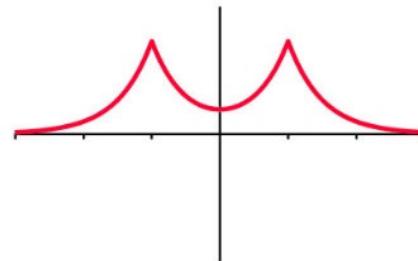
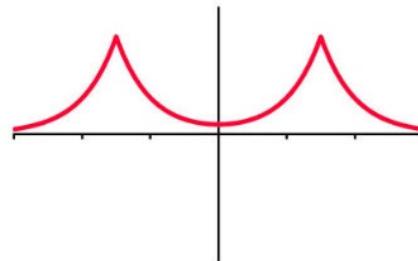
For  $H_2^+$ :  $c_A = c_B = 1$



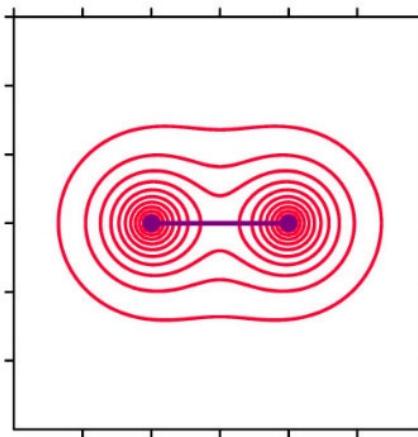
- As the atoms approach one another the energy of  $\Psi_+$  falls at first, reaching a minimum at  $R = 2.5 a_0$  (145 pm) before rising steeply
- If electron placed in this orbital, it is favorable for two atoms to come together until  $2.5 a_0$ , at which point energy is minimum: called **Bonding Orbital**
- As the atoms approach one another the energy of  $\Psi_-$  simply rises
- If electrons were placed in this orbital it would be disadvantageous in energy terms: called **Anti-Bonding Orbital**

# Contour plots of bonding and anti-bonding MO's

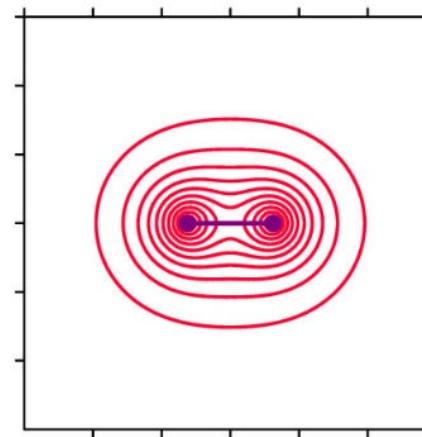
(a)



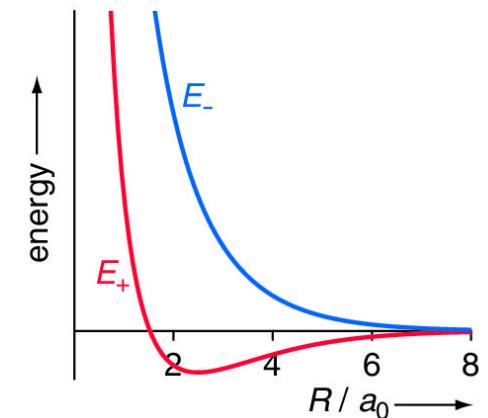
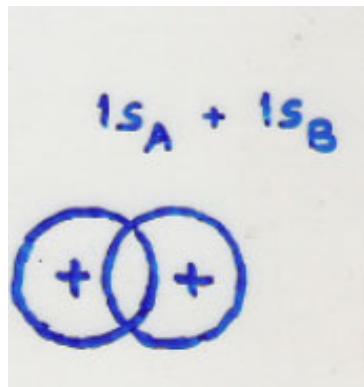
$R = 6 a_0$



$R = 4 a_0$

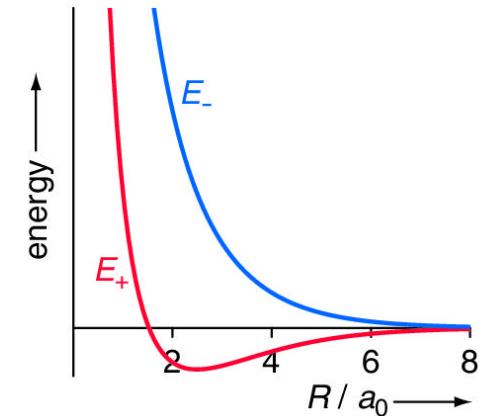
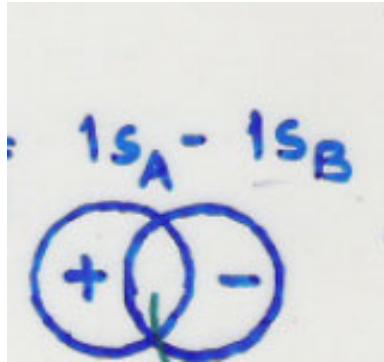
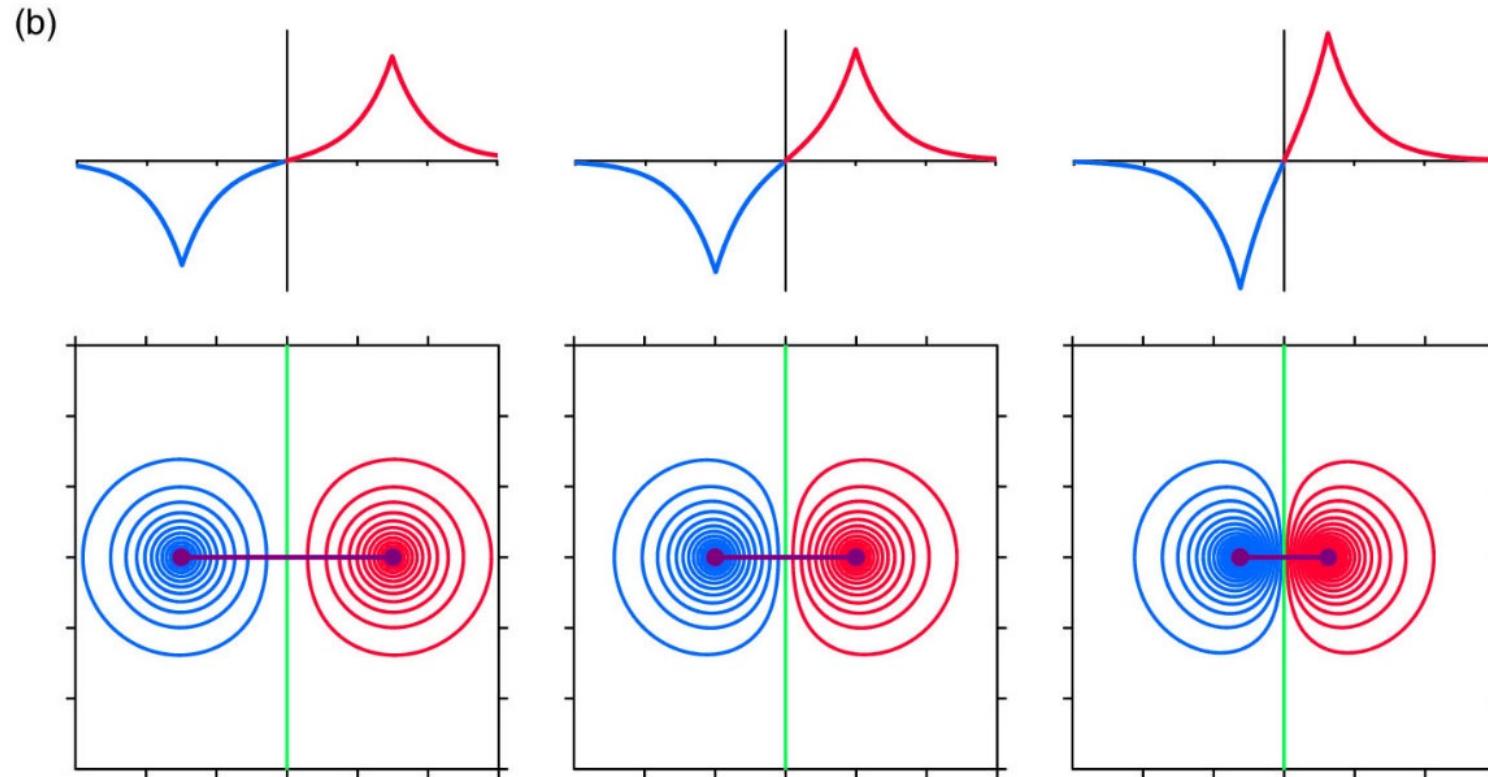


$R = 2.5 a_0$



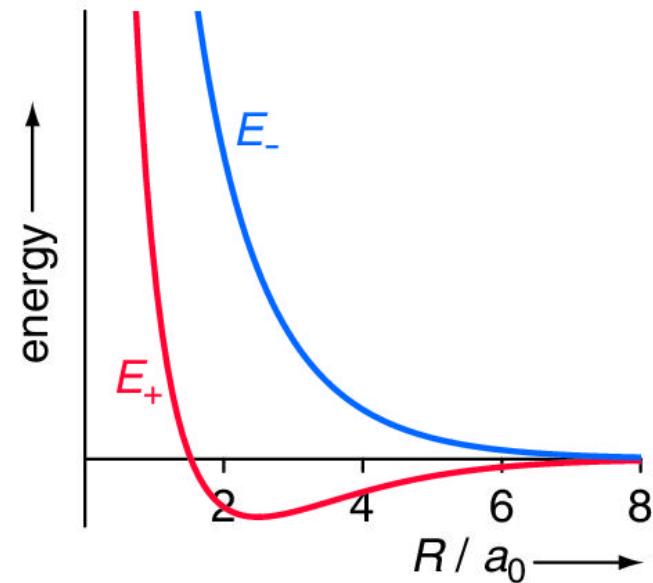


# Contour plots of bonding and anti-bonding MO's



# Overlap and Overlap Integral

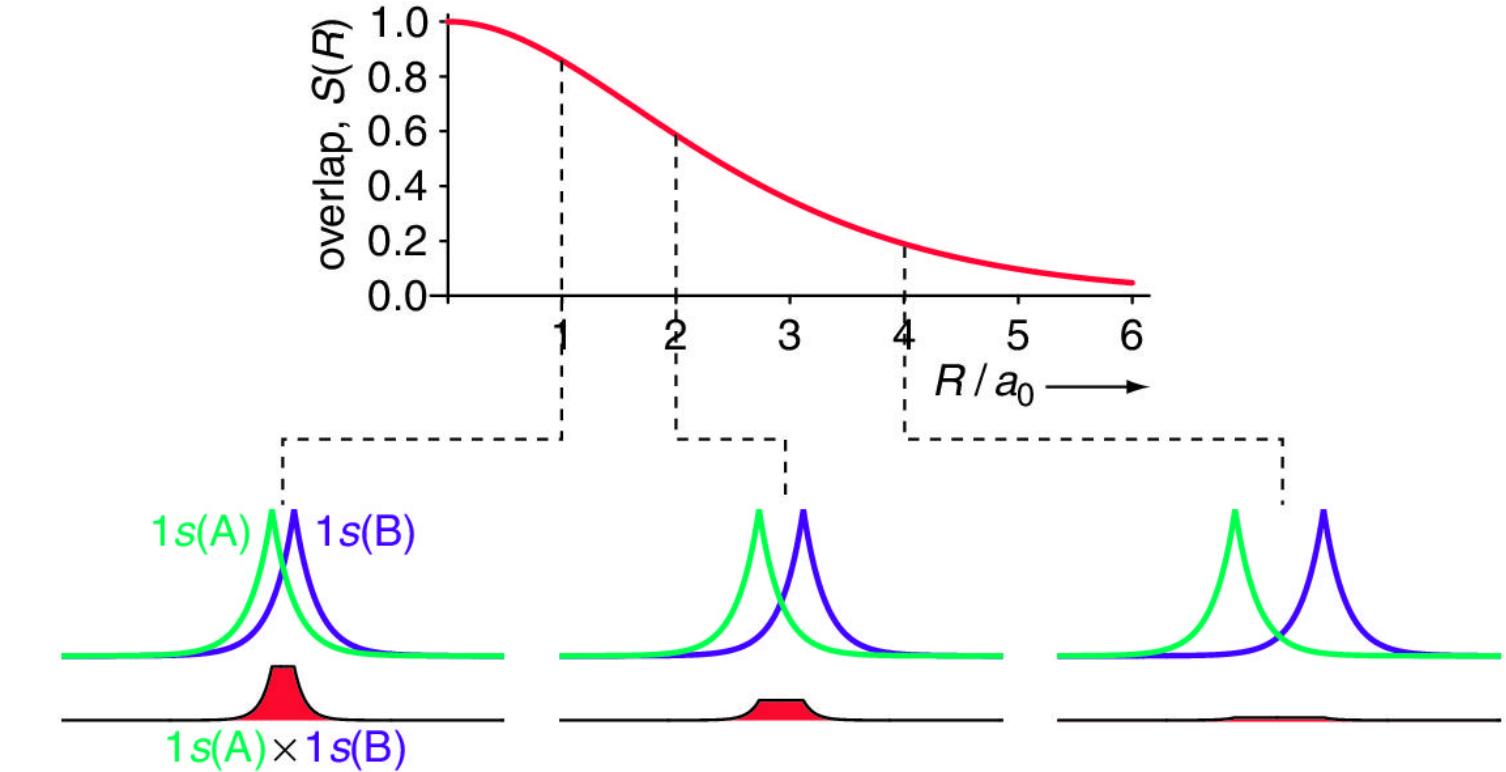
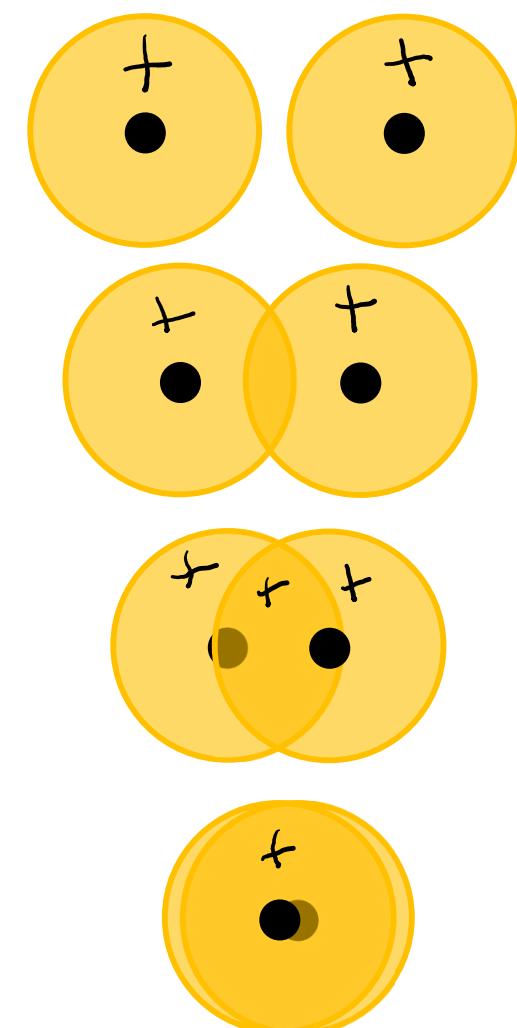
- As R decreases, MO's shift in energy further away from energy of AO's
- Calculations complicated- useful guide to the strength of the interaction of AO's (hence energy shift of MO's) can be obtained by looking at ***overlap integral (S)***
- Overlap integral between two AO's is determined by multiplying together two AO wavefunctions, and then taking the integral of the products
- *Recall: Integral of a function is the area under the curve of the function*



# Overlap Integral depends on $R_{AB}$

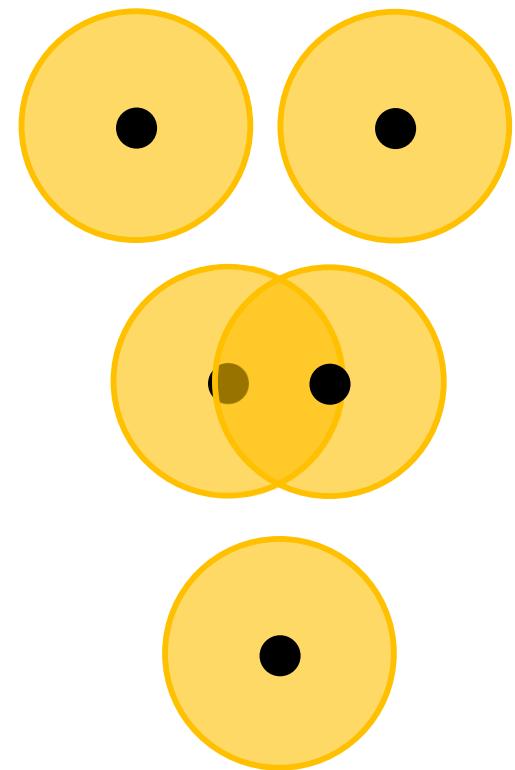
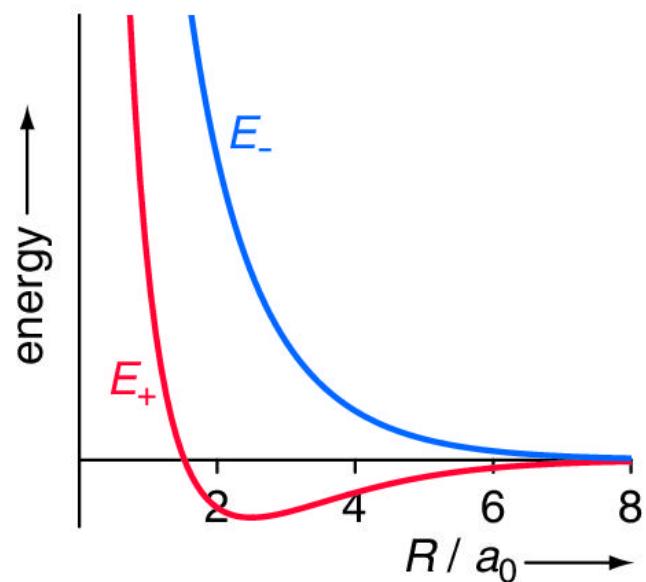
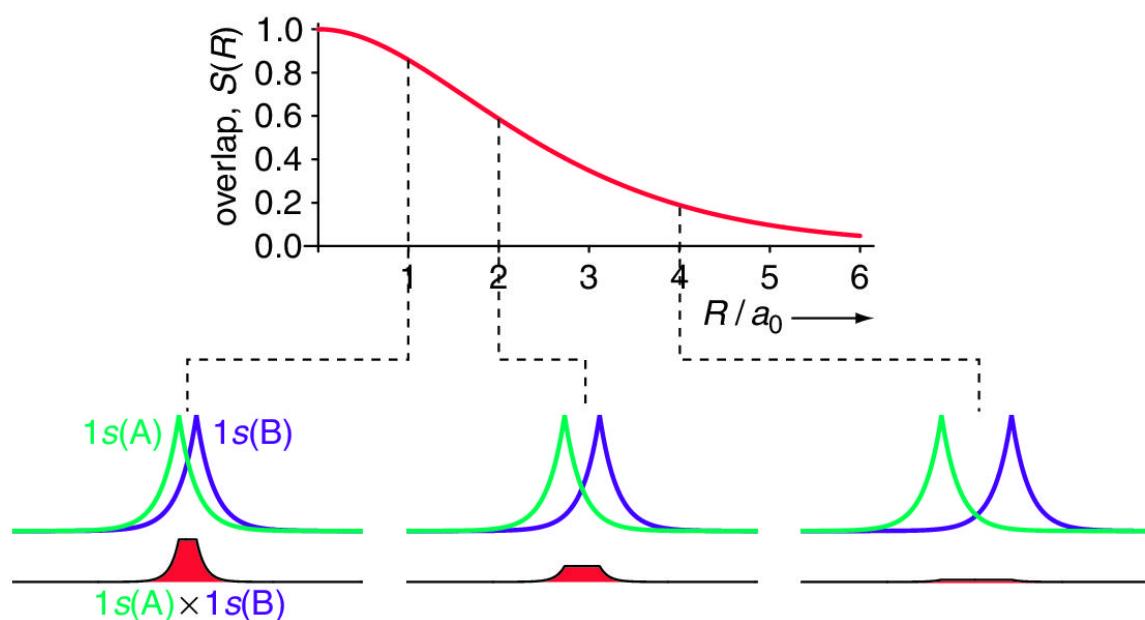
$$\text{Overlap Integral } S_{AB}(R) = \langle \psi_1 | \psi_2 \rangle = \int \psi_1 \psi_2 d\tau$$

$1s+1s$

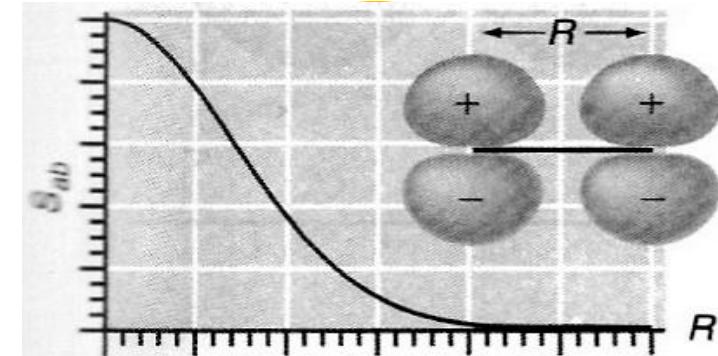
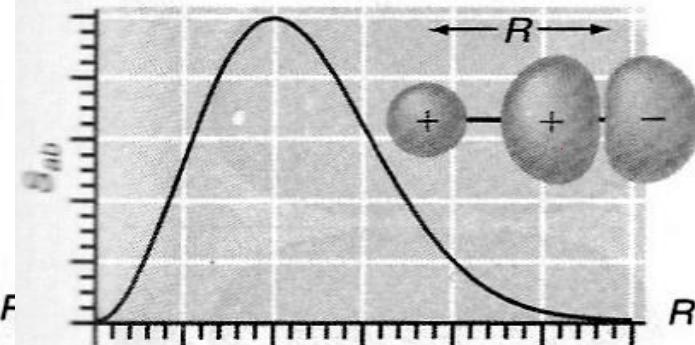
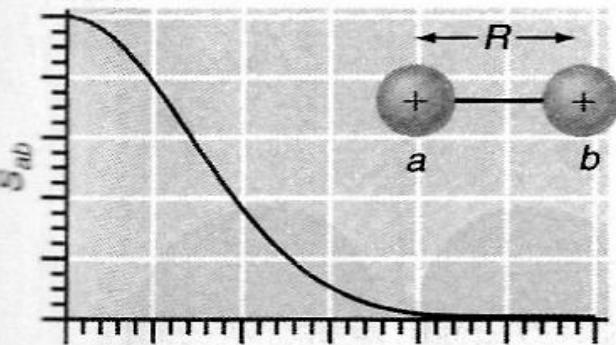
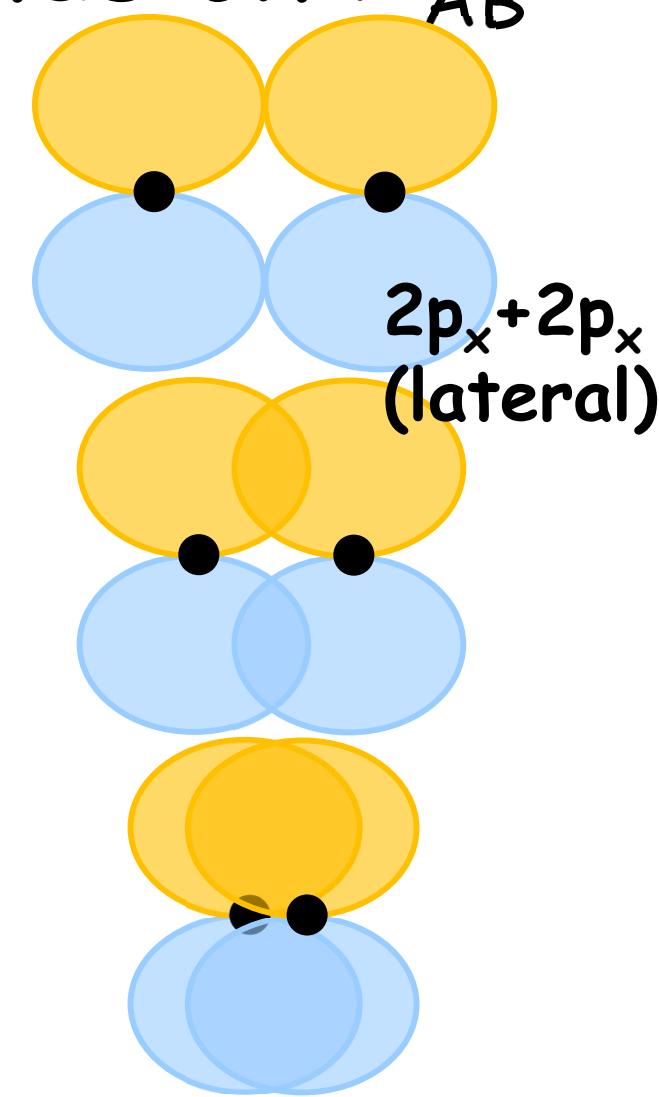
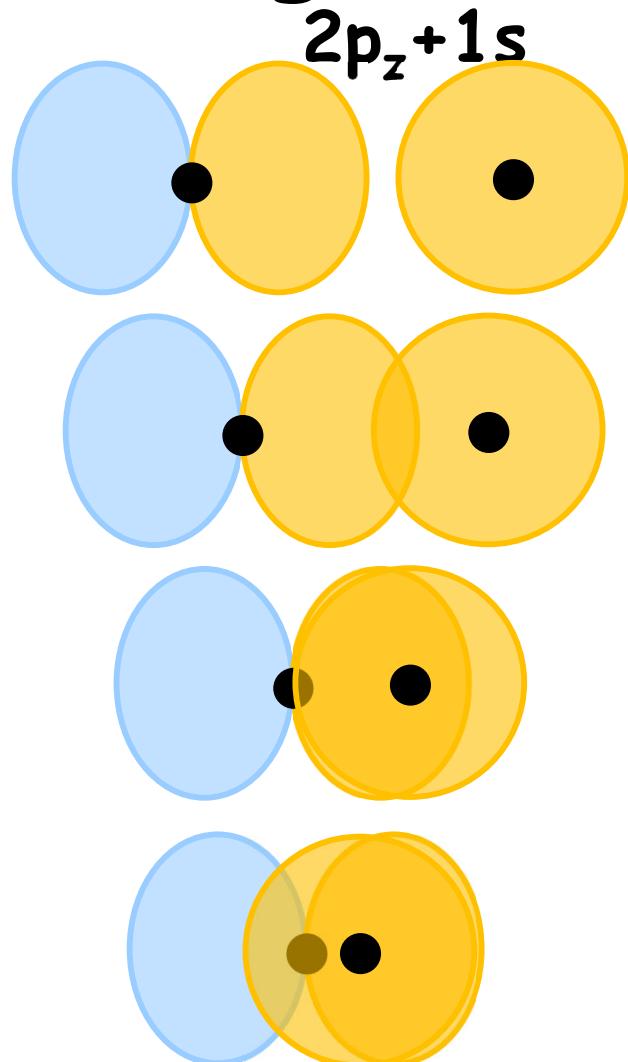
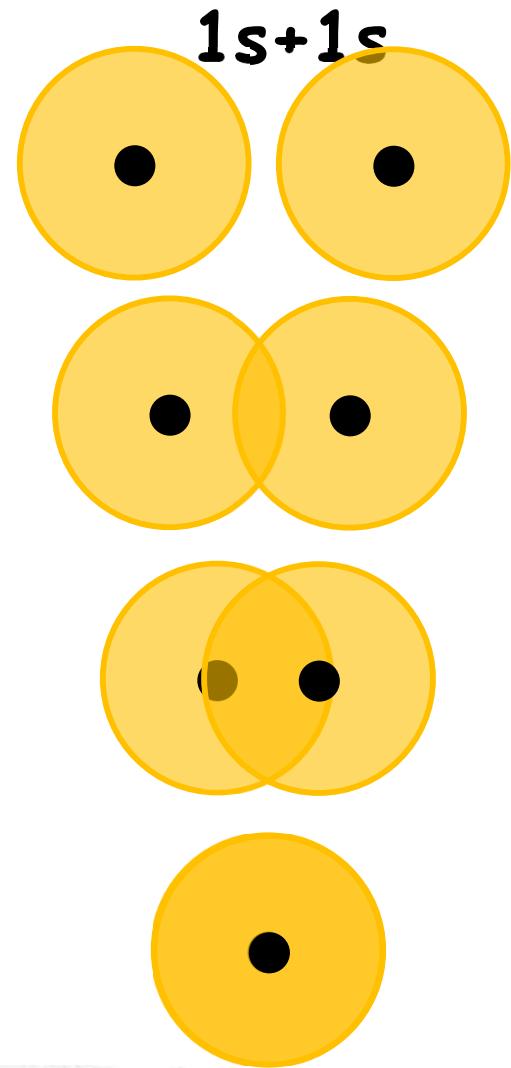


- Plot of overlap integral  $S(R)$  for two 1s orbitals as a function of  $R$
- $S(R)$  is the integral of the product of the two wavefunctions, which in this case is the area under the graph of this product

# Overlap Integral and Bond Length



# Overlap Integral depends on $R_{AB}$

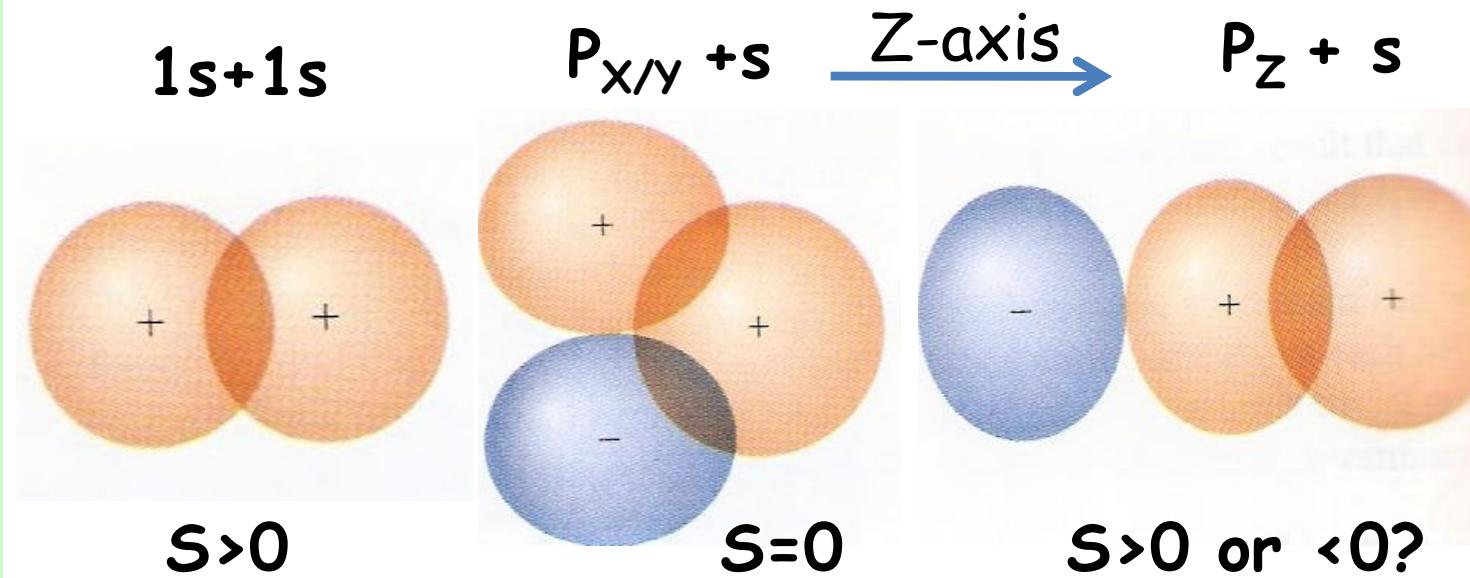


# Overlap Integral: Symmetry

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

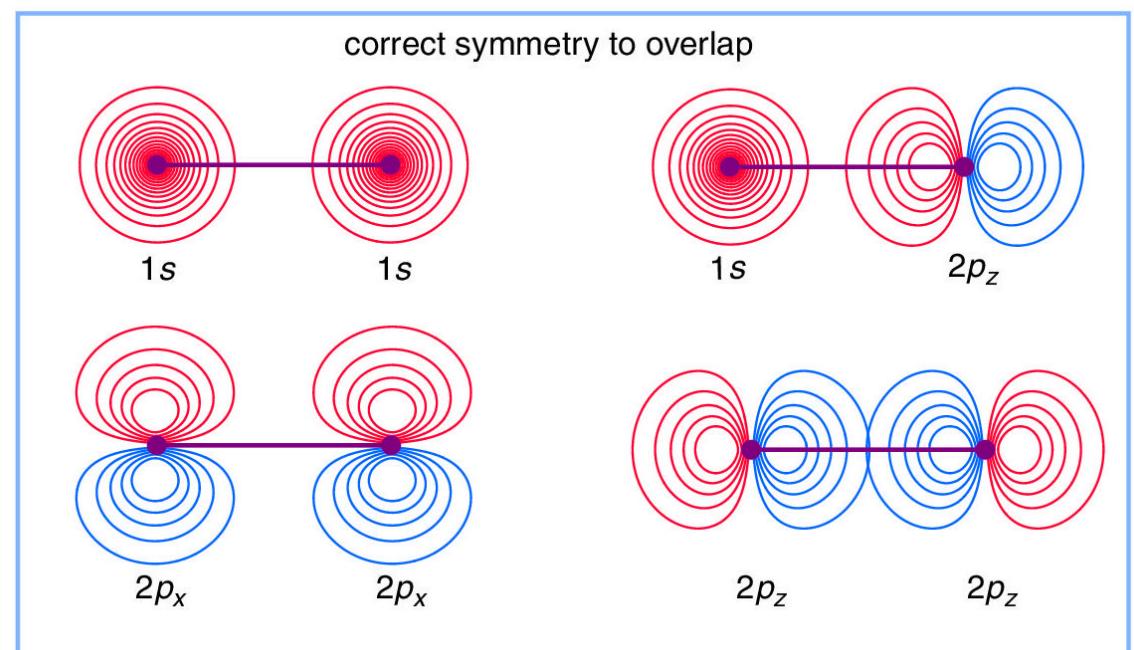
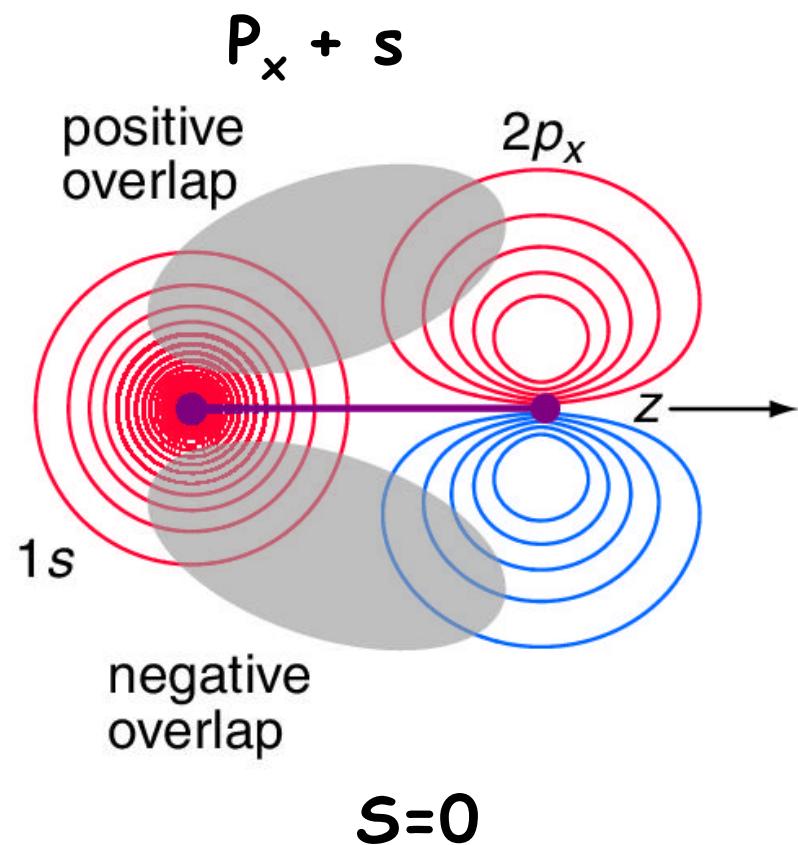
Overlapped area  
of 2 Wave-  
functions (can  
have +/- values)

Have to consider  
extent (amount)  
of both positive  
and negative  
contributions!

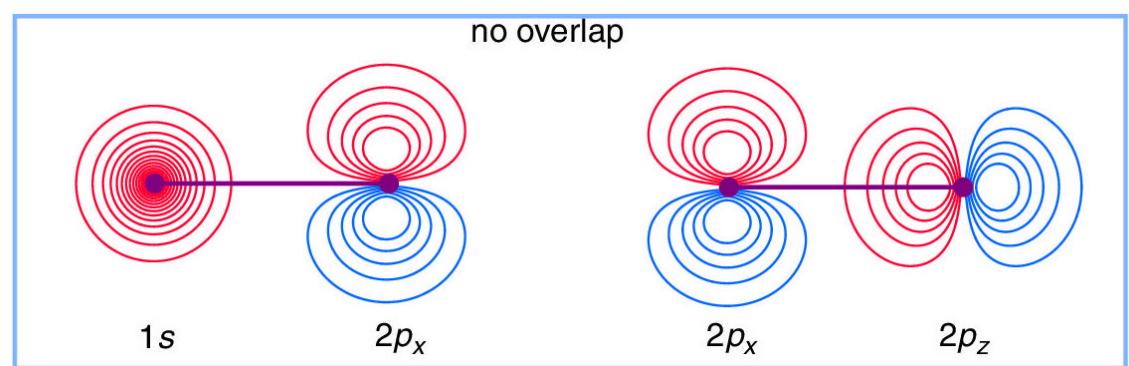
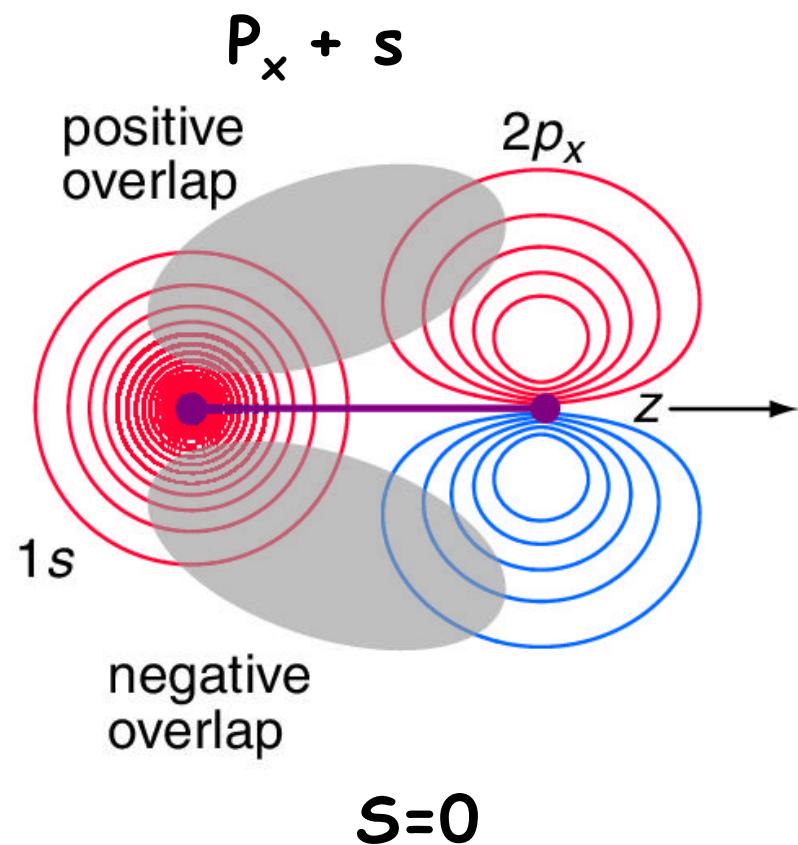


→  $S$  is a qualitative measure of bond strength  
→ If  $S \gg 0$ ; electron delocalized over molecule  
→  $S(R) = 0 \rightarrow$  bond formation cannot occur

# Overlap Integral depends on Symmetry

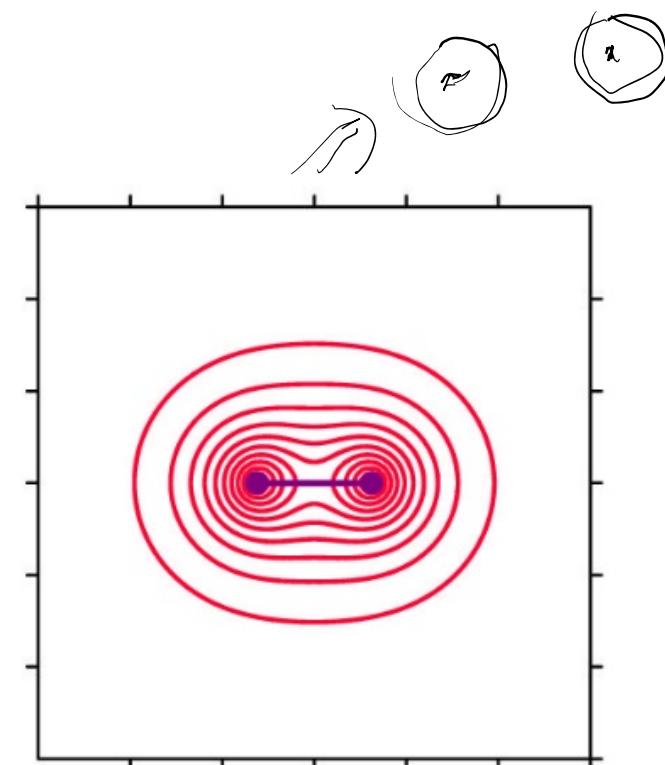


# Overlap Integral depends on Symmetry

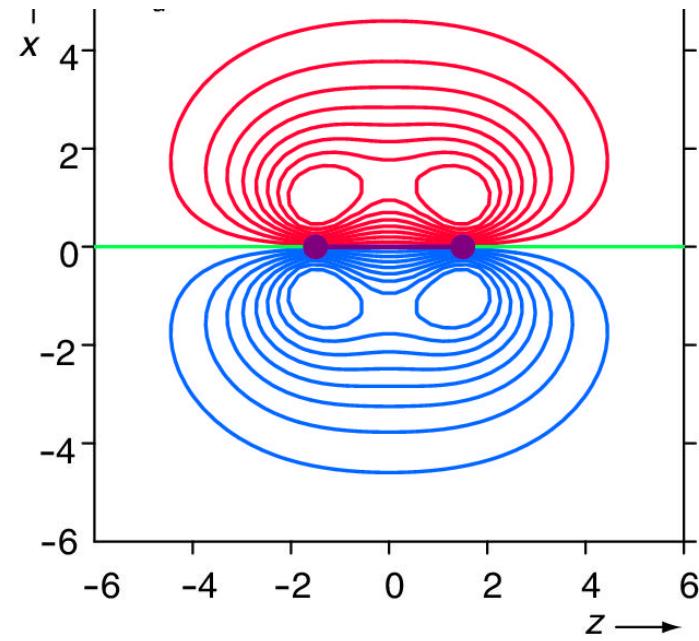


# Symmetry Labels

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

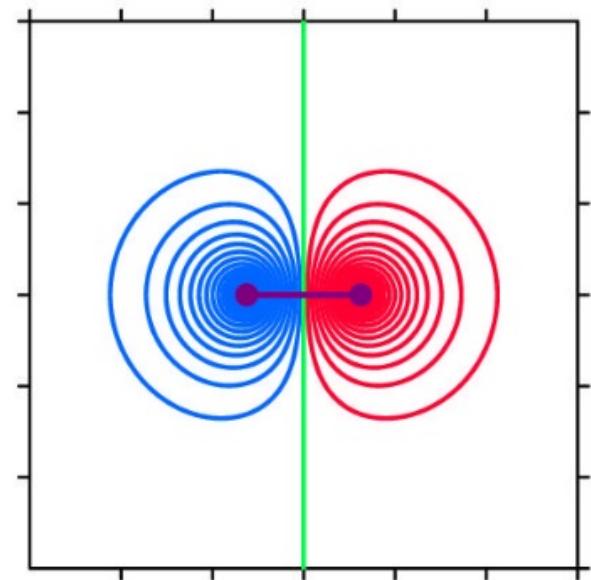


The wavefunction of MO's which changes sign through rotation by  $180^\circ$  about the internuclear axis are labelled  $\pi$  (pi)

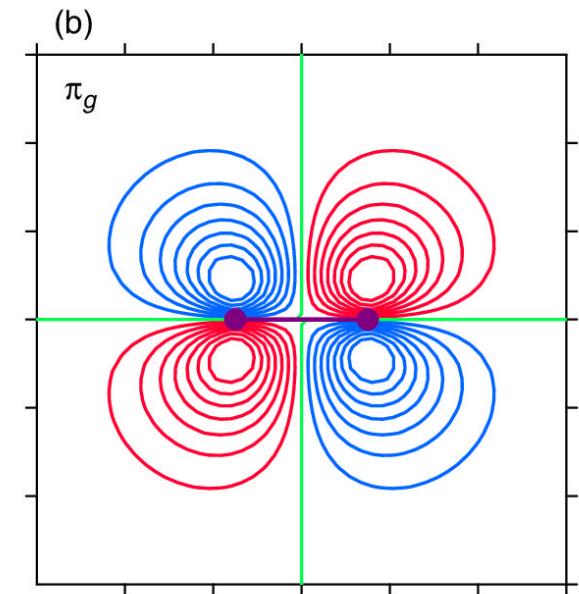


# Symmetry Labels

Anti-bonding  $\sigma^*$  (sigma)



Anti-bonding  $\pi^*$  (pi)



# Symmetry and Nomenclature of MOs

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

Inversion Operation :  $\hat{I}$

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

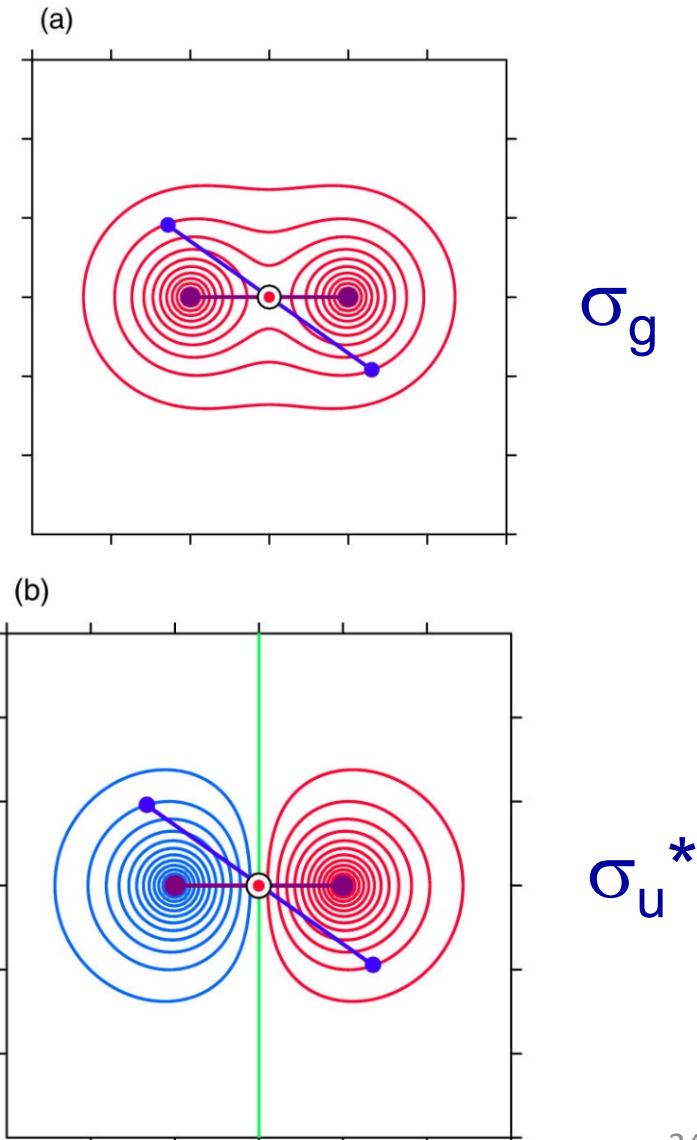
$$\hat{I}\Psi(\vec{r}) = \Psi(-\vec{r}) = +\Psi(\vec{r}): Symmetric$$

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

Hydrogen molecule ion:

"b"  $\rightarrow$  Bonding using s:  
symmetric  $\rightarrow \sigma_g$

"a"  $\rightarrow$  antibonding using s:  
antisymmetric  $\rightarrow \sigma_u^*$

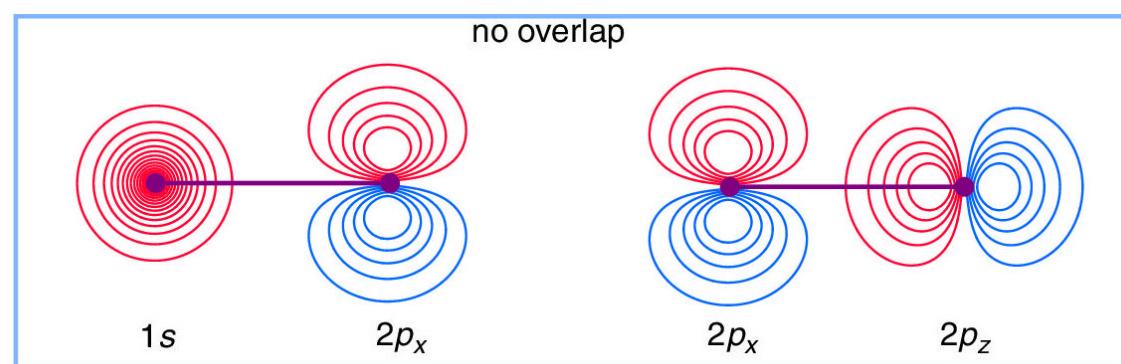
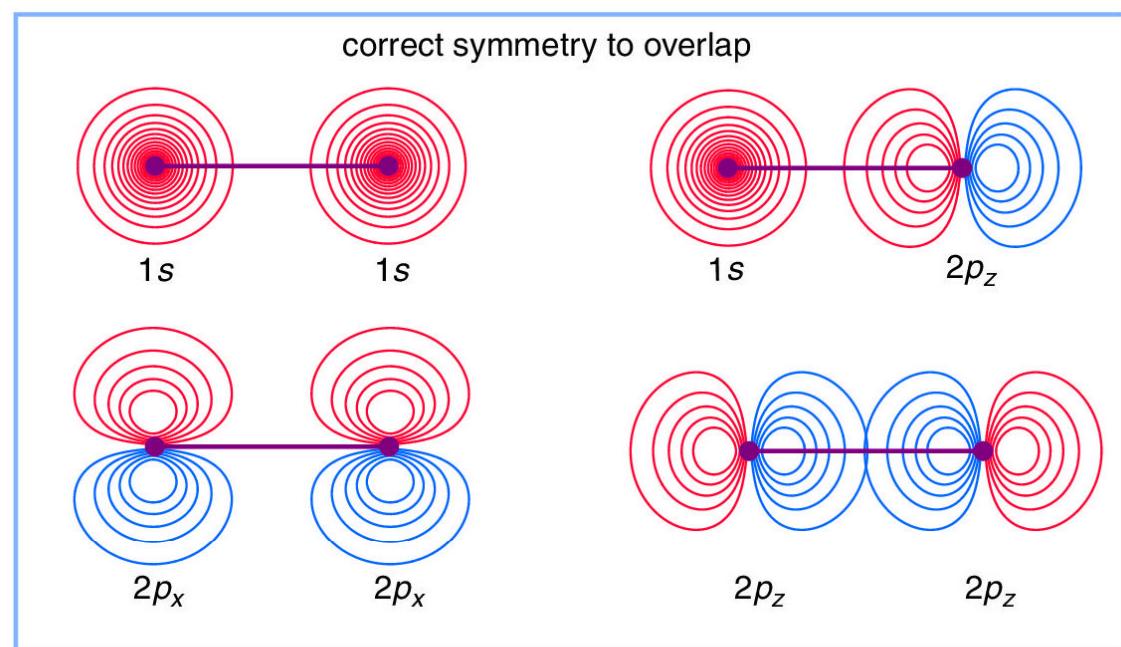
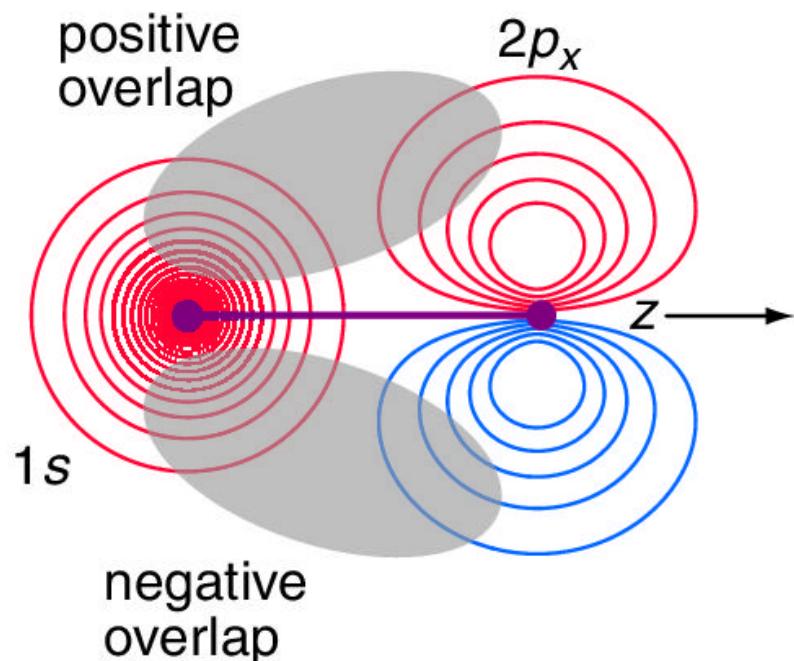


# Rules for Forming MOs: 1

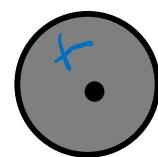
Combining certain number of AO's produces the same number of MO's e.g. combining 4 AOs give 4 MOs

# Rules for Forming MOs: 2

Recall: Only AO's of the correct symmetry will give MOs



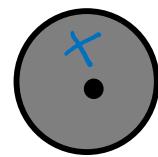
# Types of MO formed from 1s



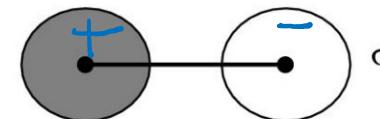
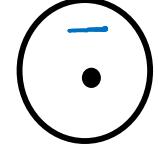
+



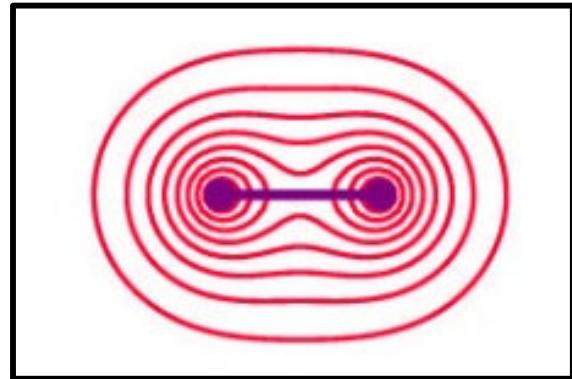
bonding  $\sigma_g$



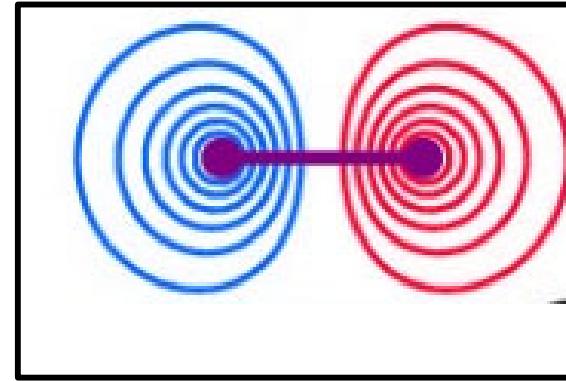
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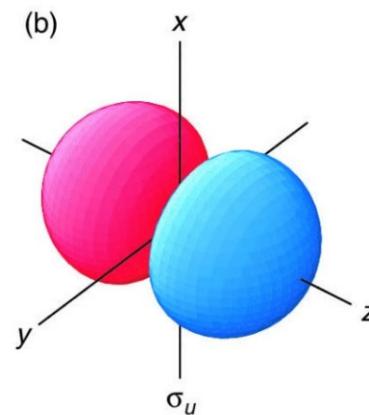
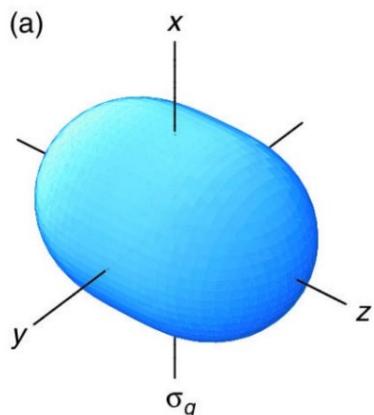
anti-bonding  $\sigma_u$



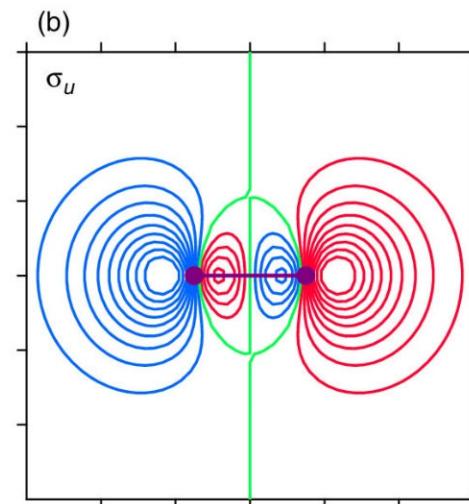
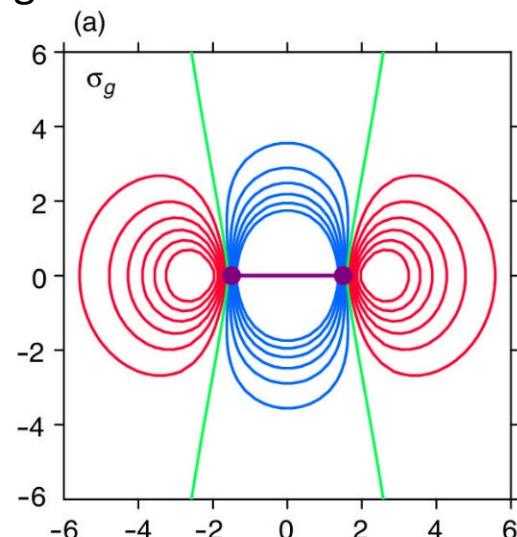
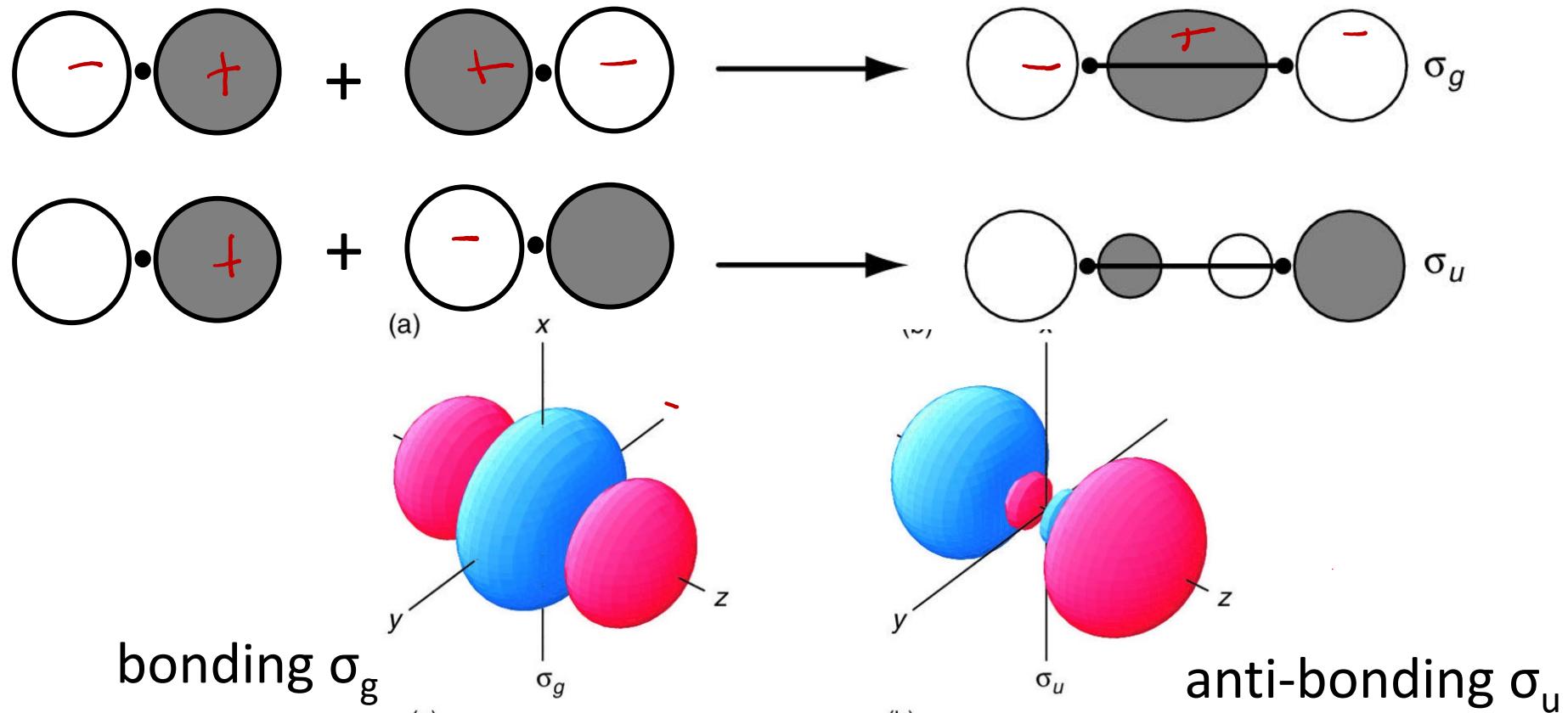
bonding  $\sigma_g$



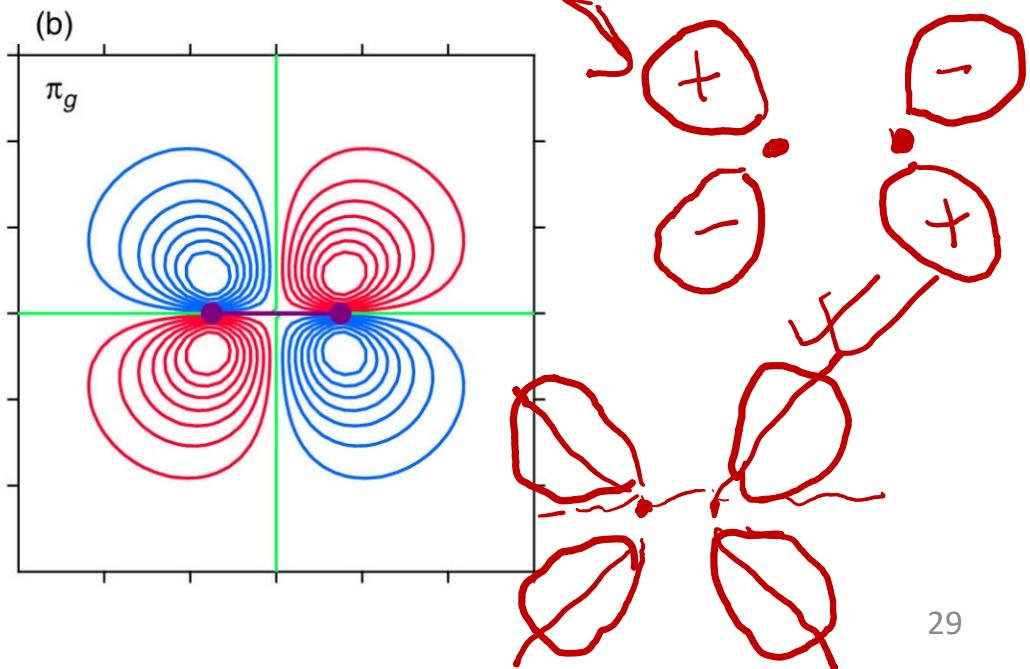
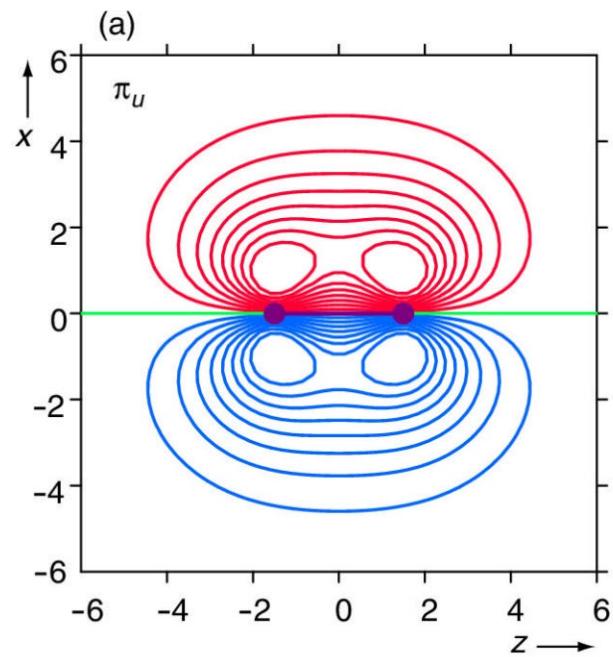
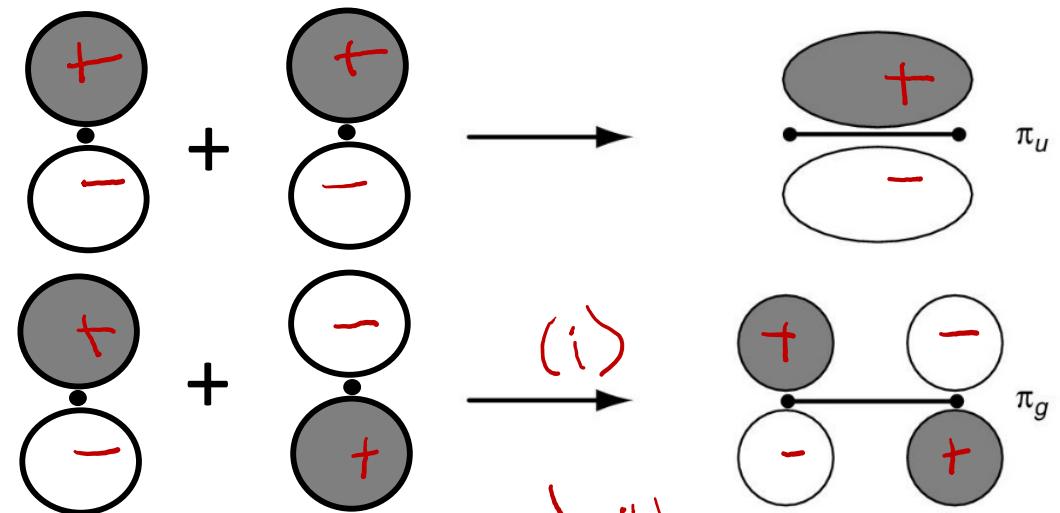
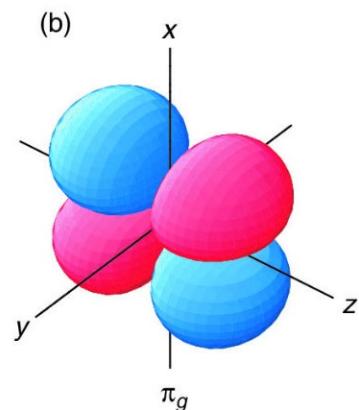
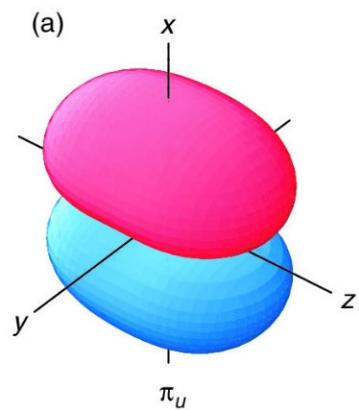
anti-bonding  $\sigma_u$



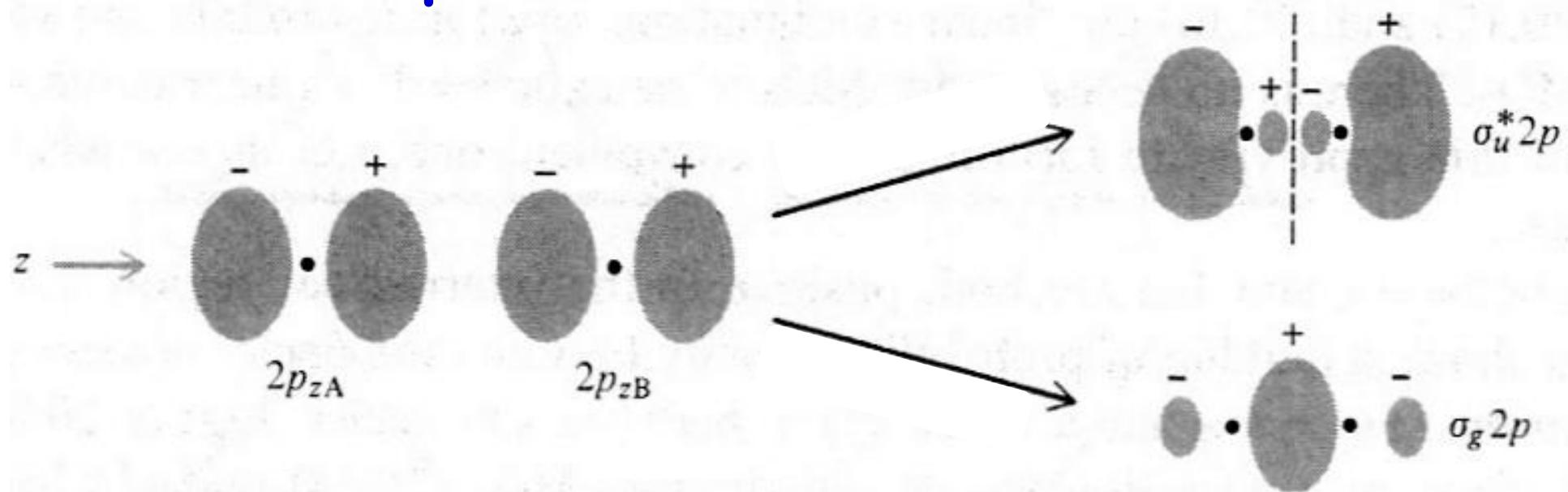
# MO formed from $2p_z \sigma$ overlap



# MO formed from $2p_y$ $\pi$ overlap



# LCAO of p-orbitals: $\sigma$ - and $\pi$ - bonds



Note the signs, symmetries and nodes

