Lecture 4

- Revision of hybridisation

  - Mixing atomic orbitals on the same atom

- Molecular Orbital Theory

  - How atomic orbitals on different atoms interact
  - The labelling of the new molecular orbitals

- Homonuclear Diatomic Molecules

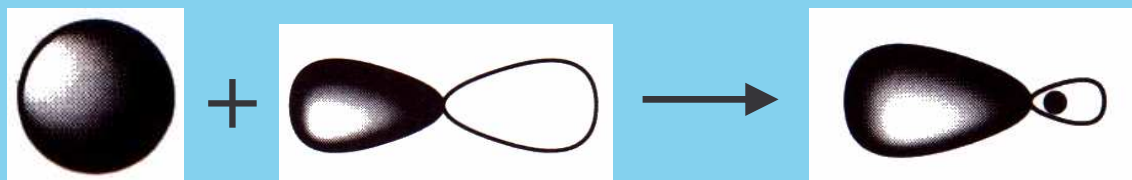 - The energies of the resulting molecular orbitals

sp hybridisation

- *sp* hybridisation
  - Mix and one *s* and one *p* orbital – two combinations $s + p_z$ and $s - p_z$
  - Two AOs → two hybrid AOs
  - Sign of the wavefunction is important when mixing atomic orbitals
  - *sp* therefore means that the hybrid orbital is 50% *s* and 50% *p*

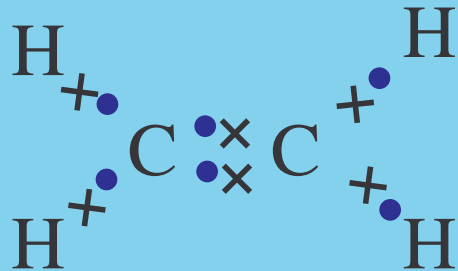$$\psi_{sp} = \frac{1}{\sqrt{2}}\left(\varphi_{2s} + \varphi_{2p_z}\right)$$

$$\psi_{sp} = \frac{1}{\sqrt{2}}\left(\varphi_{2s} - \varphi_{2p_z}\right)$$
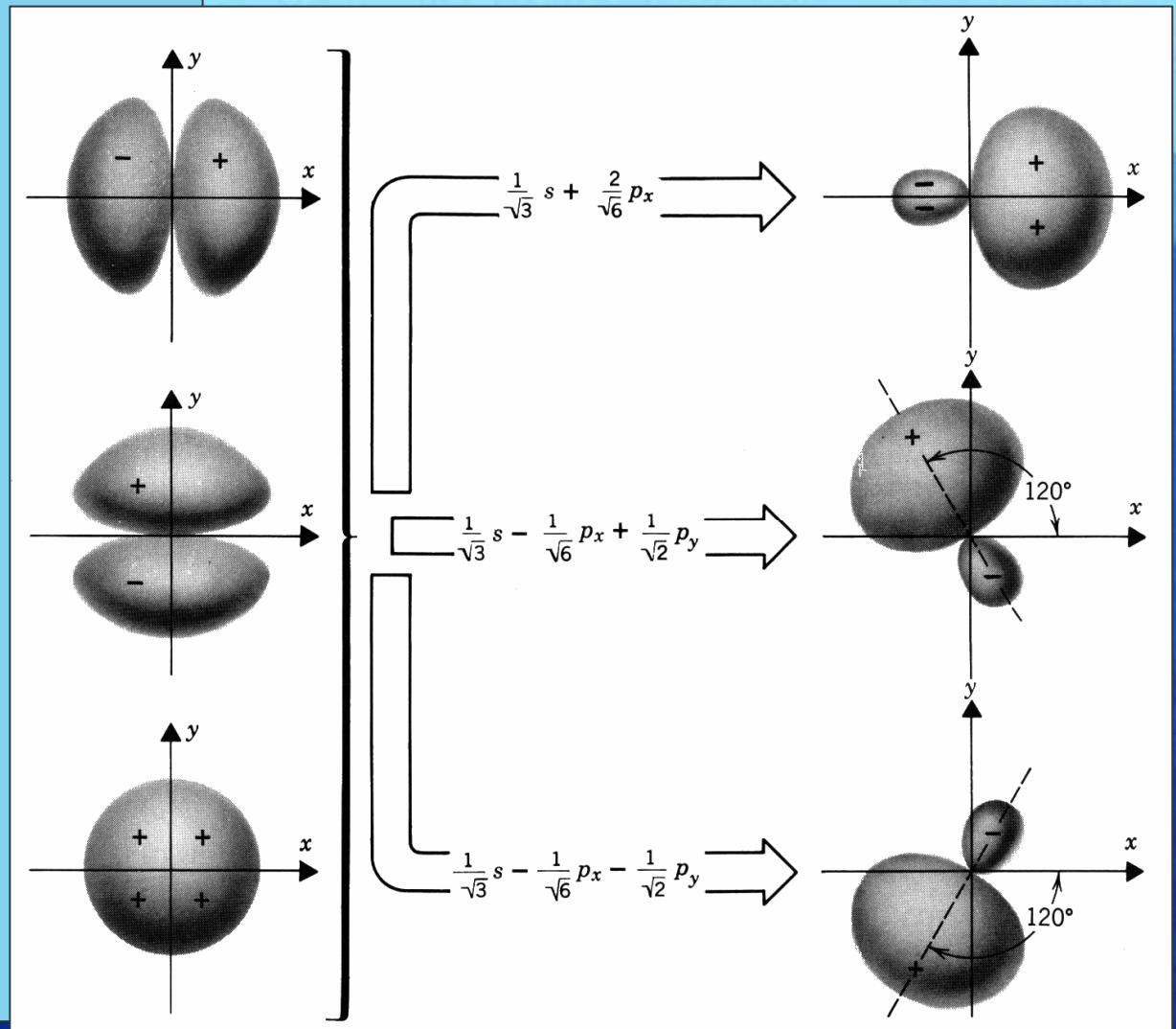
Hybridisation – sp^2 hybridisation

- Lewis structure → 3 directions
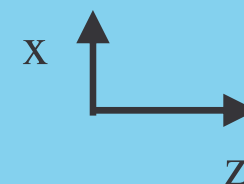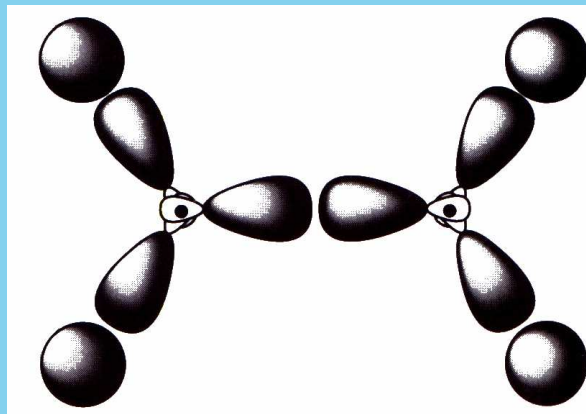

- Molecular is planar

- Three directions each at 120°

  → mix one s with two p orbitals

  → sp^2 hybridisation

$$\frac{1}{\sqrt{3}} s + \frac{2}{\sqrt{6}} p_x$$

$$\frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y$$

$$\frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y$$
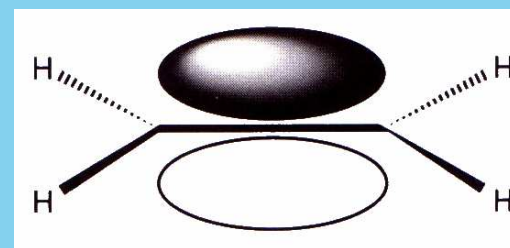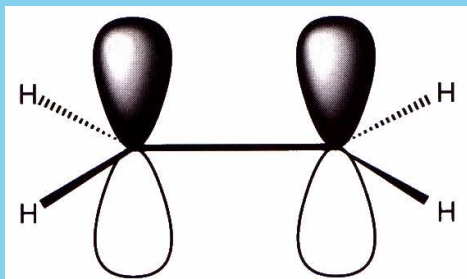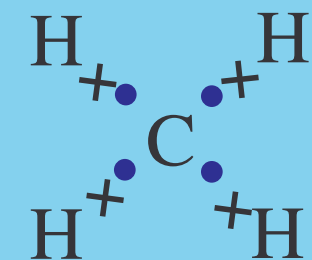
Hybridisation – π bonds

X
Z

– What about the other two electrons shared by the C atoms in ethene that are not in hybridised orbitals?

• These create a π bond above and below the plane of the molecule
  – Could think of the C as going from $2s^2\ 2p^2$ → three (sp^2) and one p_x^1
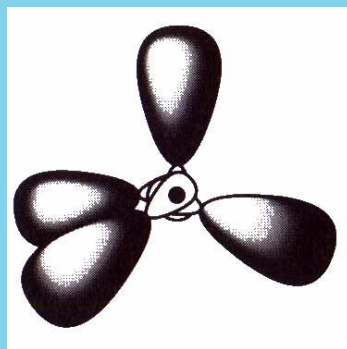
Hybridisation – sp^3
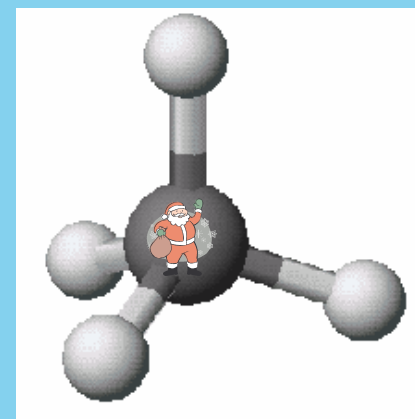
- For tetrahedral molecules we have to mix the *s* with all the *p* orbitals (sp^3)
  - e.g. methane

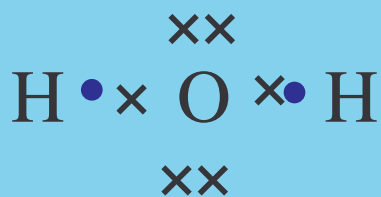4 electron pairs sp^3 hybridisation   tetrahedral
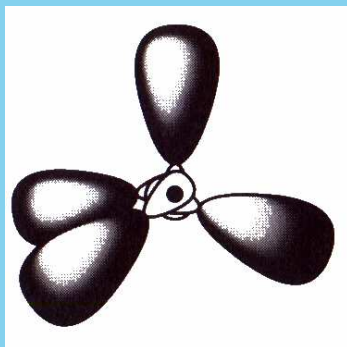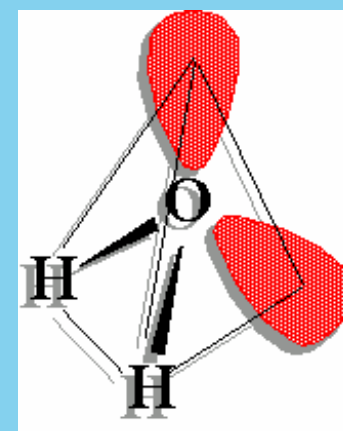
  - H_2O can also be thought of like this with two of the sp^3 orbitals occupied by lone pairs.

4 electron pairs sp^3 hybridisation   tetrahedral

Hybridisation – *d* orbitals

Trigonal Bipyramidal

sp^3d → 5 electron pairs
$(s + px + py + pz + dz^2)$

Lone pairs always go equatorial

Octahedral

sp^3d^2 → 6 electron pairs
$(s + px + py + pz + dz^2 + dx^2\text{-}y^2)$

Two Lone pairs are always *trans*

Five electron pairs

No lone pairs   One lone pair   Two lone pairs   Three lone pairs

PF_5, Trigonal bipyramidal SF_4, Seesaw ClF_3, T-shaped XeF_2, Linear

Six electron pairs

No lone pairs   One lone pairv   Two lone pairs

SF_6, Octahedral BrF_5, Square-pyramidal XeF_4, Square-planar
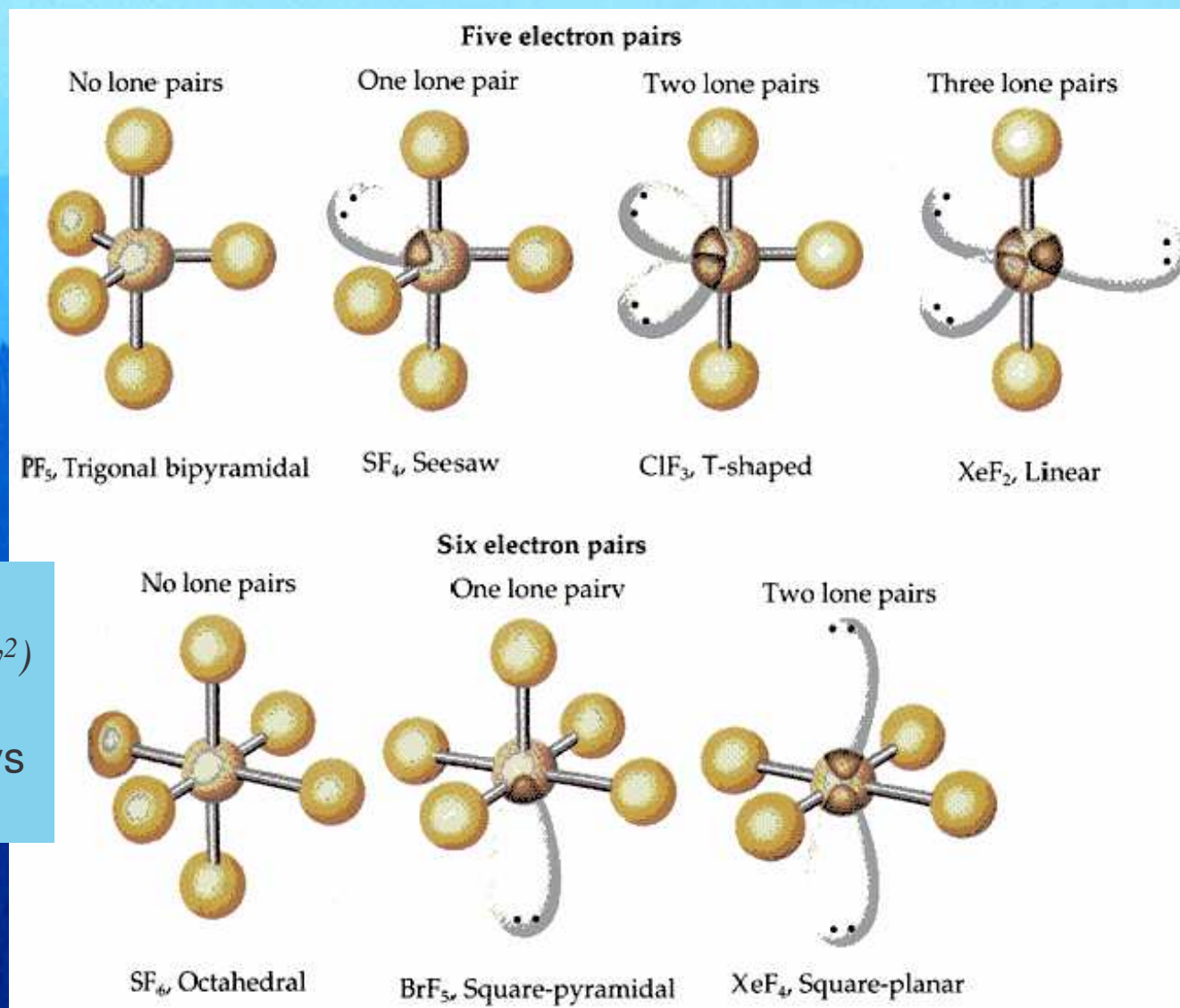
Hybridisation – Table Summary

Hybridisation	Atomic orbitals that are mixed	Geometry	General formula	Examples
sp	$s + p$	linear	AB_2	BeH_2
sp^2	$s + p_x + p_y$	trigonal planar	AB_3	BF_3, CO_3^{2-} C_2H_4
sp^3	$s + p_x + p_y + p_z$	tetrahedral	AB_4	SO_4^{2-}, CH_4, NH_3, H_2O,
sp^3d	$s + p_x + p_y + p_z + dz^2$	Trigonal Bipyramidal	AB_5	PCl_5, SF_4
	$s + p_x + p_y + p_z + dx^2$-$y^2$	square pyramidal		
sp^3d^2	$s + p_x + p_y + p_z + dz^2 + dx^2$-$y^2$	octahedral	AB_6	SF_6 $[Ni(CN)_4]^{2-}$ $[PtCl_4]^{2-}$

Molecular orbital theory

- MO theory (Robert Mullikan) assumes
  - Electrons are delocalised
  - MO's formed by addition and subtraction of AO's → Linear Combination of Atomic Orbitals (LCAO)   (like hybrid AO's but entire molecule)
- H_2 molecule – interaction of two hydrogen 1s orbitas (φ_a and φ_b)

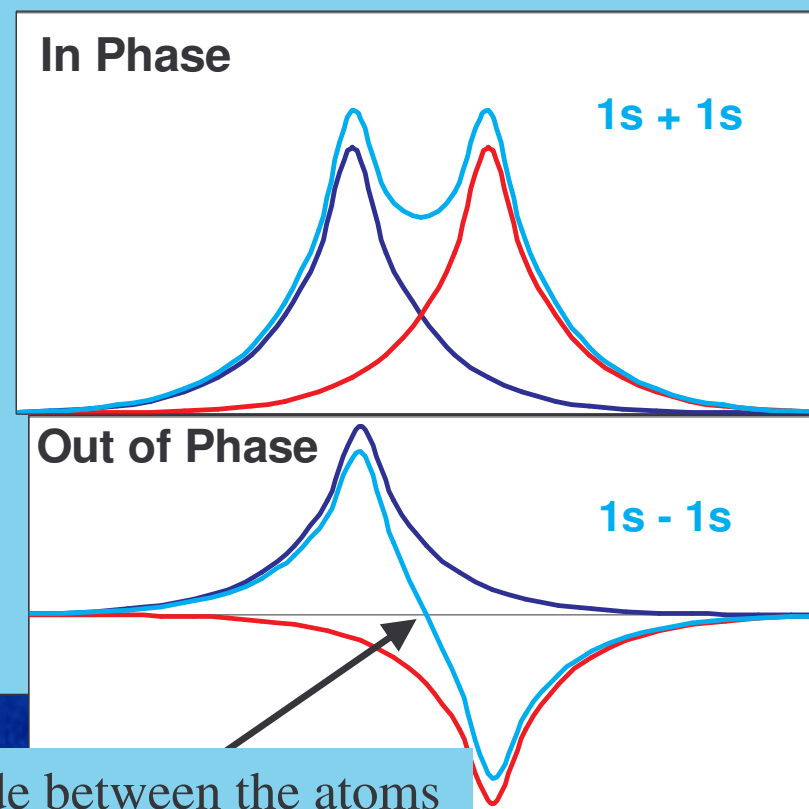In phase interaction

$$\psi_1 = (\varphi_a + \varphi_b)$$

→ Constructive interference

Out of phase interaction

$$\psi_2 = (\varphi_a - \varphi_b)$$

→ Destructive interference

Interaction of 2 AO → 2 MO's

In Phase

1s + 1s

Out of Phase

1s - 1s

Node between the atoms

Charge density associate with MO's in H_2

- Charge density given by ψ^2

  - In phase interaction → enhance density between the atoms

  $$\psi_1^2 = (\varphi_a + \varphi_b)^2 \qquad \Rightarrow \qquad \psi_1^2 = [\varphi_a]^2 + [\varphi_b]^2 + 2[\varphi_a \varphi_b]$$

  referred to a positive overlap (σ bonding) $\quad \psi_1 = \psi_\sigma$

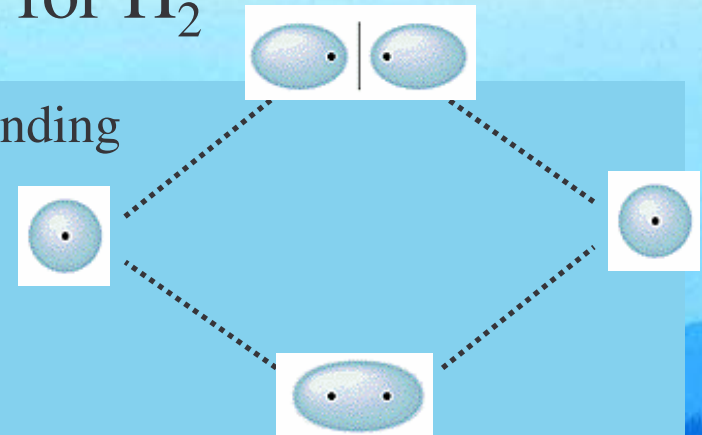 - Out of phase interaction → reduced density between the atoms

  $$\psi_2^2 = (\varphi_a - \varphi_b)^2 \qquad \Rightarrow \qquad \psi_2^2 = [\varphi_a]^2 + [\varphi_b]^2 - 2[\varphi_a \varphi_b]$$

  referred to a negative overlap (σ^* anti-bonding) $\quad \psi_2 = \psi_{\sigma^*}$

  New wave functions must be normalised to ensure probability in 1 !

Energy level diagram for H_2

- Interference between AO wave functions → bonding
  - Constructively → bonding interaction
  - Destructively → anti-bonding interaction

- Energy level diagram represents this interaction
  - Two *s* orbitals interaction to create a low energy bonding and high energy anti-bonding molecular orbital
  - Electrons fill the lowest energy orbital (same rules as for filling AO's)
  - Bonding energy = 2 ΔE

Energy

ΔE

H H_2 H
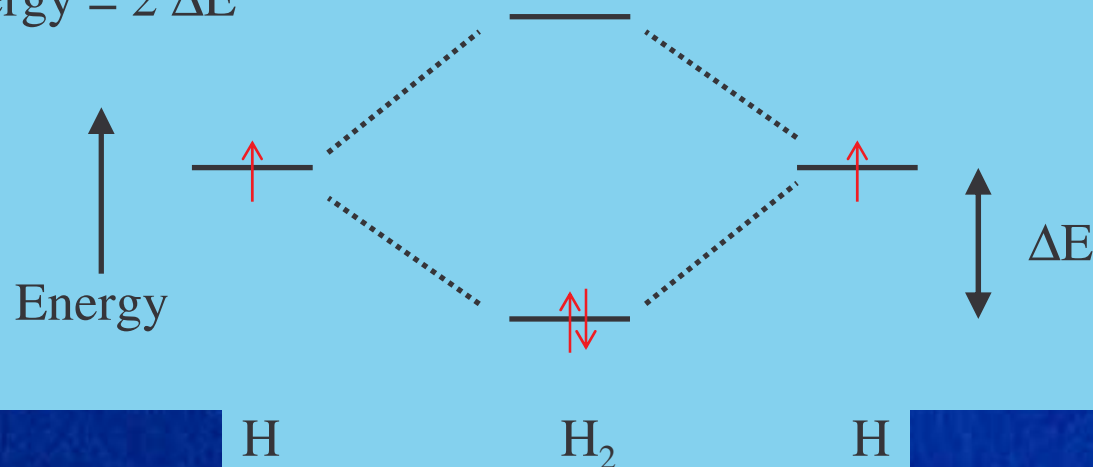
What happens when the AO's have different energies?

- Hypothetical molecule where the two *s* orbitals have different energies
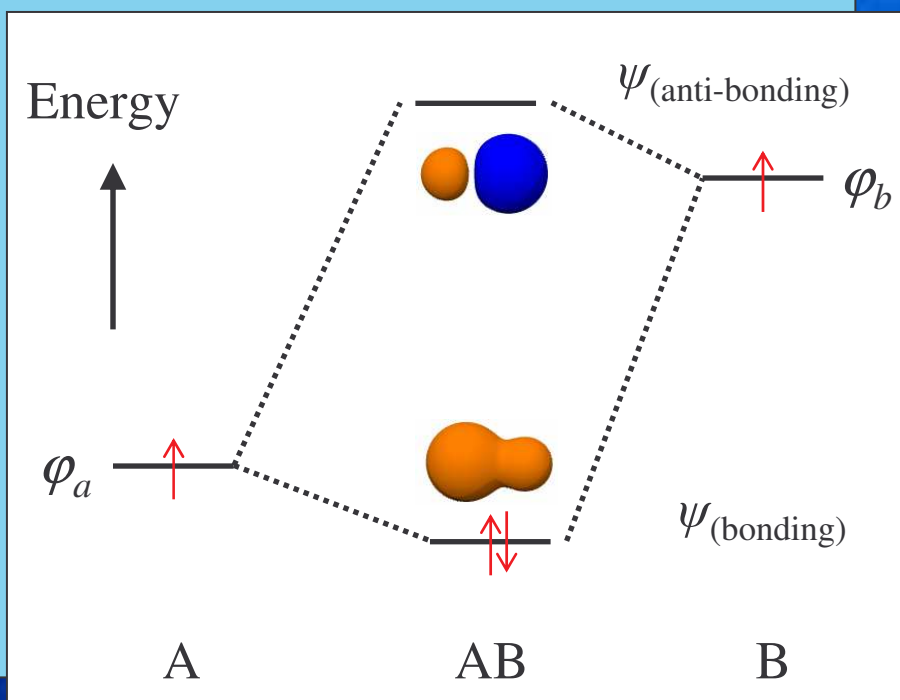
$$E(\varphi_a) < E(\varphi_b)$$

- What would the MO's be like ?
  - Bonding MO will be much more like the low energy orbital φ_a
  - Anti-bonding MO will be much more like high energy orbital φ_b

- We can say that the bonding MO is

$$\psi_\sigma = \left(C_a^\sigma \varphi_a + C_b^\sigma \varphi_b \right)$$

- Where the coefficients C, indicate the contribution of the AO to the MO

So for $\quad \psi_\sigma \quad \quad C_a^\sigma > C_b^\sigma$

Energy

ψ(anti-bonding)

φ_b

φ_a
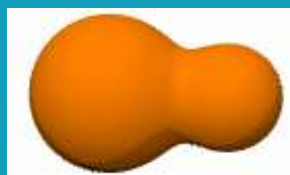
ψ(bonding)

A   AB   B

Linear Combination of Atomic Orbitals - LCAO

- We wrote an equation using coefficients for the contribution of AO's to the bonding MO, we can do the same for the anti-bonding MO
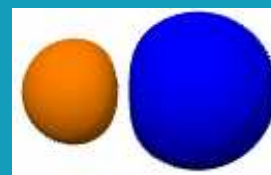
$$\psi_\sigma = \left(C_a^\sigma \varphi_a + C_b^\sigma \varphi_b \right) \qquad \psi_{\sigma^*} = \left(C_a^{\sigma^*} \varphi_a - C_b^{\sigma^*} \varphi_b \right)$$

where the coefficients are different are reflect the contribution to each MO

$$C_a^\sigma > C_b^\sigma \qquad\qquad C_a^{\sigma^*} < C_b^{\sigma^*}$$

- The sign can be adsorbed into the coefficient and we can write all of the MO's in a general way

$$\psi_n = \left(C_a^n \varphi_a + C_b^n \varphi_b \right)$$

n = 1   n = 2

$$\psi_1 = \left(C_a^1 \varphi_a + C_b^1 \varphi_b \right) \qquad\qquad \psi_2 = \left(C_a^2 \varphi_a + C_b^2 \varphi_b \right)$$

- The coefficients contains both phase (sign) of the AO's and how big their contribution (size) is to a particular MO

LCAO

- Generally we can write

$$\psi_n = \sum_{x=a...}^{No\,AO's} C_x^n \varphi_x$$

x = a,b,c …. (all of the AO's in the molecule)   n = 1,2,3…..(the resulting MO's)

- So   MO(1) = $\psi_1 = C_a^1 \varphi_a + C_b^1 \varphi_b + C_c^1 \varphi_c + C_d^1 \varphi_d + ...$

  MO(2) = $\psi_2 = C_a^2 \varphi_a + C_b^2 \varphi_b + C_c^2 \varphi_c + C_d^2 \varphi_d + ...$

  MO(3) = $\psi_3 = C_a^3 \varphi_a + C_b^3 \varphi_b + C_c^3 \varphi_c + C_d^3 \varphi_d + ...$

  C_x^1 - coefficients for MO(1), C_x^2 coefficients for MO(2) etc.

- And an examination of the coefficients tells us the bonding characteristics of the MO's

What interactions are possible

- We have seen how *s* orbitals interact – what about other orbitals

- If you have positive overlap
  reversing the sign → negative overlap

E.g. $s + s$ and $p_x + p_x$ → +ve
        $s - s$ and $p_x - p_x$ → -ve

- Must define orientation and
  stick to it for all orbitals.
  Thus
        $p_z + p_z$ → -ve
        $p_z - p_z$ → +ve
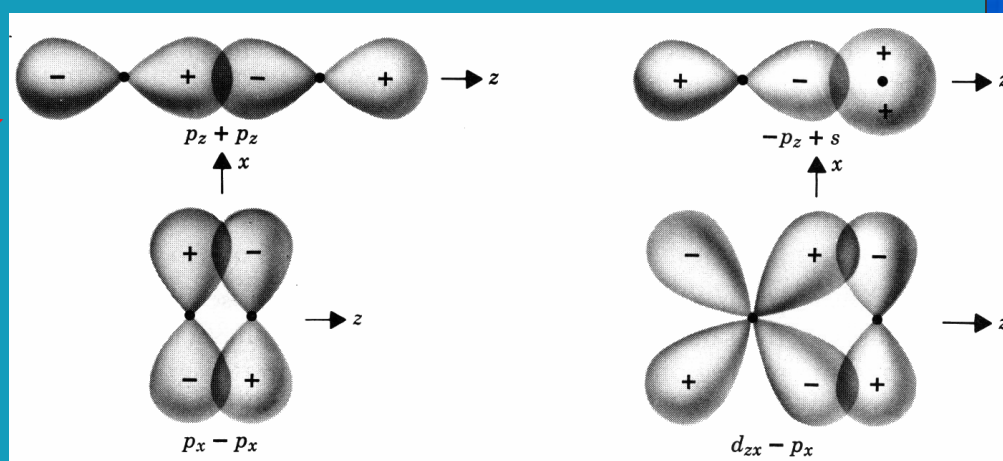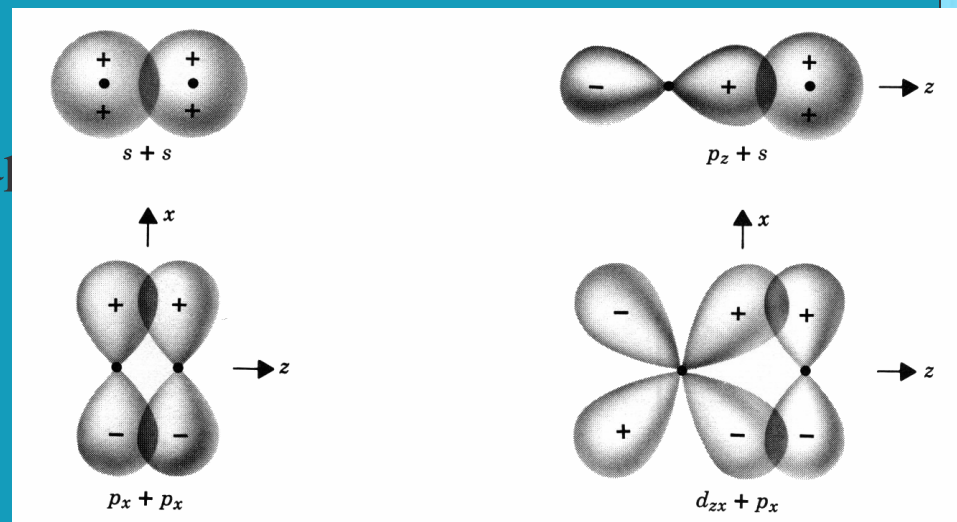
What interactions are NOT possible

- Some orbitals cannot interact – they give rise to zero overlap

- Positive overlap (constructive interference) on one side in cancelled by negative overlap (destructive interference) on the other

- $s + p_x$ positive overlap above the axis is cancelled by negative overlap below
  - Same is true for the other interactions below

Zero overlap
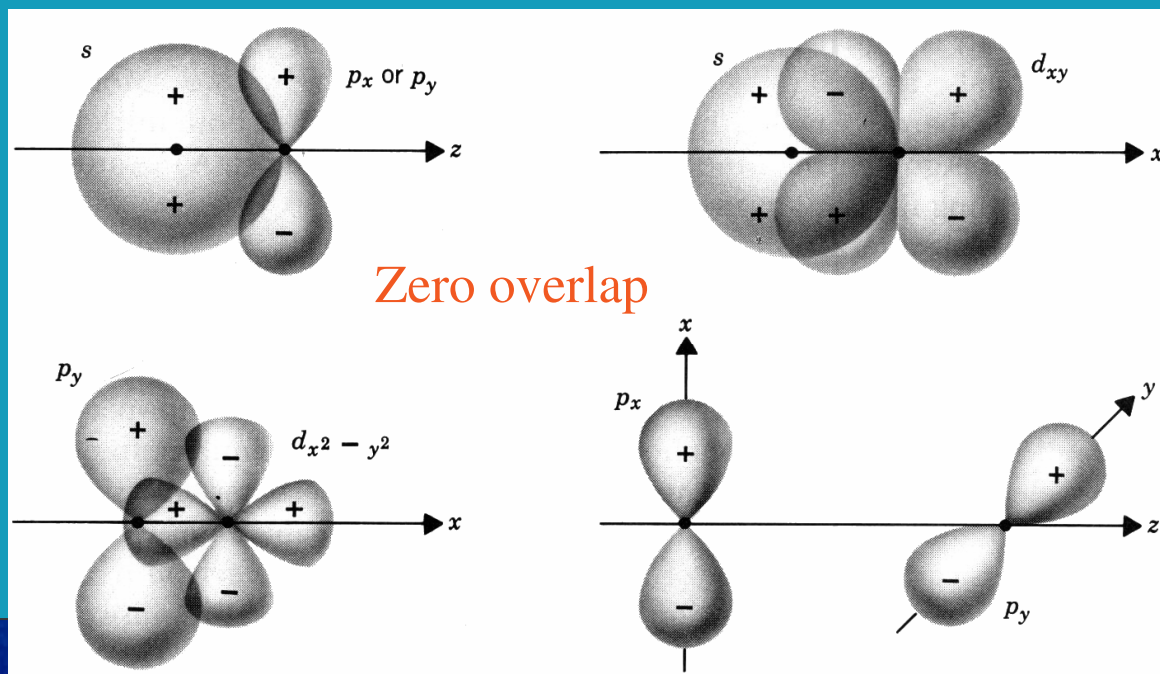
Labelling molecular orbitals

1 **Symmetry Label** (internuclear axis is always the z axis)

σ = spherical symmetry along the bond axis (same symmetry as s orbital)
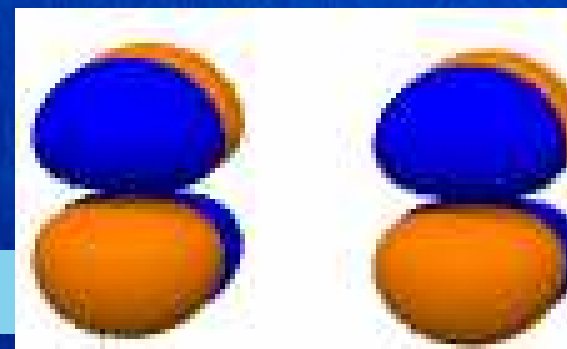
no nodes pass through the bond axis

$s + s$

$p_z + s$

$p_z + p_z$
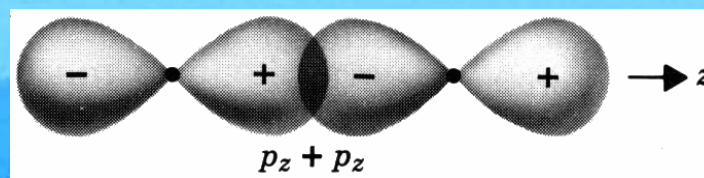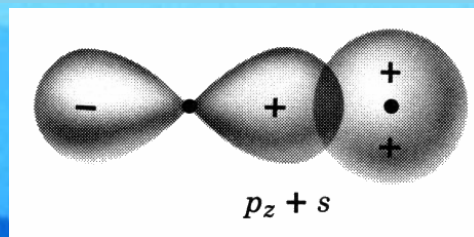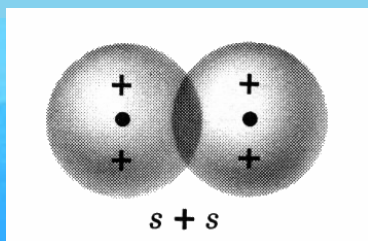
π = one nodal plane which passes through the bond axis
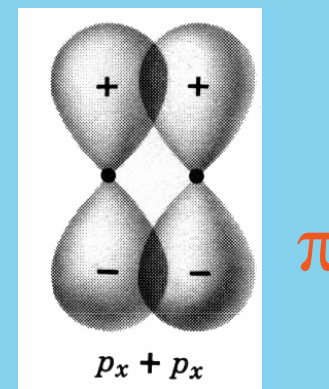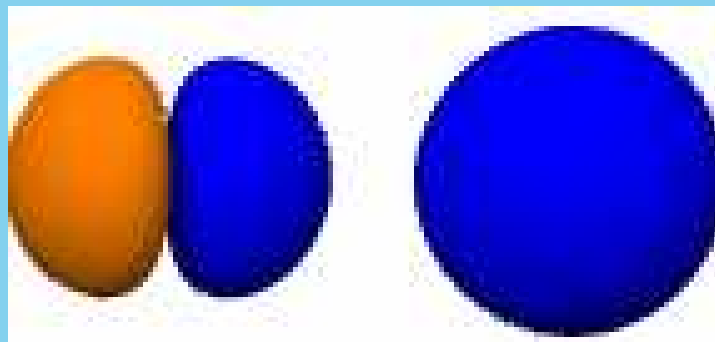

$p_x + p_x$
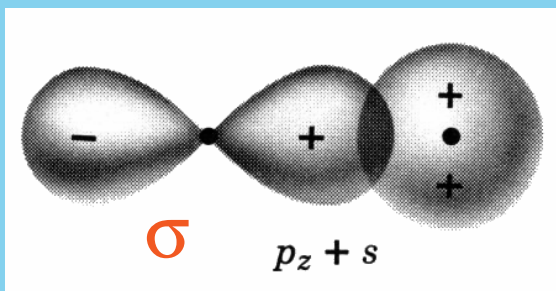

$d_{zx} + p_x$
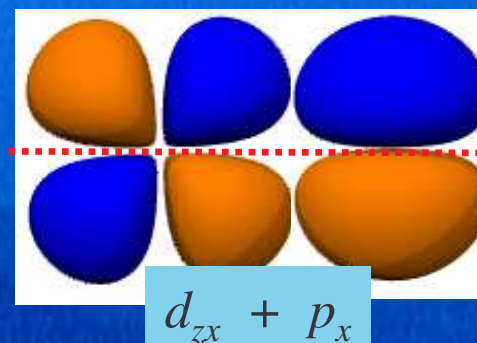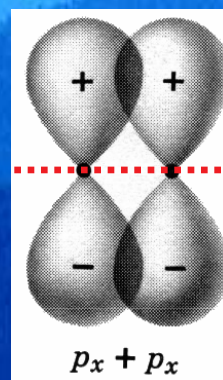
δ = two nodal plane which pass through the bond axis

(end on d_{xy} or $d_{x^2-y^2}$

Labelling molecular orbitals

2   Bonding and Anti-bonding Labels

σ $p_z + s$

π $p_x + p_x$

– Additional * if the interaction is destructive

σ^* $-p_z + s$

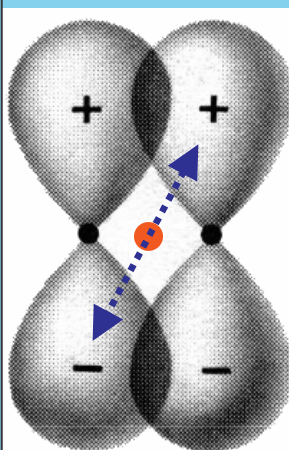π^* $p_x - p_x$
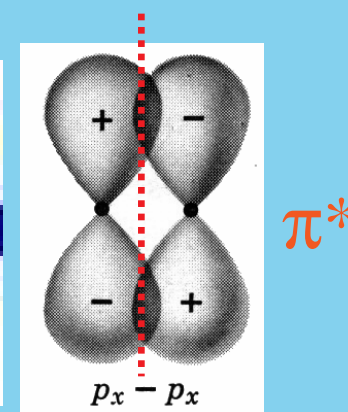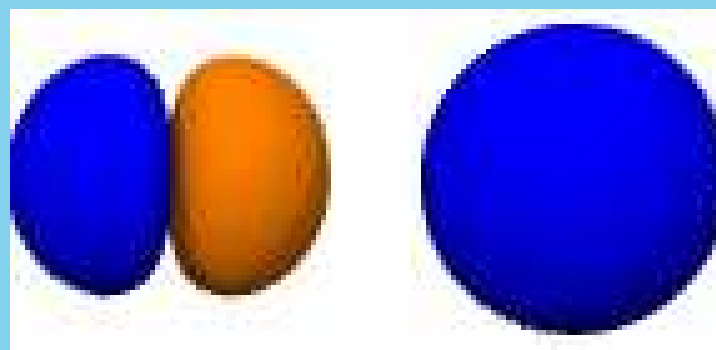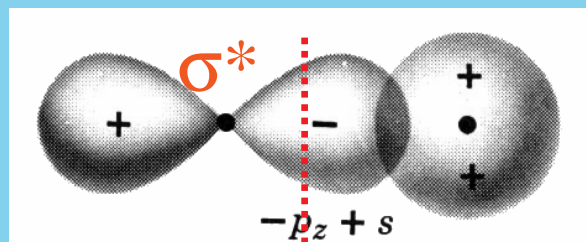
Labelling molecular orbitals

3 Label indicating the presence of a Centre of Inversion
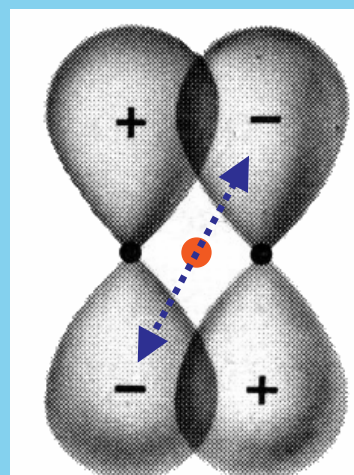
$p_x + p_x$

As you go from one side of wave function through the centre of the bond the sign of the wavefunction reverses

→ not centrosymmetric

→ **u** = ungerade or odd

$$\pi_u$$

$p_x + p_x$

$p_x - p_x$

$p_x - p_x$

Wave function does not change sign

→ centrosymmetric

→ **g** = gerade or even

$$\pi^*_g$$

- MO's sometimes labelled with the type of AO forming them e.g. σ_s or σ_p