Symmetry and Bonding

Lecture 4

Outline

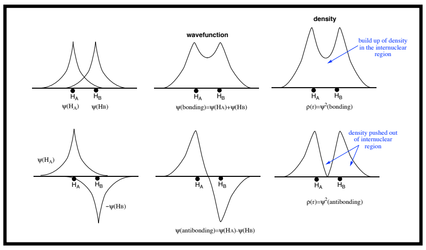
- **The Diatomic MO Diagram part 2**
  - What are LCAOs?
  - MO mixing
  - Periodic trends in X_2 MO diagrams
  - Heteronuclear diatomic molecules
  - Fragment orbital energy positioning
  - Orbital size in a MO diagram

Linear Comination of AOs

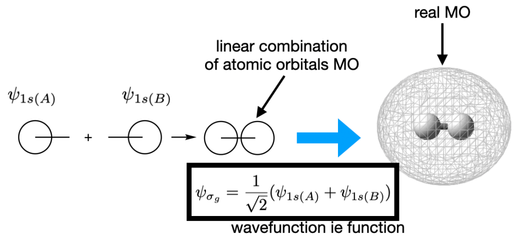
forming simple MOs by combining FOs

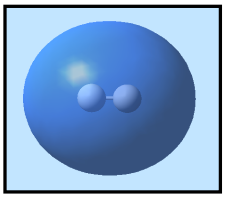
- add once “as is”, add once with phase of one FO inverted
- we draw a “cartoon”
- this cartoon represents an equation!

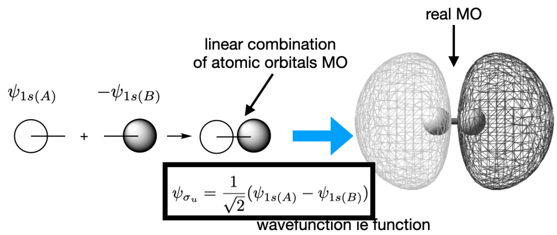
another representation of the MOs

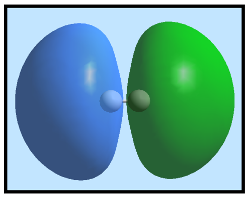


last year: wavefunctions density









Linear Comination of AOs

theory: linear combination of atomic orbitals

$$\psi_\Gamma = N(c_1\psi_1 + c_2\psi_2 + \cdots c_n\psi_n) = N\sum c_i\psi_i$$

- Γ gamma represents an unknown symmetry label
- N normalisation factor
- c's determine the magnitude of the contribution by each AO(ψ)
- i is index running over all AOs

"linear" means only addition subtraction

- no powers (eg x^2) no exponents (e^x) no logs ($\log_{10}x$)

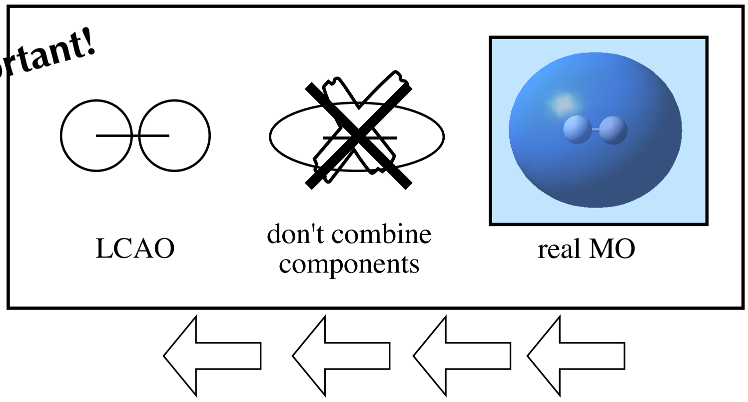
in a calculation the computer is varying the c's to find the lowest energy molecular wavefunction

- the c's give us the form of the MO
- we can make an estimate for the c's without doing complex mathematics

Linear Comination of AOs

- in this course do NOT combine AOs on different centers, we want to keep this information it tells us about how the atoms are bonding

Important!



- in research we often work backwards!
  - from computed MO to understand the bonding
  - more on this in a later lecture

MO Mixing

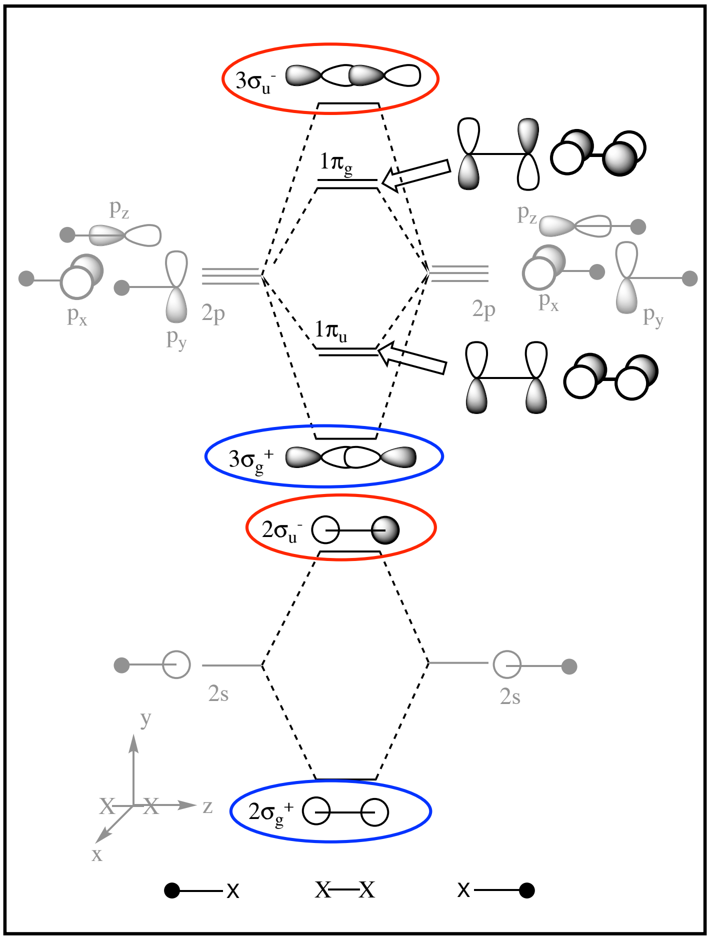
- current MO diagram is good for O_2 and F_2
- but not for C_2 or N_2 -> we need to include MO mixing
- mixing is when MOs interact to form new bonding / antibonding pairs
- Necessary MO mixing rules:
  - ONLY MOs of the same symmetry can mix
  - MOs cannot be from the same bonding/antibonding pair
  - mixing MUST stabilise the total energy of the molecule

Important!

- Large/important MO mixing when:
  - the closer in energy the MOs the larger the mixing
  - one of the MOs is non-bonding or unoccupied
  - MOs are in the HOMO-LUMO region

MO Mixing

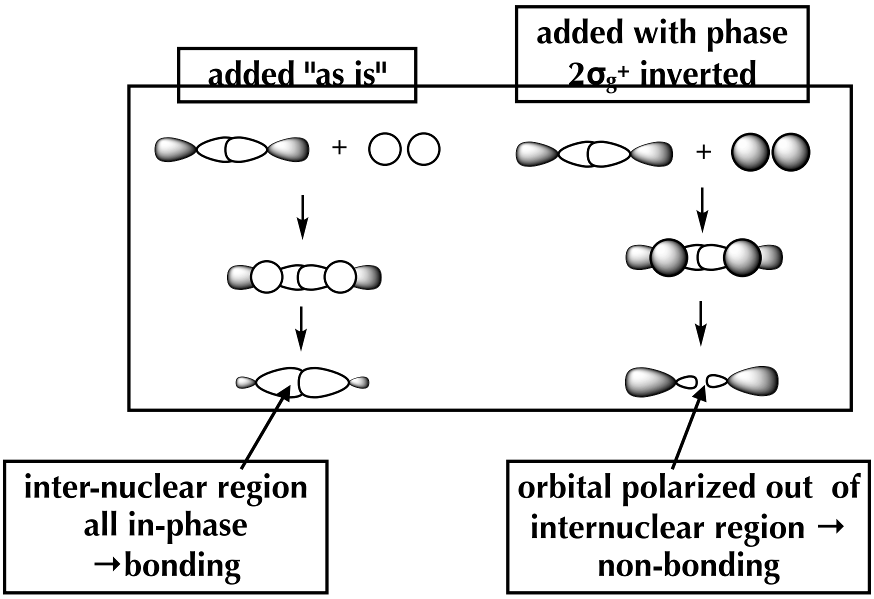
- **which MOs can mix for X_2?**
  - $2\sigma_g^+$ and $3\sigma_g^+$ (blue)
  - $2\sigma_u^-$ and $3\sigma_u^-$ (red)
- **how large will the mixing be?**
  - none of these MO pairs is close in energy => mixing is small
  - BUT in the case of diatomic molecules it is important!



MO Mixing

- **add the MOs once "as is" and once with the phase of one MO inverted**

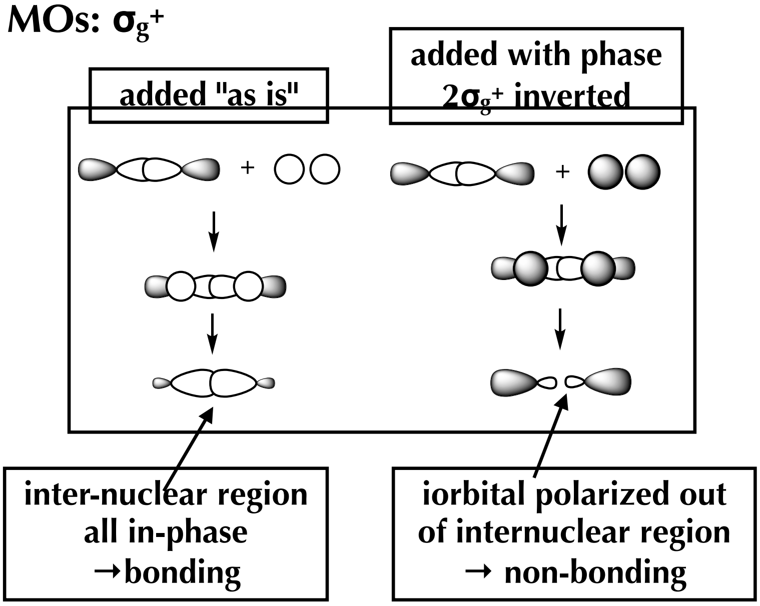
$2\sigma_g^+$

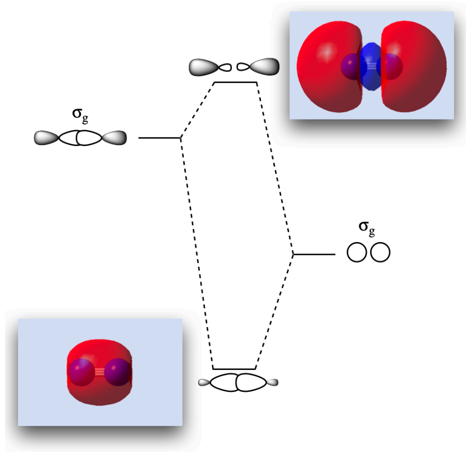


MO Mixing

- **add MOs once "as is" once with the phase of one MO inverted**
  - composite AOs look a bit like sp-hybrids
  - overall molecule must be stabilised ($2\sigma_g^+$ goes down more than $3\sigma_g^+$ goes up)

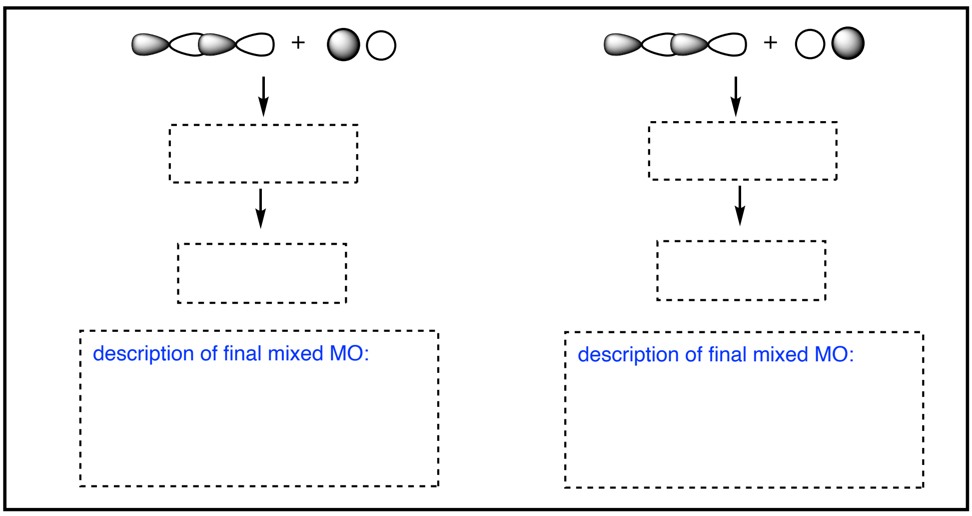
MOs: σ_g^+





In-Class Activity P1

- **determine the mixing of the $2\sigma_u^-$ and $3\sigma_u^-$ MOs**



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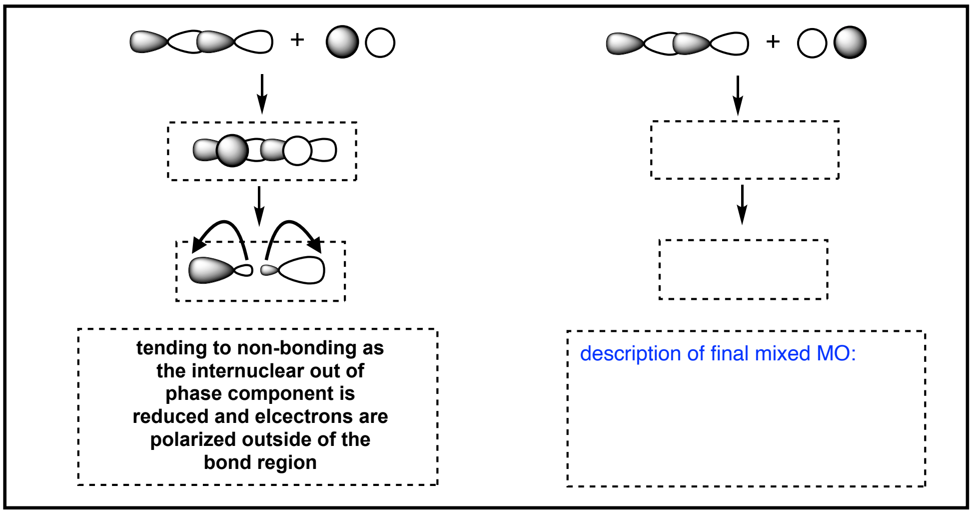

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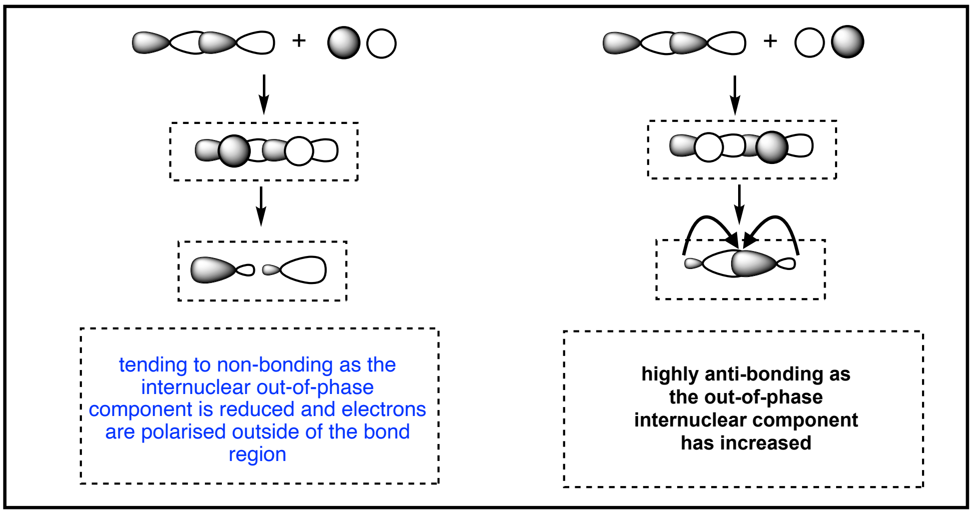
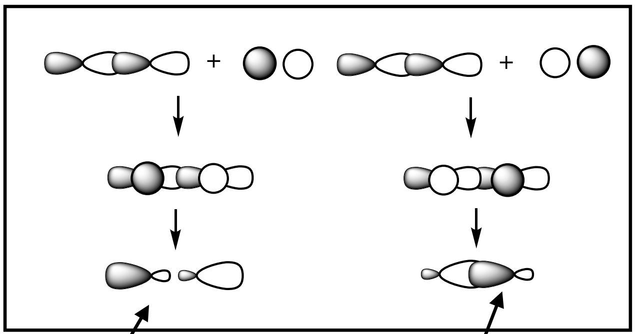


MO Mixing

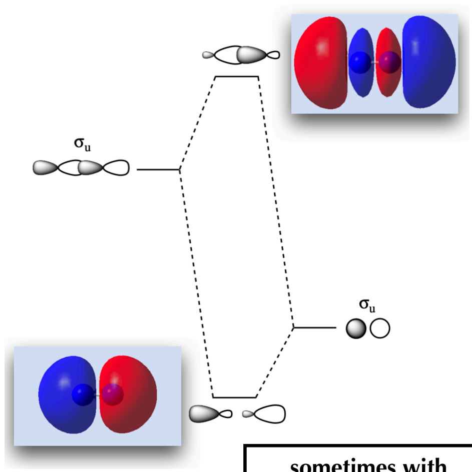
- **add MOs once "as is" once with the phase of one MO inverted**
  - anti-bonding is very strong, orbital is unoccupied therefor larger destabilisaton
  - poor match with the real MO (other effects are active)

MOs: σ_u^-



iorbital polarized out of internuclear region → non-bonding

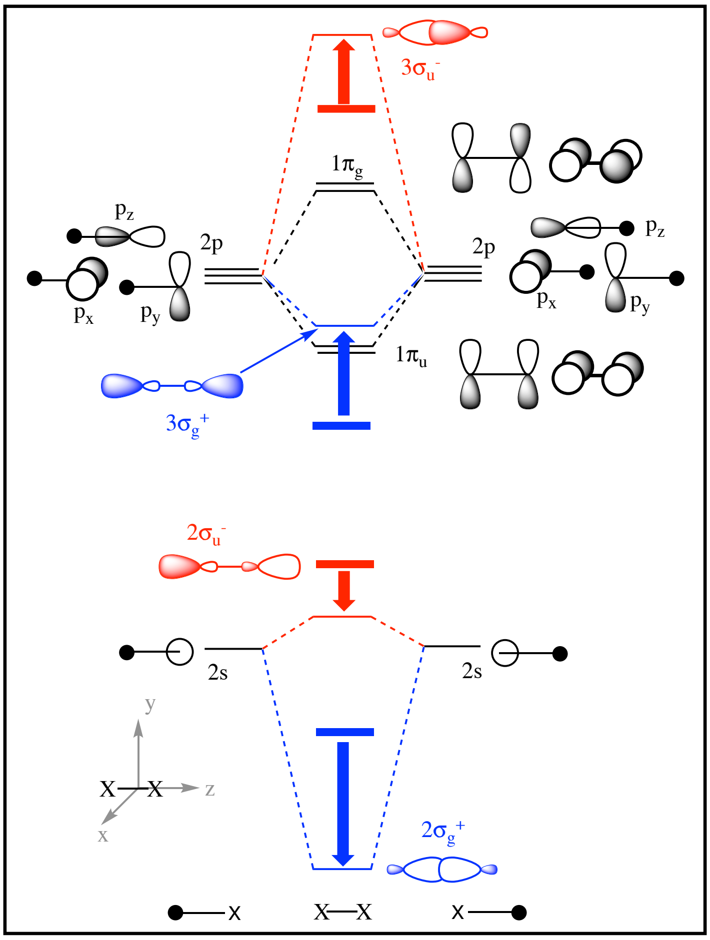
inter-nuclear region out-of-phase →anti-bonding



sometimes with mixing the qualitative MOs do not match the real MOs as well

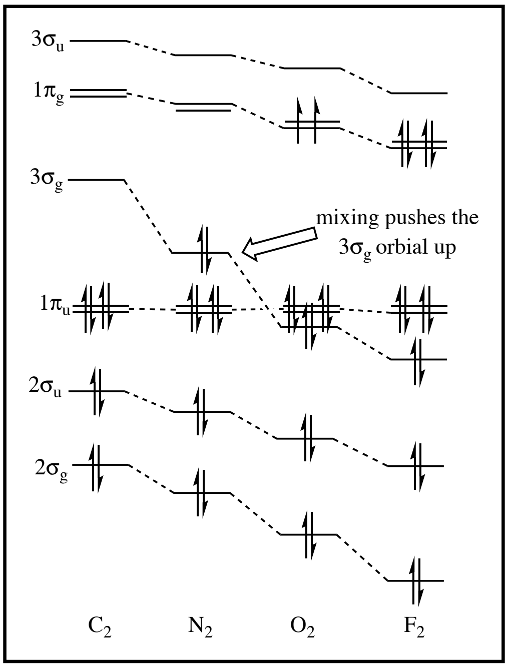
Final MO Diagram

for a homonuclear diatomic with mixing



Periodic Trend in MOs

- **molecules with the same valence orbitals have similar MO diagrams**
- **occupation changes**
- **mixing can cause changes**
- **for second row diatomic molecules the 2s-2p gap very important, switches mixing on/off**
  - O_2 and F_2 no or very small mixing
  - C_2 and N_2 large mixing
  - electronic structure changes from N_2 to O_2
  - O_2 $(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$
  - N_2 $(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$



Heteronuclear Diatomic Molecules

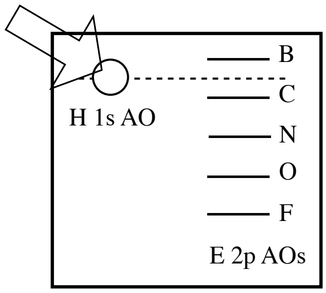
- **2nd row heteronuclear diatomic molecules**
  - examples are CO, [CN]⁻ and NO•
  - the symmetry is reduced $C_{\infty v}$
  - the FO energy levels are no-longer the same
  - the contributions of each FO to MOs also change
  - the change in symmetry means mixing changes

Fragment Orbitals

- **placing FOs is easier with a reference, we frequently use H 1sAO**
- **higest occupied AO energies can be placed based on the electrongativity**

H	Li	Be	B	C	N	O	F
2.20	0.98	1.57	2.04	2.55	3.04	3.44	3.98
	Na	Mg	Al	Si	P	S	Cl
	0.93	1.31	1.61	1.91	2.19	2.58	2.19

Pauling electronegativity



valence pAO relative to valence H1sAO

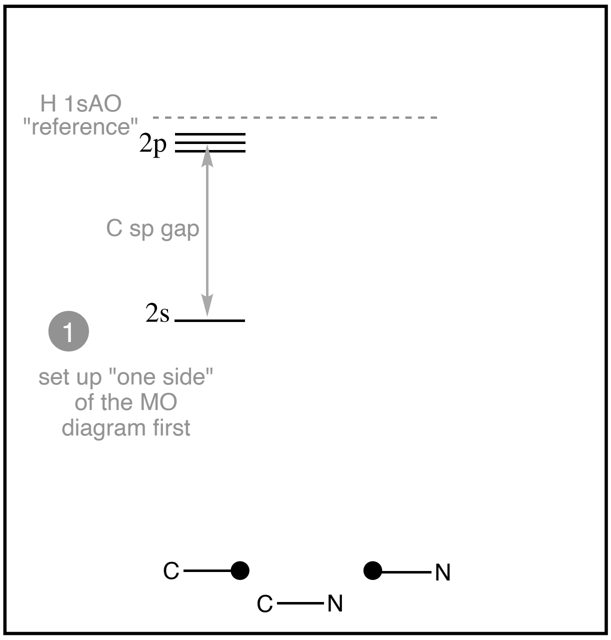
Fragment Orbitals

- **combine information on position of 2p**
- **with knowledge of the 2s-2p gap to position 2sAO**
- **2p AO always interact**
- **increasing s-p gap along the periodic table means**

2s AOs only interact for adjacent atoms

Fragment Orbitals

- **example: [CN]$^{-}$**
- **place H1sAO reference**
- **evaluate C first**
  - **C is more electronegative than H**
  - **C sp gap is relatively small**



Fragment Orbitals

- **example: [CN]$^{-}$**
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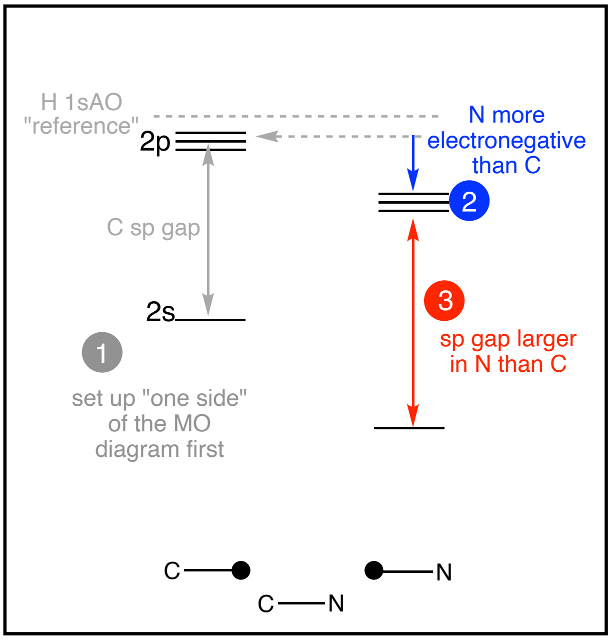
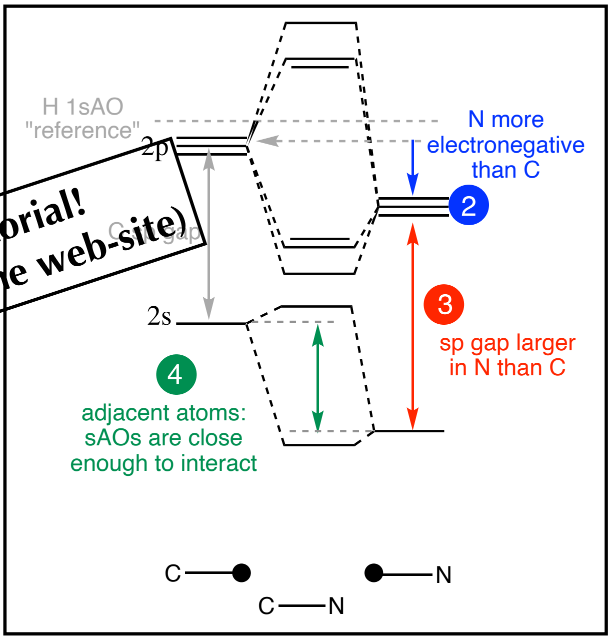
- **evaluate N relative to C**
  - **N is more electrongetive than C (and H)**
  - **N sp-gap is larger than that of C**



Fragment Orbitals

- **example: [CN]$^{-}$**
- **place H1sAO reference**
- **evaluate C first**
  - C is more electronegative than H
  - C sp gap is relatively small
- **evaluate N relative to C**
  - N is more electrongetive than C (and H)
  - N sp-gap is larger than that of C
- **decide if the 2s AOs will interact**
  - C and N are adjacent so the 2sAOs will interact

on-line tutorial!
(under L4 on the web-site)



In-Class Activity P2

- **Do the 2sAOs of NO interact?**
- **Do the 2sAOs of CO interact?**

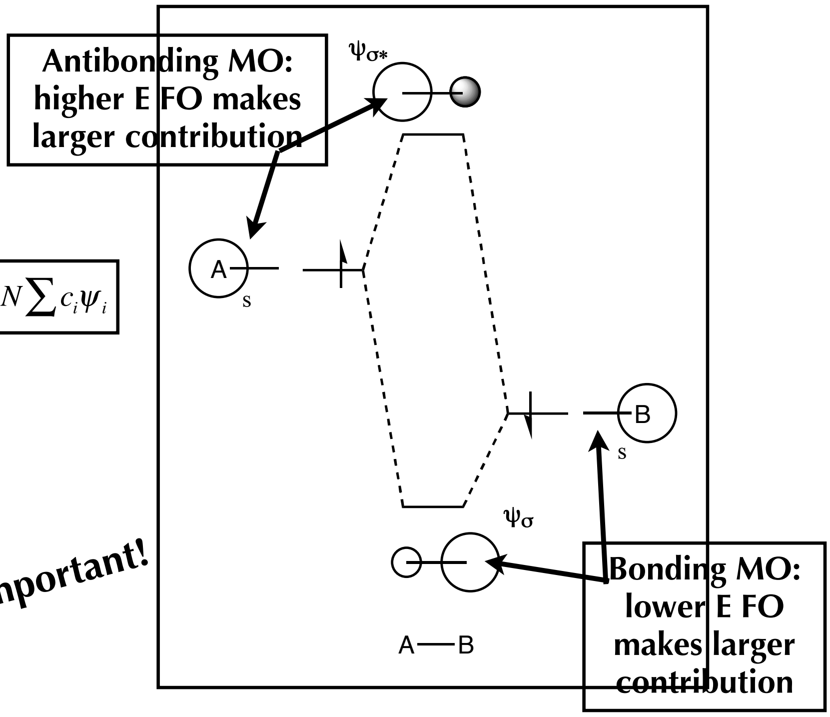
In-Class Activity P2

- **Do the 2sAOs of NO interact?**
  - yes N and O are adjacent on the PT
- **Do the 2sAOS of CO interact?**
  - no C and O are NOT adjacent on the PT
- **GoSoapBox correct answer is 2**
  - 2sAOs interact for NO but not for CO

LCAOs

- **C's are represented in the size of the AO contributions**

$$\psi_\Gamma = N(c_1\psi_1 + c_2\psi_2 + \cdots c_n\psi_n) = N\sum c_i\psi_i$$



Important!

In-Class Problem P3

a) draw the MO diagram for N_2

b) use the MO diagram to explain why N_2 is so stable

c) use the MO diagram to rank N_2, $[N_2]^-$ and $[N_2]^+$ in order of stability

tutorial style

Key Points

- **be able to explain the acronym LCAO, give the general equation, describe each of the components and illustrate the process on a diagram**
- **be able to describe and illustrate MO mixing**
- **be able to draw MO diagrams for diatomic molecules that exhibit mixing**
- **be able to use the MO diagram to interpret or discuss the electronic structure and bonding in a diatomic molecule**
- **be able to rationalise the relative position of FO energy levels**
- **be able to explain and predict the relative size of AO contributions to MOs**
- **be able to draw the MO diagram for a heteronuclear diatomic molecule**