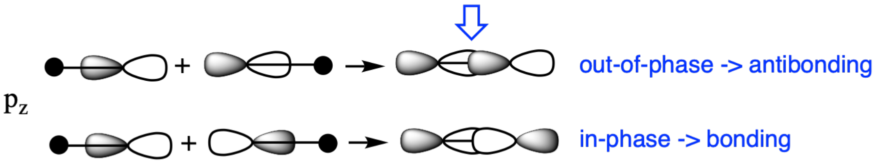
In-Class Problems / Self-study Problems / Test Preparation: Lecture 3

- **In-Class P1** complete the diagram showing how the p_z AOs "along the bond" combine in a bonding and antibonding pair, label the internuclear region for the in-phase bonding and out-of-phase antibonding MOs

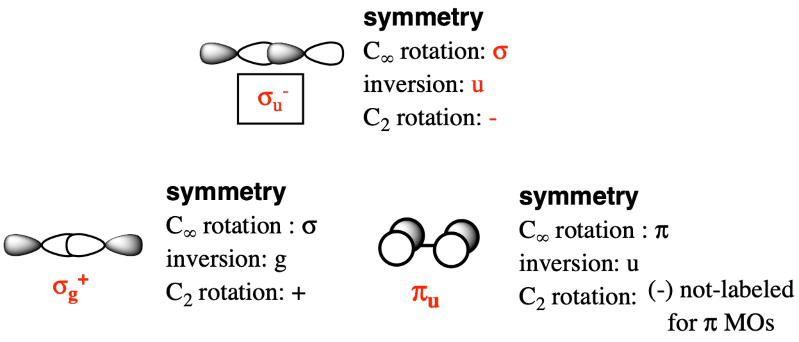


out-of-phase -> antibonding

in-phase -> bonding

Figure 1 Combining AOs to form MOs

- **In-Class P2** determine the full symmetry label for the following MOs, I have done the first example for you.



symmetry
C_∞ rotation: σ
inversion: u
C_2 rotation: -

symmetry
C_∞ rotation : σ
inversion: g
C_2 rotation: +

symmetry
C_∞ rotation : π
inversion: u
C_2 rotation: (-) not-labeled for π MOs

Figure 2 Combining AOs to form MOs

- **Q1** draw the MO diagram for F_2
  - follow the same procedure as for the O_2 molecule
  - however the number of electrons is different F has 7 valence electrons and F_2 14 electrons in the MO diagram

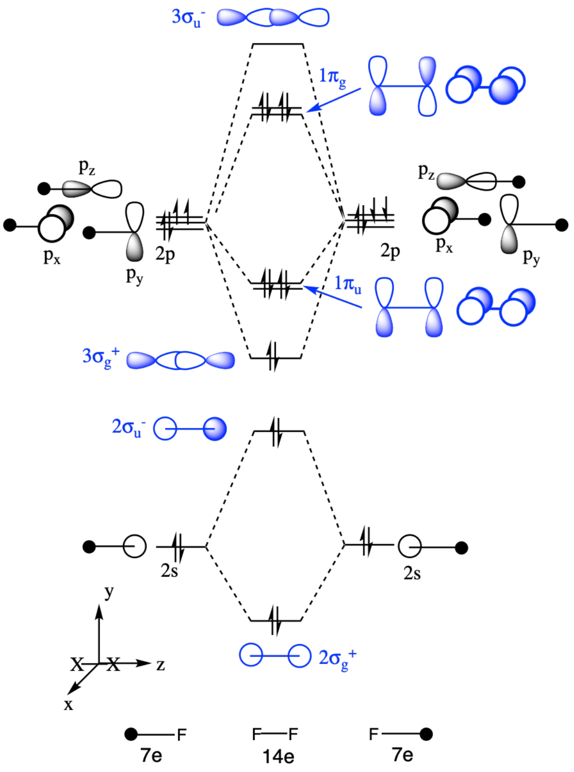


Figure 3 MO diagram for F_2

- **Q2** draw the MO diagram for He_2, and use it as a basis to discuss the electronic structure of $[He_2]^+$ and $[He_2]^-$. Use your MO diagram to rationalize which of these diatomic molecules is stable. Identify if each molecule will be diamagnetic or paramagnetic.
  - we would normally only determine the valence MO diagram (ie for the 1s AOs) however for $[He_2]^-$ we will need to add the 2sAOs as well.
  - the electronic configurations are

    He_2 $(1\sigma_g^+)^2 (1\sigma_u^-)^2$

    $[He_2]^+$ $(1\sigma_g^+)^2 (1\sigma_u^-)^1$

    $[He_2]^-$ $(1\sigma_g^+)^2 (1\sigma_u^-)^2 (2\sigma_g^+)^1$
  - He_2 is unstable, because the antibonding MOs are destabilised more than the bonding MOs are stabilised, thus there will be an energy cost to forming He_2. He_2 would be diamagnetic, no unpaired spins
  - (information) there is no experimental evidence for the existence of He_2 at room temperature, however at very low temperatures a Van der Waals bound dimer exists; in liquid Helium!
  - $[He_2]^+$ has one electron removed from the antibonding MO, now there are 2 stabilised electrons and only 1 destabilised electron, this molecule might be stable. $[He_2]^+$ would be paramagnetic, one unpaired spin

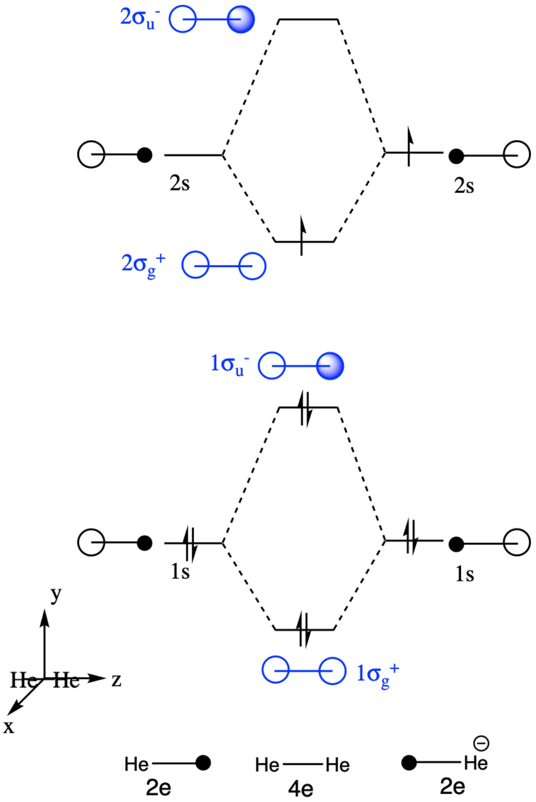


Figure 4 MO diagram for $[He_2]^-$

  - (information) $[He_2]^+$ has been found experimentally, the dissociation energy has been measured to be 241 kJ/mol
  - To a first approximation $[He_2]^-$ has a core electronic structure like He_2, but has one additional electron which would go into the stabilised $2\sigma_g^+$ MO. The stabilisation would need to overcome the net destabilisation of the $(1\sigma_g^+)^2 (1\sigma_u^-)^2$ configuration. In this configuration $[He_2]^-$ is paramagnetic, one unpaired spin.
  - (information) $[He_2]^-$ has been found experimentally, but it is only found in a metastable excited state which has theoretically been determined to actually be $(1\sigma_g^+)^2(1\sigma_u^-)^1(2\sigma_g^+)^1(1\pi_u)^1$
- **Q3** using the MO diagram of O_2 discuss the O-O bond distances for the following molecules $[O_2]^{\bullet+}$(dioxygenyl), O_2 (dioxygen) $[O_2]^-$ (superoxide) $[O_2]^{2-}$ (peroxide)
  - O_2 forms a strong O-O bond, the 2p manifold has the $(2\sigma_g^+)$ occupied forming a strong σ-bond, the 6π electrons mean that while there are 4e in π-bonding MOs 2e go into an antibonding MO thus the π-bonding is weakened.
  - $[O_2]^+$ has one less electron in an antibonding π-MO meaning that the π-bonding is stronger than in O_2, $[O_2]^+$ will have a shorter O-O bond than O_2
  - in contrast $[O_2]^{\bullet-}$ is a radical anion has one extra electron in an antibonding π-MO meaning that the π-bonding is weaker than in O_2, $[O_2]^-$ will have alonger O-O bond than O_2
  - $[O_2]^{2-}$ has the π-MO manifold completely occupied, because antibonding is destabilised more than bonding is stabilised this will significantly weaken the bonding, $[O_2]^{2-}$ will only be weakly stable and the O-O bond will be even longer.