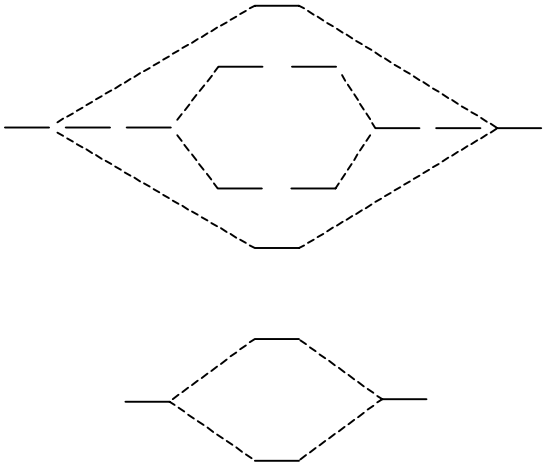
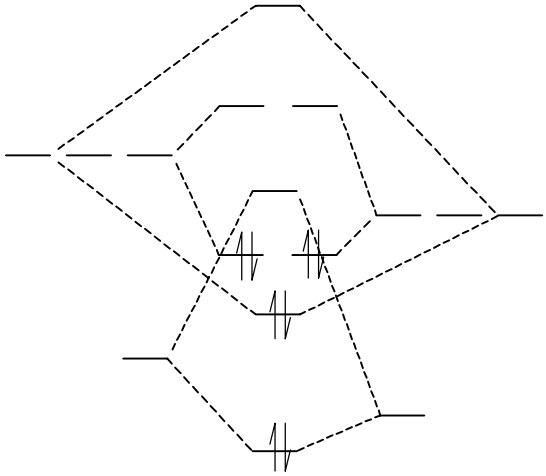
Section 5 – Questions from Shriver and Atkins

2.14 The blank diagram for O_2 looks like this: Filling in the electrons will give,



The diagram for the heterodiatomic BN is:



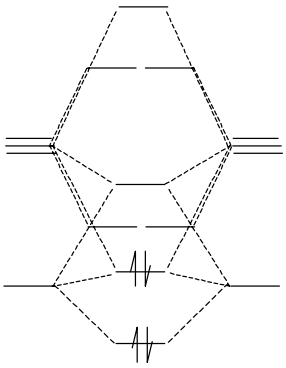
(a) 13 e^- total, 1 unpaired

(b) 11 e^- total, 1 unpaired

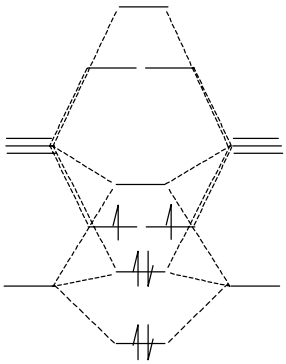
(c) With 8 e^- total, there are 0 unpaired

2.15 Molecular orbital configurations are identical to atomic, except using the MO name instead of the AO name.

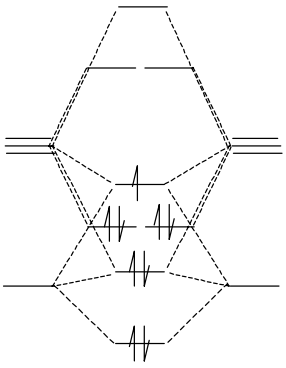
(a) $1\sigma_g^2 1\sigma_u^2$ (b) $1\sigma_g^2 1\sigma_u^2 1\pi_u^2$ (c) $1\sigma_g^2 1\sigma_u^2 1\pi_u^3$ (d) $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^3$



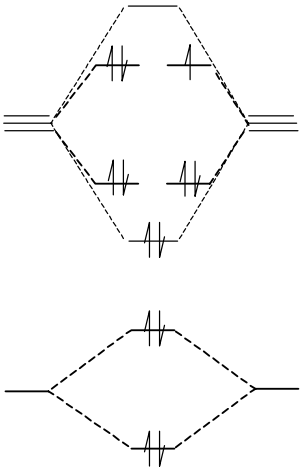
Be_2



B_2



C_2^-



F_2^+

2.16 C_2^{2-} will have two more electrons than C_2 (see 2.15(c) above, and add 1 more electron). The net result is that, because the added two electrons are in non-bonding orbitals, there is no effect on the bonding propeties (*i.e.* C_2^{2-} also has a triple bond, just like acetylene).

2.17 (a) Just like in Figure 2.24, except Br has 4*s* and 4*p* orbitals instead.
(b) Same as any halogen or interhalogen, bond order = 1.

2.18 (a) S_2 is the same as O_2, B.O. = 2.
(b) 6(bonding) – 4(anti) – 0(4 non) = 2 bonding e^- = B.O. = 1
(c) NO same as CO with 1 fewer e^-; it is lost from a non-bonding orbital, thus NO has B.O. = 3

2.19 (a) B.O. increases by 0.5, bond length shortens
(b) B.O. decreases by 0.5 (extra electron goes into π^*), bond lengths lengthens
(c) B.O. and bond length remain the same, as electron is lost from a non-bonding orbital

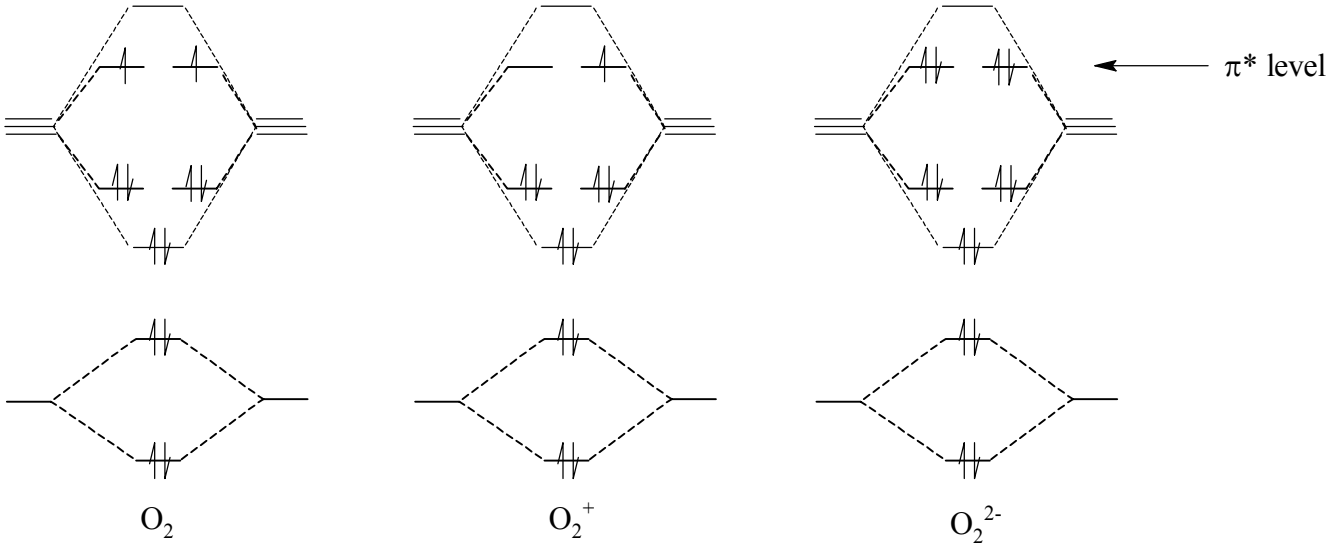
2.23 The 1e orbitals are purely F in character (no line to the S at all); the $2t_1$ orbitals are slightly closer in energy to the S, therefore they have more S character.

6.5 (a) An *s*-orbital has all the symmetry elements in ∞ amounts (i.e. C_∞ and S_∞ axes)
(b) E, C_∞, σ_v
(c) E, 3 mutually perpendicular C_2, σ_h, σ_v, i
(d) E, C_∞, perpendicular C_2, σ_h, σ_v, i, S_∞

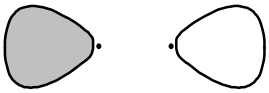
6.6 (a) C_{3v}
(b) point group has an E in it, therefore doubly degenerate
(c) E has the $3p_x$ and $3p_y$ orbitals being degenerate

6.7 (a) D_{3h}
(b) point group has an E in it, therefore doubly degenerate
(c) E' has the $3p_x$ and $3p_y$ orbitals being degenerate

16.p1 As can be seen in the diagram, the differences all relate to the amount of filling of the π* level. It is ½-filled in O_2, which has a B.O. of 2. It is ¼-filled in O_2^+, so the bond order increases to 2.5 (shorter and stronger bond. It is fully-filled in O_2^{2-}, thus the B.O. drops to 1 and gives the longest bond.

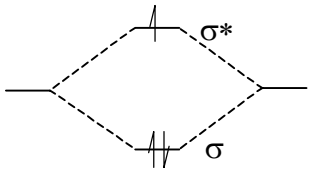


17.4 The orbital is a σ* derived from the *ns* orbitals on the halogen, *i.e.*,

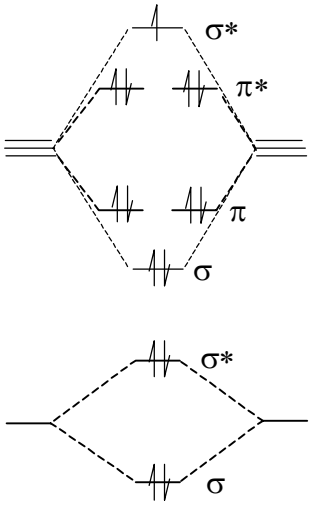


If X_2 acts as a Lewis acid, it is accepting electron density from the Lewis base, and therefore electrons will go into the LUMO. If this orbital is populated, it would serve to weaken the X-X bond (in fact, if it was fully populated, the B.O. would go to 0 and the X-X bond would cleave).

18.7



He^+, B.O. = 1/2



Ne^+, B.O. = 1/2

19.11 Note that all these have 2+ oxidation states, therefore,
(a) and (b) d^4 on each metal gives $\sigma^2\pi^4\delta^2$
(c) d^9 on each metal gives $\sigma^2\pi^4\delta^4\delta^{*4}\pi^{*4}$