Marks
6

- The electronic energies of the molecular orbitals of diatomics consisting of atoms from H to Ne can be ordered as follows (with energy increasing from left to right):

$$\sigma\ \sigma^{*}\ \sigma\ \sigma^{*}\ 2{\times}\pi\ \sigma\ 2{\times}\pi^{*}\ \sigma^{*}$$

(the ‘2×’ denotes a pair of degenerate orbitals)

Use this ordering of the molecular orbitals to identify the following species.

(i) The lowest molecular weight diatomic ion (homo- or heteronuclear) that has **all** of the following characteristics:

a) a single negative charge,
b) a bond order greater than zero *and*
c) is diamagnetic.

HBe^- has 6 electrons (1 from He, 4 from Be and 1 from the negative charge) so has a configuration $\sigma^2\ \sigma^{*2}\ \sigma^2$. It has a bond order of 1 and is diamagnetic.

(ii) A diatomic species that has the same electronic configuration as O_2.

There are many: simply substitute one or both O by a cation with the same number of electrons (F^+, Ne^{2+} etc) or an anion with the same number of electrons (N^-, C^{2-} etc). For example:

NO^-, OF^+, NF, F_2^{2+}, CN^{3-}, N_2^{2-} .....

(iii) All of the atoms with atomic numbers less than or equal to 10 that cannot form stable, neutral, homonuclear diatomic molecules.

The neutral, homonuclear diatomic molecule would have a bond order of zero: He, Be and Ne.

He_2 $\sigma^2\ \sigma^{*2}$
Be_2 $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}$
Ne_2 $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}\ \pi^4\ \pi^{*4}\ \sigma^2\ \pi^{*4}\ \sigma^{*2}$

Given that there are three degenerate *p* orbitals in an atom, why are there only two degenerate π orbitals in a diatomic molecule?

One *p*-orbital on each atom overlaps end-on with the matching *p*-orbital on the other atom. This produces a *σ*-bond.

This leaves only two *p*-orbitals on each atom to overlap in the side-on manner required for π bonding.