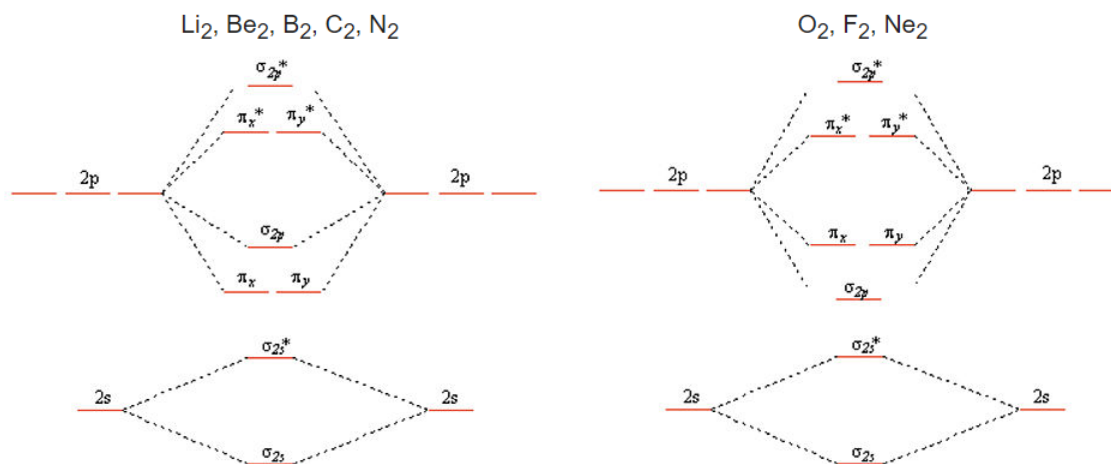


2.5: Diatomic Molecules

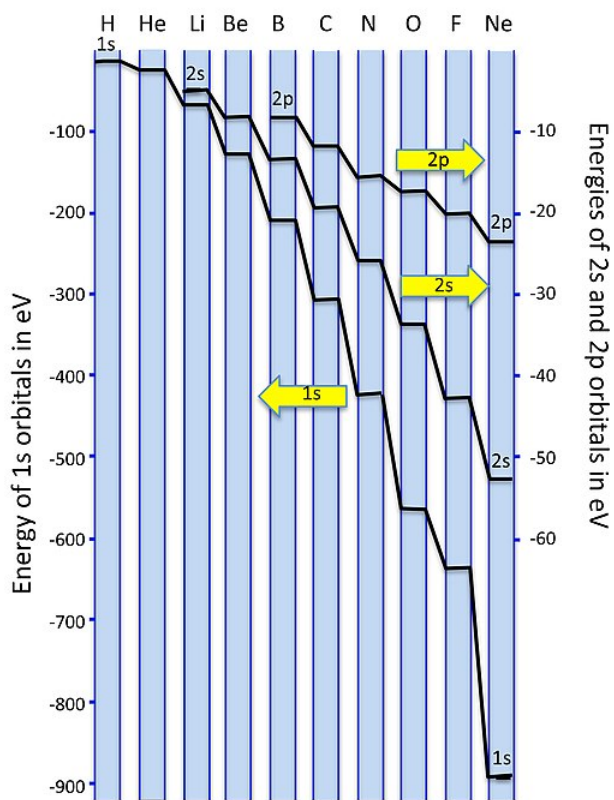
Valence bond theory fails for a number of the second row diatomics, most famously for O_2 , where it predicts a diamagnetic, doubly bonded molecule with four lone pairs. O_2 does have a double bond, but it has two unpaired electrons in the ground state, a property that can be explained by the MO picture. We can construct the MO energy level diagrams for these molecules as follows



We get the simpler diatomic MO picture on the right when the $2s$ and $2p$ AOs are well separated in energy, as they are for O, F, and Ne. The picture on the left results from mixing of the σ_{2s} and σ_{2p} MO's, which are close in energy for Li_2 , Be_2 , B_2 , C_2 , and N_2 . The effect of this mixing is to push the σ_{2s}^* down in energy and the σ_{2p} up, to the point where the π_{2p} orbitals are below the σ_{2p} . Asymmetric diatomic molecules and ions such as CO, NO, and NO^+ also have the ordering of energy levels shown on the left because of sp mixing. A good animation of the molecular orbitals in the CO molecule can be found on the University of Liverpool [Structure and Bonding](#) website.

Why don't we get sp -orbital mixing for O_2 and F_2 ? The reason has to do with the energies of the orbitals, which are not drawn to scale in the simple picture above. As we move across the second row of the periodic table from Li to F, we are progressively adding protons to the nucleus. The $2s$ orbital, which has finite amplitude at the nucleus, "feels" the increased nuclear charge more than the $2p$ orbital. This means that as we progress across the periodic table (and also, as we will see later, when we move down the periodic table), the **energy difference between the s and p orbitals increases**. As the $2s$ and $2p$ energies become farther apart in energy, there is less interaction between the orbitals (i.e., less mixing).

A plot of orbital energies is shown below. Because of the very large energy difference between the $1s$ and $2s/2p$ orbitals, we plot them on different energy scales, with the $1s$ to the left and the $2s/2p$ to the right. For elements at the left side of the 2nd period (Li, Be, B) the $2s$ and $2p$ energies are only a few eV apart. The energy difference becomes very large - more than 20 electron volts - for O and F. Since single bond energies are typically about 3-4 eV, this energy difference would be very large on the scale of our MO diagrams. For all the elements in the 2nd row of the periodic table, the $1s$ (core) orbitals are very low in energy compared to the $2s/2p$ (valence) orbitals, so we don't need to consider them in drawing our MO diagrams.



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