Figure 2.4.1: Oxygen molecules have two unpaired electrons and are therefore paramagnetic. In this photograph, liquid oxygen is suspended between the poles of a strong permanent magnet.

Valence bond theory fails for a number of the second row diatomics, most famously for \( \text{O}_2 \), where it predicts a diamagnetic, doubly bonded molecule with four lone pairs. \( \text{O}_2 \) 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:

![MO Energy Level Diagrams](image)

Figure 2.4.2: MO’s for homonuclear diatomics. Left - \( \text{Li}_2 \), \( \text{Be}_2 \), \( \text{B}_2 \), \( \text{C}_2 \), \( \text{N}_2 \). Right - \( \text{O}_2 \), \( \text{F}_2 \), \( \text{Ne}_2 \).
We get the simpler picture on the right when the $\langle 2s \rangle$ and $\langle 2p \rangle$ AOs are well separated in energy, as they are for $\langle \text{O} \rangle$, $\langle \text{F} \rangle$, and $\langle \text{Ne} \rangle$. The picture on the left results from mixing of the $\langle \sigma_{2s} \rangle$ and $\langle \sigma_{2p} \rangle$ MO's, which are close in energy for $\langle \text{Li}_2 \rangle$, $\langle \text{Be}_2 \rangle$, $\langle \text{B}_2 \rangle$, $\langle \text{C}_2 \rangle$, and $\langle \text{N}_2 \rangle$. The effect of this mixing is to push the $\langle \sigma_{2s} \rangle$ down in energy and the $\langle \sigma_{2p} \rangle$ up, to the point where the $\langle p\pi \rangle$ orbitals are below the $\langle \sigma_{2p} \rangle$.

**Why don't we get sp-orbital mixing for $\langle \text{O}_2 \rangle$ and $\langle \text{F}_2 \rangle$?** 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 $\langle \text{Li} \rangle$ to $\langle \text{F} \rangle$, we are progressively adding protons to the nucleus. The $\langle 2s \rangle$ orbital, which has finite amplitude at the nucleus, “feels” the increased nuclear charge more than the $\langle 2p \rangle$ 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 (Figure 2.4.3). Because of the very large energy difference between the $\langle 1s \rangle$ and $\langle 2s/2p \rangle$ orbitals, we plot them on different energy scales, with the $\langle 1s \rangle$ to the left and the $\langle 2s/2p \rangle$ to the right. For elements at the left side of the 2nd period ($\langle \text{Li} \rangle$, $\langle \text{Be} \rangle$, $\langle \text{B} \rangle$) the $\langle 2s \rangle$ and $\langle 2p \rangle$ energies are only a few eV apart. The energy difference becomes very large - more than 20 electron volts - for $\langle \text{O} \rangle$ and $\langle \text{F} \rangle$. 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 $\langle 1s \rangle$ (core) orbitals are very low in energy compared to the $\langle 2s/2p \rangle$ (valence) orbitals, so we don't need to consider them in drawing our MO diagrams.

![Figure 2.4.3: Orbital Energy trends.](image-url)
Contributors

- Adapted from the Wikibook constructed by Chemistry 310 students at Penn State University.