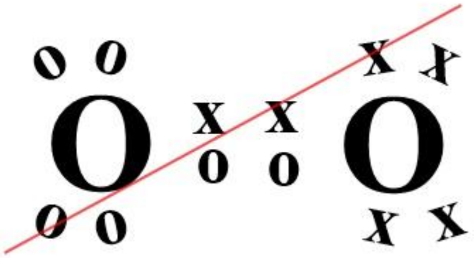
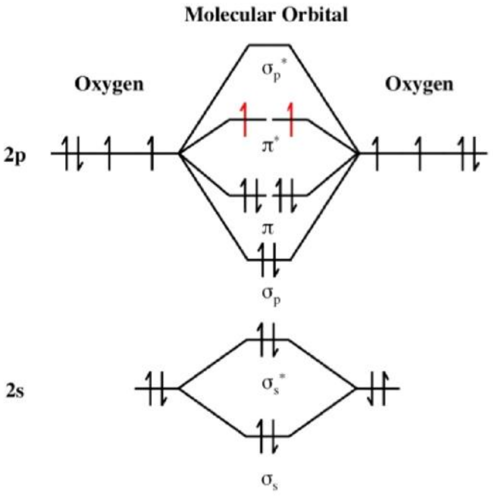
DIOXYGEN - O_2

The common allotrope of elemental oxygen is often just called oxygen, O_2, but to help distinguish it from the element may be called dioxygen or molecular oxygen. Elemental oxygen is most commonly encountered in this form, as about 21% (by volume) of the Earth's atmosphere is O_2, the remainder largely being dinitrogen, N_2. At STP, dioxygen is a colourless, odourless gas, in which the two oxygen atoms are chemically bonded to each other giving rise to two unpaired electrons occupying two degenerate molecular orbitals. The electron configuration of O_2 molecules in this form, a diradical, indicates that they should be paramagnetic. This is a classic example of where a simple Lewis structure fails to account for the properties and where an MO approach correctly provides the explanation.

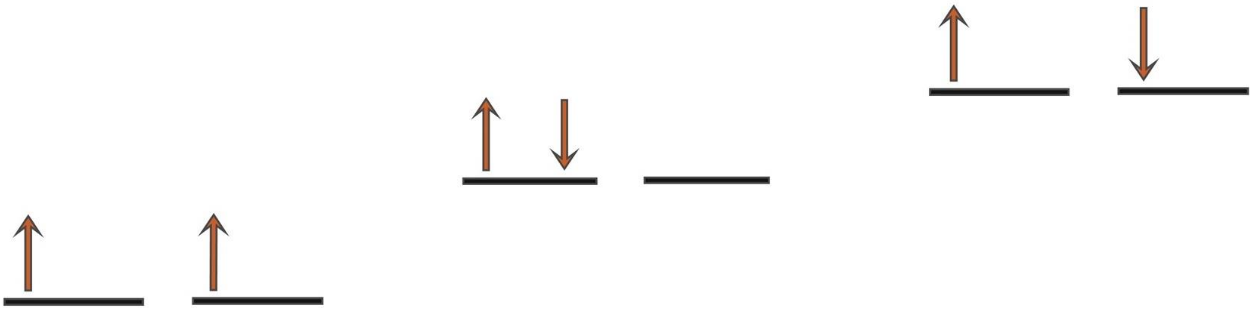




The electron configuration (ignoring 1s orbitals) is:
$(\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\sigma_{2p})^2\ (\pi_{2p})^4\ (\pi_{2p}^*)^2$ and from this the Bond Order is found to be $\frac{1}{2}(2 - 2 + 2 + 4 - 2) = 2$ that is, a double bond as shown in the Lewis structure as well. The difference though is that the Lewis structure does not predict the molecule to be paramagnetic. The bond length is 121 pm and the bond energy is 498 $kJmol^{-1}$.

A video clip showing liquid dioxygen being poured between the faces of a magnet and attracted into the magnet field has been prepared as a Harvard Natural Sciences Lecture Demonstration.

With 2 electrons to be placed in 2 degenerate orbitals, a number of variations are possible and the arrangement above where the 2 electrons are parallel is considered to be the most stable. Note that the spin multiplicity is given by the formula, 2S+1 and so for S=1 from s=½ + ½ then 2S+1 = 3 i.e. a spin triplet.



a) e$^-$s parallel (triplet $^3\Sigma_g$), b) 2 e$^-$s in 1 orbital (singlet $^1\Delta_g$), c) e$^-$s opposed (singlet $^1\Sigma_g$)

Singlet oxygen is the name commonly used for the electronically excited state shown in b) and it is less stable than the normal triplet state a) by 94.7 kJmol^{-1}. In isolation, singlet oxygen can persist for over an hour at room temperature. The other singlet state at 157.8 kJmol^{-1} shown in c) is very short lived and relaxes quickly to b). Because of differences in their electron shells, singlet and triplet oxygen differ in their chemical properties. Singlet oxygen is highly reactive.

Reactions of triplet dioxygen are restricted by conservation of spin state rules and at ambient temperatures this prevents direct reaction with all but the most reactive substrates, e.g. white phosphorus. At higher temperatures, or in the presence of suitable catalysts, reactions proceed more readily. For instance, most flammable substances are characterised by an autoignition temperature above which they will undergo combustion in air without an external flame or spark.

The energy difference between the ground state and singlet oxygen is 94.7 $kJmol^{-1}$ which would correspond to a transition in the near-infrared at ~1263 nm. In the isolated molecule, this transition is strictly forbidden by spin, symmetry and parity selection rules, making it one of nature's most forbidden transitions. In other words, direct excitation of ground state oxygen by light to form singlet oxygen is very improbable. As a consequence, singlet oxygen in the gas phase is extremely long lived (72 minutes). Interaction with solvents however, can reduce the lifetime to microseconds or even nanoseconds.

Various methods for the production of singlet oxygen exist. A photochemical method involves the irradiation of normal oxygen gas in the presence of an organic dye as a sensitizer, such as methylene blue. Singlet oxygen can be produced chemically as well. One of the chemical methods is by the reaction of hydrogen peroxide with sodium hypochlorite. This is convenient in small laboratories and for demonstrative purposes:

$$H_2O_2 + NaOCl \rightarrow O_2(^1\Delta_g) + NaCl + H_2O$$

In photosynthesis, singlet oxygen can be produced from the light-harvesting chlorophyll molecules. One of the roles of carotenoids in photosynthetic systems is to prevent damage caused by any singlet oxygen that is produced by either removing excess light energy from chlorophyll molecules, or quenching the singlet oxygen molecules directly.

Source :
http://wwwchem.uwimona.edu.jm:1104/courses/CHEM1902/IC10K_MG_oxygen.html