Molecular Orbitals

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1 Linearity of Schrödinger's Equation

All electron orbitals can be fully described by quantum theory and must satisfy Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\ddot{\psi}(x) = [E - V(x)]\,\psi(x)$$

Solutions for ψ must in addition be probability amplitude functions, meaning that $\psi^2(x)$ is the probability of finding the electron at x. While the particulars of this equation are too complicated, we can observe one important property of it at a glance: it is a linear differential equation, because ψ and its derivatives are never raised to any exponent greater than 1 (and are never multiplied with each other). The theory of differential equations tells us that any linear combination of two solutions to a linear differential equation is itself a solution. This means that if ψ_1 and ψ_2 are both solutions, then $\psi_1 + \psi_2$ is another solution. Moreover, it is possible to find two orthogonal functions such that every solution is a linear combination of those two. Two functions $a(x)$ and $b(x)$ are orthogonal if the following holds:

$$\int_{-\infty}^{\infty} a(x)b(x)\,dx = 0$$

Given this information, we can attempt to construct the orthogonal solutions to Schrödinger's equation given any two solutions ψ_1 and ψ_2. Because these two functions are probability amplitudes, their squares are probability densities, and the following relations must hold:

$$\int_{-\infty}^{\infty} \psi_1^2(x)\,dx = 1$$
$$\int_{-\infty}^{\infty} \psi_2^2(x)\,dx = 1$$

We can then subtract these integrals and factor the new integrand:

$$\int_{-\infty}^{\infty} \psi_1^2(x) - \psi_2^2(x)\,dx = \int_{-\infty}^{\infty} (\psi_1(x) + \psi_2(x))(\psi_1(x) - \psi_2(x))\,dx = 0$$

We have now constructed two functions which satisfy the above relation for orthogonality: $(\psi_1(x) + \psi_2(x))$ and $(\psi_1(x) - \psi_2(x))$. However, they should also individually be probability amplitudes. To satisfy this last condition, we must scale them each by a constant. The reader can verify (or accept) that this constant is $\frac{1}{\sqrt{2}}$. We therefore arrive at the orthogonal functions:

$$\psi = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$$
$$\psi^* = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$$

The process just developed of transforming any two solutions to the Schrödinger equation into orthogonal functions forms the basis of molecular orbital theory.
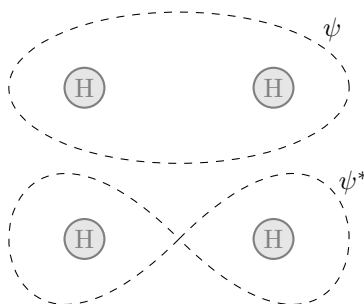
2   Molecular Orbitals

When two atoms come together and form a bond, their atomic orbitals combine to form new molecular orbitals. These molecular orbitals can be approximately represented by linear combinations of the atomic orbitals; in fact, the functions ψ and $\psi*$ defined above can represent the two molecular orbitals formed by two atomic orbitals ψ_1 and ψ_2.

For example, consider two hydrogen atoms forming a bond:
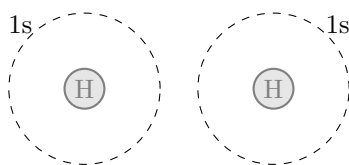
We can represent the molecular orbitals of the H_2 molecule as the sum and difference of the two 1s orbitals, like so:


Although the two 1s orbitals had equal energy, we observe that these two molecular orbitals cannot have the same energy. The first, ψ, has most of its electron density between the two protons. This is the position with the lowest energy. However, ψ^* has most of its electron density left of the leftmost proton or right of the rightmost proton. These positions have higher energy. In general, when two atomic orbitals form two molecular orbitals, they form one with lower energy and one with higher energy. The lower energy orbital, which is formed by the sum of the atomic orbitals, is called a *bonding orbital*. The higher energy orbital, formed by the difference of the atomic orbitals, is called an *antibonding orbital*.

Molecular orbitals are denoted according to their symmetry. The orbitals shown above are rotationally symmetric with respect to the axis along the nuclei. They therefore have σ symmetry, and we may call them σ_{1s} and σ_{1s}^*. Other bonds have π symmetry, and would be denoted similarly.

3   Molecular Orbital Diagrams

Molecular orbital diagrams are used to show how atomic orbitals combine to form molecular orbitals of varying energy, and how electrons are placed into those molecular orbitals. The following is a molecular orbital diagram for the H_2 molecule.
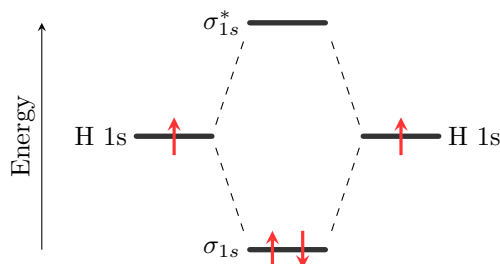
It shows that the original two 1s orbitals combine to form one orbital of lower energy and one of higher energy. The two electrons are placed according to the Aufbau principle and Hund's rule, spin-opposed into the bonding orbital.

We can draw a similar diagram for diatomic molecules more complicated than hydrogen, such as nitrogen. Nitrogen has the added complication of 2p orbitals. They can form either σ or π bonds, like so:
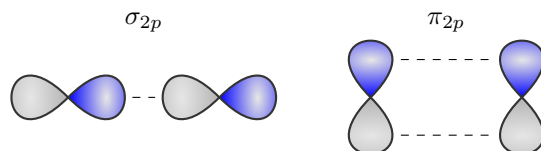
Only one pair of p orbitals can form a σ bond. The other two form *pi* bonds. We also need to know the relative energies of the σ_{2p} and π_{2p} bonds. In oxygen and fluorine, the π_{2p} orbitals have higher energy than the σ_{2p} orbitals. In nitrogen and elements with lower atomic number, the opposite is true. With this information, we can now draw the molecular orbital diagram of nitrogen.
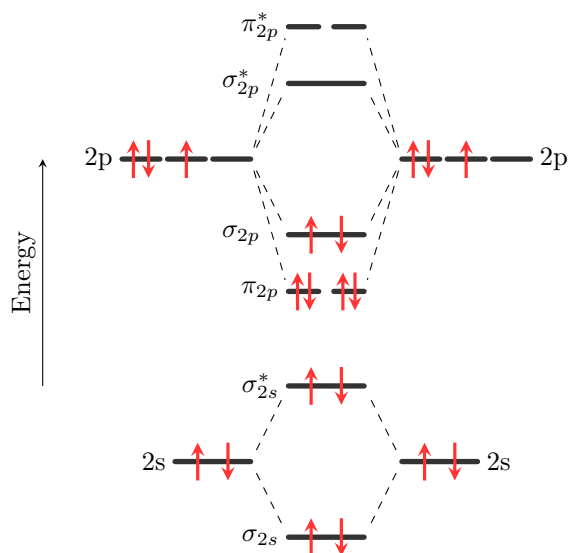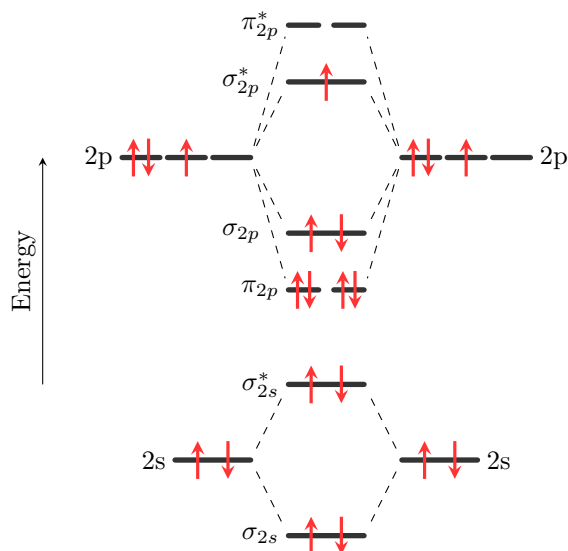

4   Bond Order

After drawing a molecular orbital diagram, it is simple to compute the order of a bond:

$$\text{bond order} = \frac{(\#\ \text{bonding electrons}) - (\#\ \text{antibonding electrons})}{2}$$

It is simple to verify that this formula yields a bond order of 1 for H_2 and 3 for N_2 according to the diagrams above, both of which agree with other predictions. We could also draw a molecular orbital diagram for the (contrived) N_2^- ion:

This is very similar to the diagram of N_2, except for an added electron in the σ_{2s}^* orbital. This is one extra antibonding electron, which changes the bond order to 2.5. This shows that the bond order need not be integral in molecular orbital theory.

5 Magnetism

Molecular orbital diagrams enable us to determine the magnetic properties of simple molecules, just as similar diagrams for single atoms did. When all the electrons are spin-paired, we say a molecule is *diamagnetic*. On the contrary, when one or more electrons is alone in an orbital, we say the molecule is *paramagnetic*. We can see above that N_2 and H_2 are both diamagnetic. However, oxygen is paramagnetic, as can be seen from its molecular orbital diagram (remembering that in oxygen, the σ_{2p} and π_{2p} orbitals switch positions).
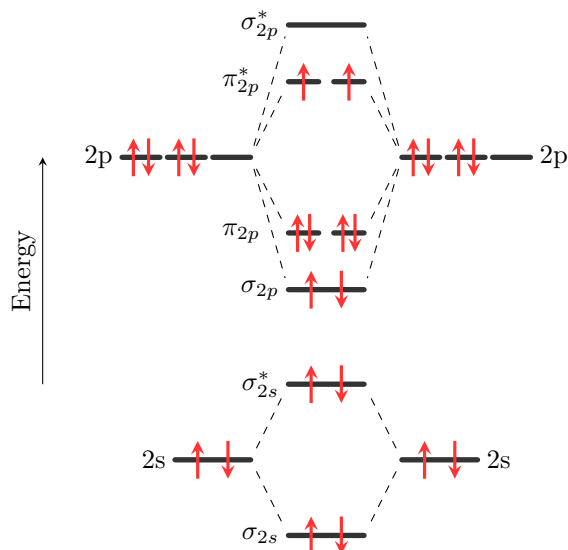
Both electrons in the π_{2p} orbitals are not spin-paired, and therefore oxygen is paramagnetic. We can also see that its bond order is 2, in agreement with other theories.