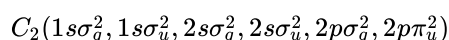


10.5: Homonuclear Diatomic Molecules

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. Quantitative theories are described in subsequent sections.

First consider diatomic carbon, C_2 . The first question to ask is, “Are the electrons paired or unpaired?” For example, if we start with acetylene and remove 2 hydrogen atoms, we get C_2 with an unpaired electron on each carbon. On the other hand, it might be possible for these electrons to pair up and give C_2 with a quadruple bond. Let's examine the molecular orbital theory of C_2 to see what that theory predicts.

Just as for the hydrogen molecule, we combine the two corresponding atomic orbitals from each atom. We are using the smallest possible basis set for this discussion. From each combination, we get a bonding molecular orbital and an antibonding molecular orbital. We expect the p_z orbitals on the two atoms to have more overlap than the p_x and p_y orbitals. We therefore expect the exchange integrals to be larger and the resulting molecular orbital $2p_z\sigma_g$ to have a lower energy, i.e. be more bonding, than the $2p_x\pi_u$ and $2p_y\pi_u$, which are degenerate since the x and y directions are equivalent. Using the Aufbau Principle, we assign 2 electrons to each orbital as shown in Figure 10.5.1, and end up with two electrons to put in two degenerate orbitals. Because of electron-electron repulsion, the lowest energy state will have each electron in a different degenerate orbital where they can be further apart than if they were in the same orbital. This separation reduces the repulsive Coulomb potential energy. Thus in C_2 we have 2 unpaired electrons, each in a bonding molecular orbital. The bond order, which is given by the number of electrons in bonding molecular orbitals minus the number of electrons in antibonding molecular orbitals divided by 2, is however 2, and each unpaired electron is not localized on a single C atom. So we see that the electronic structure of



is quite different from what we would expect by thinking it is acetylene without the two H atoms. The acetylene structure naively predicts a triple bond and two nonbonded electrons on each carbon atom.

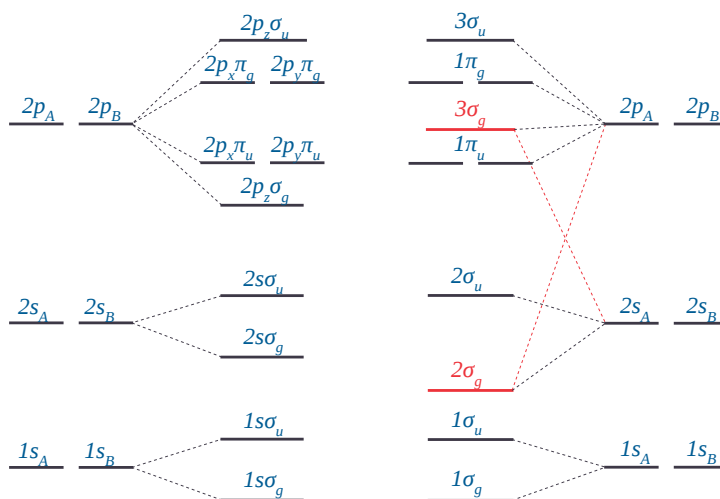


Figure 10.5.1: Ordering of molecular orbitals by energy for homonuclear diatomic molecules with (right side) and without (left side) significant mixing of molecular orbitals. The vertical energy axis is not to scale. (CC BY-NC; Ümit Kaya)

The two unpaired electrons in the two $2p\pi_u$ orbitals of C_2 predicted by this simple theory produce a singlet or a triplet ground state. The singlet ground state results if the electron spins are antiparallel ($\alpha\beta$), and the triplet ground state results if the electron spins are parallel (the three triplet spin functions are $\alpha\alpha$, $\alpha\beta$ and $\beta\beta$). Hund's rules predict the triplet state to have the lower energy, but the ground state of C_2 is known experimentally to be a singlet state. The singlet state results from a configuration where the $2p\sigma_g$ orbital has a higher energy than the $2p\pi_u$ orbitals, and all electrons are paired ($1s\sigma_g^2, 1s\sigma_u^2, 2s\sigma_g^2, 2s\sigma_u^2, 2p\pi_u^4, 2p\sigma_g^0$). The bond order is still 2, but there are no unpaired electrons. All the molecular orbitals are doubly occupied.

This configuration is accounted for theoretically by a more complete theory that allows the molecular orbitals to be written as linear combinations of all the valence atomic orbitals not just a pair of atomic orbitals. The $2\sigma_g$ molecular orbital, which in the simple

scheme is $2s_A + 2s_B$, is stabilized by mixing with $2p_{zA} + 2p_{zB}$, which is the $3\sigma_g$ orbital. As a result of this mixing, the $3\sigma_g$ orbital is destabilized and pushed to higher energy, above the $2p\pi_u$ orbitals. This mixing is just an example of hybridization. Better wavefunctions and better energies are obtained by using hybrid functions, which in this case is a linear combination of $1s$ and $2p_z$ functions. The relative energies of these hybrid orbitals also are shown on the right hand side of Figure 10.5.1.

For such mixing to be important, the orbitals must have the same symmetry and be close to each other in energy. Because of these constraints, this mixing is most important for the $2s\sigma_g$ and $2p\sigma_g$ orbitals, both of which have symmetry. This ordering is found for all the diatomic molecules of the first row elements except O_2 and F_2 . For these two molecules, the energy separation between the $2s$ and $2p$ orbitals is larger, and consequently the mixing is not strong enough to alter the energy level structure from that predicted by using the simple two-function basis set.

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