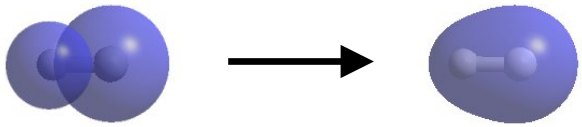
Exercise 3.1
Linear Combination of Atomic Orbitals: Heteronuclear Diatomics

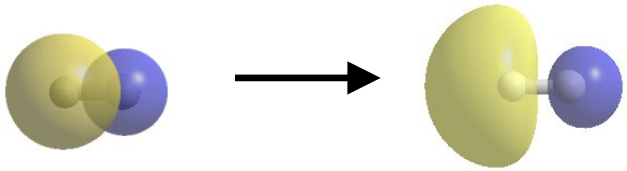
Linear Combination of Atomic Orbitals with Different Energies

A heteronuclear diatomic molecule is a molecule containing two atoms of different elements. As such, the atomic orbitals (AOs) combining to make molecular orbitals (MOs) have different energies. Each of the resulting MOs more closely resembles the AO to which it is closer in energy. This effect is called polarization of the MO.

When two AOs with different energies combine constructively (in-phase), the AO from the atom with the larger ionization energy contributes more to the resulting MO. This is because a large ionization energy is due to low energy atomic orbitals. Since the lower energy AO contributes more to the lower energy MO, you can imagine that you are combining more of that AO. This can be represented by drawing it proportionally larger than the other AO:

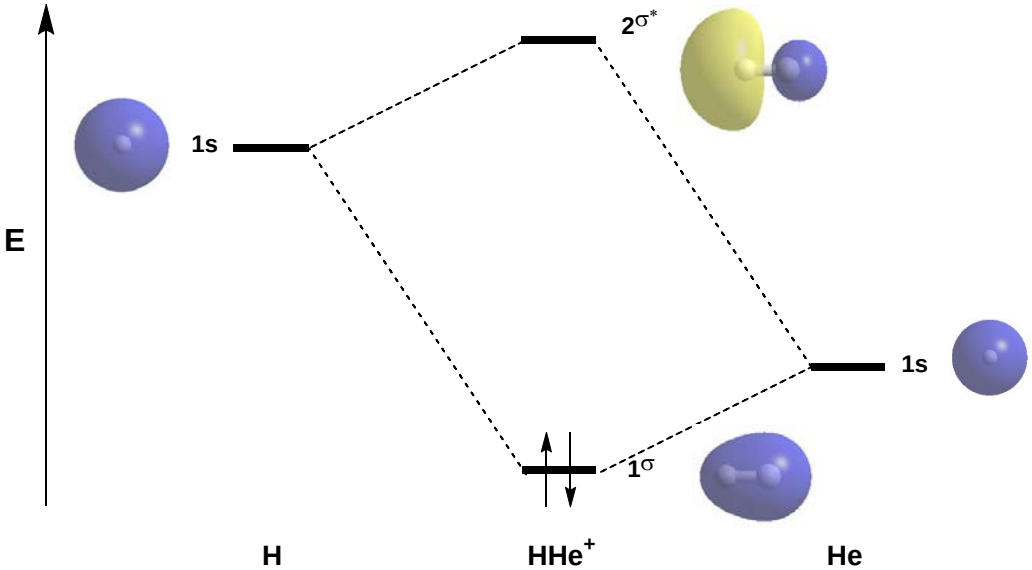


When two AOs with different energies combine destructively (out-of-phase), the AO from the atom with the smaller ionization energy contributes more to the resulting antibonding MO. This is because a small ionization energy is due to high energy atomic orbitals. Since the higher energy AO contributes more to the higher energy MO, you can imagine that you are combining more of that AO. This can be represented by drawing it proportionally larger than the other AO:



Because the trends for electronegativity are the same as the trends for ionization energy, some people describe this behavior in terms of electronegativity instead of ionization energy. That's less accurate, and it doesn't address noble gases.

The MO energy level diagram below is for HHe^+, one of the simplest heteronuclear diatomic species. HHe^+ is isoelectronic with H_2, meaning that it has the same number of electrons as H_2. As such, the MO energy level diagram for HHe^+ is very similar to the one for H_2.



1. In HF, the $1s$ orbital of H and the $2p_z$ orbital of F combine to make two MOs. The energy of the $1s(H)$ orbital is -1.00 Ry, and the energy of the $2p(F)$ orbitals is -1.37 Ry.

(a) Draw the molecular orbital formed from constructive overlap of these two atomic orbitals. Is it sigma or pi symmetric? Is it bonding or antibonding?

(b) Draw the molecular orbital formed from destructive overlap of these two atomic orbitals. Is it sigma or pi symmetric? Is it bonding or antibonding?

2. In CO, the $2p_y$ orbital of C and the $2p_y$ orbital of O combine to make two MOs. The energy of the $2p(C)$ orbitals is -0.79 Ry, and the energy of the $2p(O)$ orbitals is -1.17 Ry.

(a) Draw the molecular orbital formed from constructive overlap of these two atomic orbitals. Is it sigma or pi symmetric? Is it bonding or antibonding?

(b) Draw the molecular orbital formed from destructive overlap of these two atomic orbitals. Is it sigma or pi symmetric? Is it bonding or antibonding?

3. Rank the following isoelectronic species according to how much polarization you would expect to see in their π-symmetric molecular orbitals: CN^-, N_2, CO. Explain your ranking.