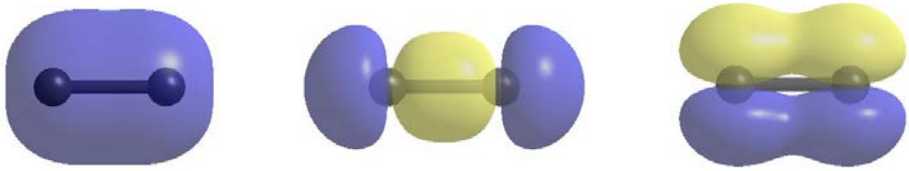
Exercise 3.3
Bonding, Antibonding and Nonbonding Molecular Orbitals

Generally speaking, electrons in bonding orbitals pull the nuclei closer together, grouping atoms as a molecule and increasing bond order. On the other hand, electrons in antibonding orbitals pull the nuclei away from each other, decreasing bond order. Electrons in nonbonding orbitals do neither; they function like a lone pair and have no impact on bond order.

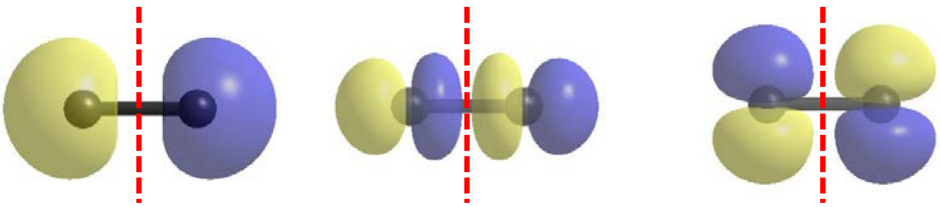
The following three methods can be used to distinguish between bonding, antibonding and nonbonding molecular orbitals (MOs).

Shape

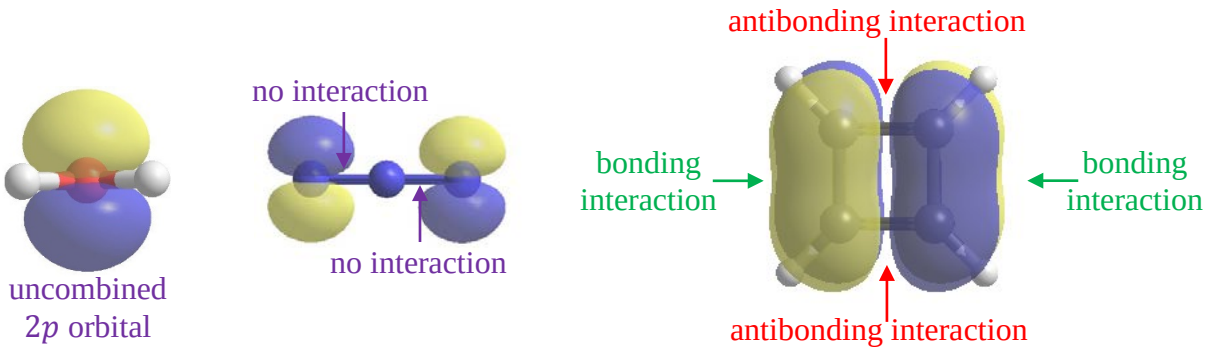
Bonding MOs are largest in the region between the nuclei. The high electron density in this region in a filled bonding MO pulls the nuclei closer together as a result of the attraction between the negatively charged electrons and the positively charged nuclei. This decreases bond length and increases bond energy.



Antibonding MOs have a perpendicular node passing through the region between the nuclei. Since a node is, by definition, a region of zero electron density, this means that most of the electron density in a filled antibonding MO is outside the region between the nuclei. The electrons therefore pull the nuclei away from each other as a result of the attraction between the negatively charged electrons and the positively charged nuclei. This increases bond length and decreases bond energy. In the diagrams below, the perpendicular nodes are shown as red dashed lines.

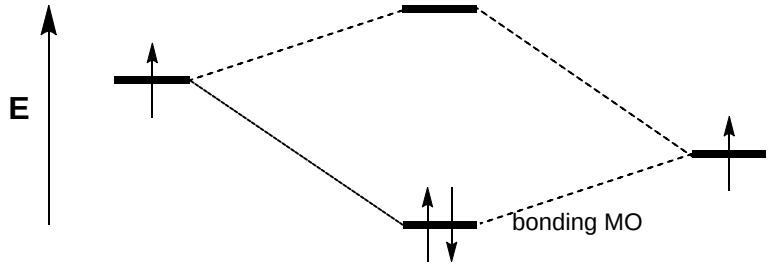


Nonbonding MOs are MOs that are neither bonding nor antibonding. They are not largest in the region between the nuclei, but they do not have a perpendicular node passing through that region either. (They may have perpendicular nodes passing through the nuclei, but those are not relevant to bond order.) The easiest nonbonding MOs to recognize are those which formed because an atomic orbital (AO) was not able to interact with any other AOs in the molecule *(see below left)*. Other nonbonding MOs that you are likely to encounter include MOs with no density on an atom *(see below middle)* and MOs which are equally bonding and antibonding *(see below right)*.

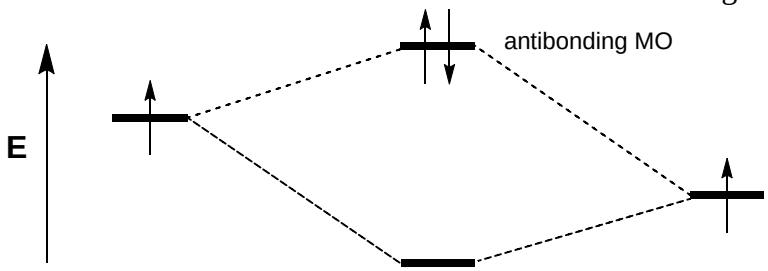


Energy

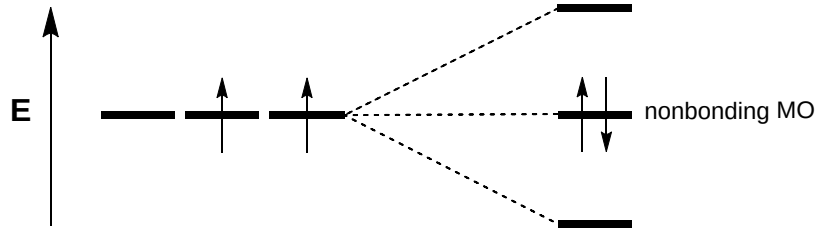
The energy of a bonding MO is always lower than the average of the energies of the AOs which combined to make it. So, if you only had two electrons, the system would be lower in energy as a molecule with the electrons in the bonding MO than as free atoms:



The energy of an antibonding MO is always higher than the average of the energies of the AOs which combined to make it. So, if you only had two electrons, the system would be lower in energy as free atoms than as a molecule with the electrons in the antibonding MO:

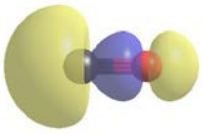


The energy of a nonbonding MO is equal (or close to equal) to the average of the energies of the AOs which combined to make it. So, if you only had two electrons, the system would have the same energy regardless of whether it existed as free atoms or as a molecule with the electrons in a nonbonding MO:



Spectroscopy

Both methods discussed so far depend on theoretical calculations, and they can sometimes lead to ambiguous situations. Consider the MO below. At first glance, it might appear bonding, but it doesn't appear to be largest in the region between the nuclei, so it doesn't really meet the description of bonding. It doesn't have a perpendicular node between the nuclei, so it doesn't meet the description of antibonding. Could it be nonbonding?



Spectroscopy can answer that question. Photoelectron spectroscopy, in particular, allows us to measure both the energy of each MO and whether it is bonding, nonbonding or antibonding.

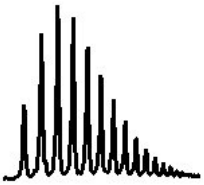
Photoelectron spectroscopy (PES) is an application of the photoelectric effect that you learned about in CHEM 1000. A molecule (X) is irradiated with light that is high enough in energy to eject an electron from the molecule, generating a cation (X^+). By subtracting the kinetic energy of the ejected electron from the energy of the photon used to eject it, we can calculate the energy required to eject the electron from the molecule (and therefore the energy of the MO):

$$E_{ionization} = E_{photon} - E_{kinetic(ejected\ electron)}$$

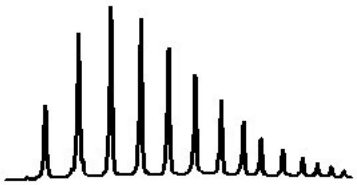
Ionization energy is, by definition, zero minus the energy of the electron in the MO.

In addition to allowing calculation of the energy of electrons in each MO, PES also shows how the bond order changes as a result of removing the electron. This indicates whether the MO was bonding, antibonding or nonbonding.

Exciting an electron out of a bonding MO decreases the bond order, weakening the bond and reducing the gaps between vibrational energy levels. In PES, signals for bonding MOs appear as a series of closely spaced lines:



Exciting an electron out of an antibonding MO increases the bond order, strengthening the bond and increasing the gaps between vibrational energy levels. In PES, signals for antibonding MOs appear as a series of widely spaced lines:

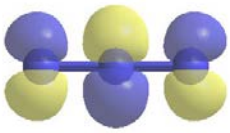


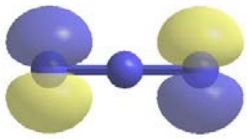
Exciting an electron out of a nonbonding MO has no effect on the bond order and therefore no significant effect on the gaps between vibrational energy levels. In PES, signals for nonbonding MOs tend to be very narrow and may appear as a single line:

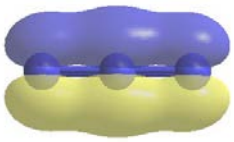
It is easiest to evaluate whether a signal on a PES spectrum corresponds to a bonding or antibonding MO if both types of MO appear on the same spectrum so that you can compare the sizes of the gaps between the lines.

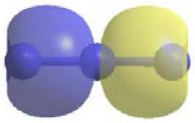
1. If the shape of the MO, the energy of the MO and a PES spectrum of the molecule give conflicting information about whether the MO is bonding, antibonding or nonbonding, how can you resolve the dilemma? Which information should you trust the most and why?

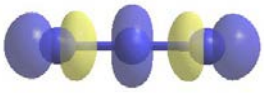
2. Categorize each of the following MOs as bonding, antibonding or nonbonding.
For practice, also categorize each MO as σ-symmetric or π-symmetric.

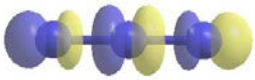
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

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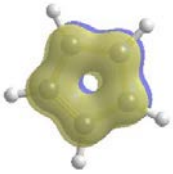
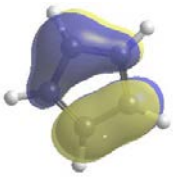
(a) 

(b) 

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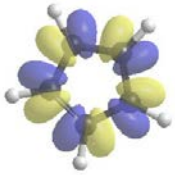
(e) 

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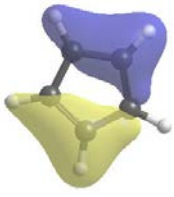
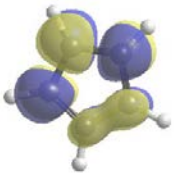
(g) 

(h) 

(i)