Exercise 4.2
Molecular Orbital Energy Level Diagrams: Linear Polyatomic Molecules

This exercise assumes that you are familiar with the "count and sort" algorithm described in Exercise 2.3 (which also contains a table of atomic orbital energies).

Molecular Orbital Energy Level Diagram for BeH_2

First, write electron configurations for beryllium and hydrogen: $1s^2 2s^2$ for Be and $1s^1$ for H

This tells us that the valence shell for Be is $n = 2$, so its valence AOs are the $2s$ and $2p$ orbitals. The valence shell for each H is $n = 1$, so their valence AOs are the $1s$ orbitals.

It also tells us that BeH_2 has four valence electrons, two from Be and one from each H.

A Lewis diagram for BeH_2 is shown below. This is a linear molecule.

H—Be—H

Grouping the valence AOs by symmetry and energy gives:

- one pi-symmetric $2p_x$ orbital from Be,
- one pi-symmetric $2p_y$ orbital from Be,
- four sigma-symmetric orbitals: $2s(Be)$, $2p_z(Be)$ and two $1s(H)$.

The two "groups" of one pi-symmetric AO each give one pi-symmetric MO identical to the AO.

The four sigma-symmetric AOs interact to give a set of four sigma-symmetric MOs: one lower in energy than all four AOs, one higher in energy than all four AOs and two with intermediate energies. Because the molecule is symmetrical, all four sigma-symmetric MOs are either symmetric or antisymmetric:

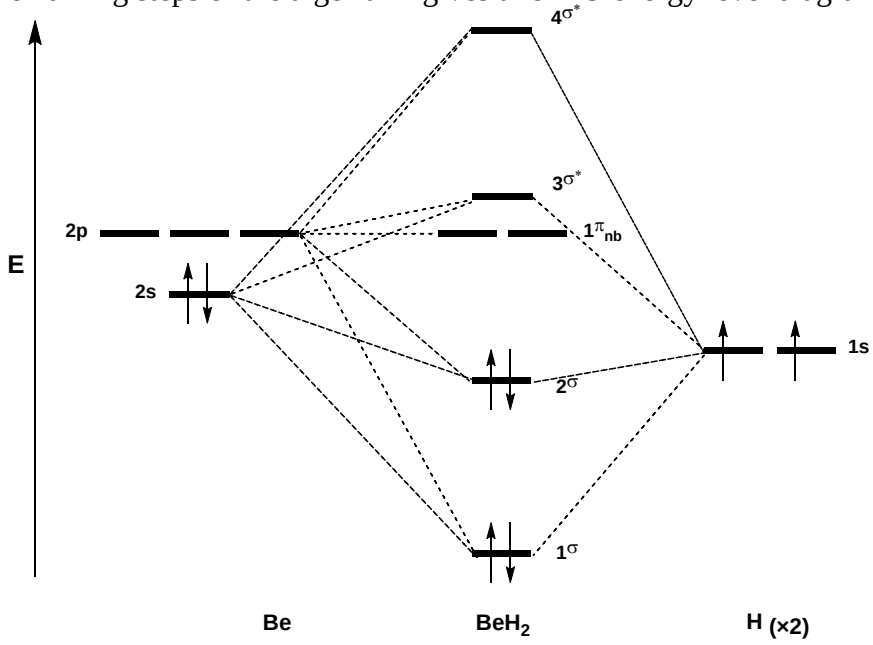
1σ
0 nodes

2σ
1 node

3σ*
2 nodes

4σ*
3 nodes

Following the remaining steps of the algorithm gives this MO energy level diagram:

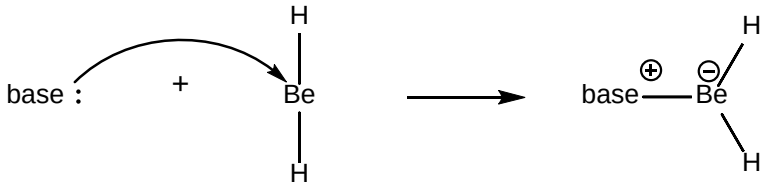


Now that there are more than two atoms, an additional step is added to the bond order calculation. We still start by subtracting antibonding electrons from bonding electrons to calculate net bonding electrons (in this case, $4 - 0 = 4$ net bonding electrons). BUT we must now recognize that those net bonding electrons are spread over two $Be - H$ bonds! So, that's $\frac{4}{2} = 2$ net bonding electrons per $Be - H$ bond. Divide that number by two to get a net bond order of 1 per $Be - H$ bond:

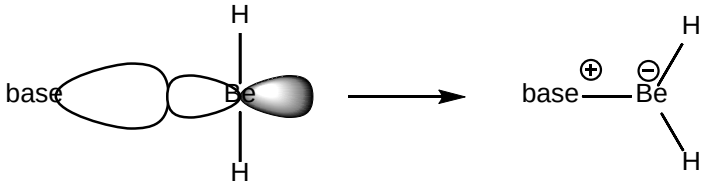
$$Bond\ Order = \frac{\#\ bonding\ electrons - \#\ antibonding\ electrons}{\#\ bonds\ over\ which\ electrons\ are\ shared} \times \frac{1}{2}$$

The bond order of 1 is consistent with the single bonds shown on the Lewis diagram of BeH_2.

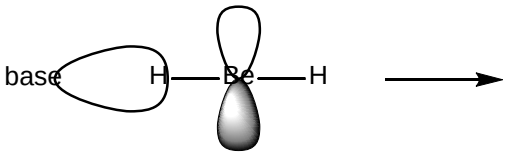
The HOMO of BeH_2 is 2σ; the LUMO is $1\pi_{nb}$. Since BeH_2 is a good Lewis acid, its LUMO is more relevant to its chemical behavior. Since each $1\pi_{nb}$ is essentially a $2p$ orbital on Be, that means that a Lewis base would attack Be (and not either H)



When we look at the shape of the LUMO, we can also see that the base would have to attack BeH_2 from the side so that the HOMO of the base could overlap with the LUMO of BeH_2:[1]



The base could *not* attack BeH_2 end-on:



overlap not constructive so no reaction

It is important to recognize that there are cases where it is not easy to predict the exact order of the MO energy levels when you generate an energy level diagram "by hand". You should be able to predict the correct order for the sigma-symmetric MOs and the correct order for the pi-symmetric MOs, but there may be times where you cannot be sure whether a particular sigma-symmetric MO is higher or lower in energy than a particular pi-symmetric MO. That's okay! If it's an important distinction, molecular modeling software can be used to calculate the correct order. The same software can be used to calculate the shapes of the MOs for molecules complex enough to make that a difficult task to do by hand.

[1] Note that the HOMO of the Lewis base has been simplified for clarity. An actual HOMO of an actual Lewis base would be more complex in appearance, but would have the sigma symmetry suggested by these pictures.

1. The energy of the $2s(Be)$ orbital is -0.69 Ry; the energy of the $2p(Be)$ orbitals is slightly higher (a reasonable approximation might be about -0.5 Ry).

   The energy of the $2s(F)$ orbital is -2.95 Ry; the energy of the $2p(F)$ orbitals is -1.37 Ry.

(a) How would you expect the molecular orbital energy level diagram for BeF_2 to be similar to the one for BeH_2?

(b) How would you expect the molecular orbital energy level diagram for BeF_2 to be different from the one for BeH_2?

(c) Construct a molecular orbital energy level diagram for BeF_2.
Include pictures of the orbitals on your diagram.

(d) Label the HOMO and LUMO on your molecular orbital energy level diagram.
What does each tell you about how BeF_2 reacts?

2.

(a) Construct a molecular orbital energy level diagram for the azide ion (N_3^-).
The energy of the $2s(N)$ orbital is -1.88 Ry; the energy of the $2p(N)$ orbitals is -0.95 Ry.
Hint: You drew pictures of all the σ MOs in question 3 of Exercise 4.1.

(b) Label the HOMO and LUMO on your molecular orbital energy level diagram.
Which of these orbitals is more likely to be relevant to the reactivity of N_3^-, and what does it tell you about how N_3^- reacts?