

Exercise 2.3

Molecular Orbital Energy Level Diagrams: Hydrogen and Helium

“Count and Sort” Algorithm for Building Molecular Orbital Energy Level Diagrams

1. Write the electron configuration for each atom, and count the total number of valence electrons. If you're working with an ion, adjust the valence electron count according to the charge.
2. Identify the valence shell for each atom. You will need to use all the atomic orbitals (AOs) in the valence shell of each atom to build your molecular orbital (MO) energy level diagram.
3. Draw a Lewis diagram for the molecule. Where necessary, re-draw the molecule with the correct molecular geometry according to VSEPR.
4. Sort the AOs into those with sigma (σ) symmetry and those with pi (π) symmetry.
5. Within each symmetry group, sort the AOs into groups which can interact. Recall that p_x orbitals cannot interact with p_y orbitals, and that AOs must have energies within approximately 1 Ry of each other to interact significantly. There is a table of AO energies on the next page.
6. Draw the energy levels for the AOs of each atom: one atom at the left side of your energy level diagram and one atom at the right side of the diagram. *This is typically only done for diatomic molecules and ions.*
7. Consider each group of AOs separately. (*This refers to the groups that you sorted in steps 4 and 5*). It is usually easiest to start with the group containing fewest AOs. For each group:
 - a. If there is only one AO in the group, it has nothing to interact with so its energy does not change. Draw a line in the middle column (MO column) of the diagram at the same energy as the AO. This is a nonbonding MO.
 - b. If there are two AOs in the group, they interact in-phase to make a bonding MO and out-of-phase to make an antibonding MO. The bonding MO is lower in energy than either AO, and the antibonding MO is higher in energy than either AO. Draw a line in the middle column (MO column) of the diagram for the energy of each MO.
 - c. If there are three or more AOs in the group, they interact to make a set of MOs. The number of MOs **must** equal the number of AOs in the group. It is usually easiest to find the most in-phase interaction (which generates a bonding MO lower in energy than any of the contributing AOs) and the most out-of-phase interaction (which generates an antibonding MO higher in energy than any of the contributing AOs) then work out the “in the middle” MOs. Draw a line in the middle column (MO column) of the diagram for each MO.

Each time you draw an MO in your diagram, label it with σ or π to show its symmetry.

8. Number the MOs on your energy level diagram. There is one set of numbers ($1\sigma, 2\sigma, 3\sigma, \dots$) for the σ MOs and one set of numbers ($1\pi, 2\pi, 3\pi, \dots$) for the π MOs.
9. Where possible, assign the dominant bonding character of each MO (no symbol for bonding, σ_{nb} or π_{nb} for nonbonding, σ^* or π^* for antibonding).
10. Add electrons to the MOs on your diagram. The total number of valence electrons in the molecule (or ion) **must** be the same as the total number of valence electrons in all atoms in the molecule (or ion). Fill the lowest energy MOs first, and follow Hund's rule (one electron per orbital; spins aligned) whenever there is more than one MO with the same energy.
11. Label the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital). These are the Frontier Molecular Orbitals, and they determine how the molecule reacts.

Table of Atomic Orbital Energies. All Energies are in Ry.

	1s	2s	2p
H	-1.00		
He	-1.81		
Li	-4.77	-0.40	
Be	-8.9	-0.69	
B	-14.5	-1.03	-0.42
C	-21.6	-1.43	-0.79
N	-30.0	-1.88	-0.95
O	-39.9	-2.38	-1.17
F	-51.2	-2.95	-1.37
Ne	-64.0	-3.56	-1.59

All energies are from J.C. Slater Physical Review (1955) **98**, 1039-1045.

Molecular Orbital Energy Level Diagram for H_2

Now, apply the algorithm to H_2 .

First, the electron configuration for each hydrogen atom is written: $1s^1$

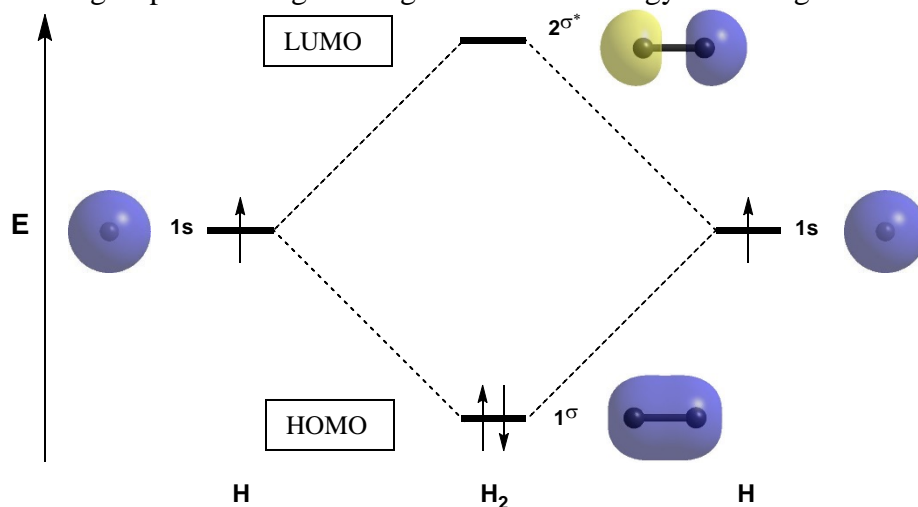
This tells us that the valence shell for each hydrogen atom is $n = 1$, and that the only valence AOs are the $1s$ orbitals. It also tells us that H_2 has two valence electrons.

A Lewis diagram for H_2 is shown below and, since there are only two atoms, it must be linear.



Both $1s$ orbitals have sigma symmetry, and their energies are within 1 Ry, so they interact.

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



It can be helpful to draw pictures of the orbitals on the energy level diagram, as was done above; however, they are not technically part of the energy level diagram. For diatomic molecules, we usually also include tie lines (the dotted lines) to show which MOs came from which AOs.

We can also calculate the bond order for H_2 by subtracting the number of antibonding electrons from the number of bonding electrons then dividing by two (since there are two electrons in a bond). In this case, that gives a bond order of $\frac{2-0}{2} = \frac{2}{2} = 1$, consistent with the single bond on the Lewis diagram. In most cases, the bond order from the MO energy level diagram will be the same as that shown on the Lewis diagram. If they differ, the MO bond order is generally correct.

The orbital occupancy for H_2 is $(1\sigma)^2$. Essentially, it is the electron configuration of a molecule.

1. Construct a molecular orbital energy level diagram for He_2 .
 Use your diagram to explain why helium does not exist as diatomic molecules.
2. Construct a molecular orbital energy level diagram for H_2^- .
 Write the orbital occupancy for H_2^- .
 Does the extra electron make the H-H bond stronger compared to H_2 ? Why or why not?