3.091: Introduction to Solid State Chemistry
Maddie Sutula, Fall 2018
Recitation 10

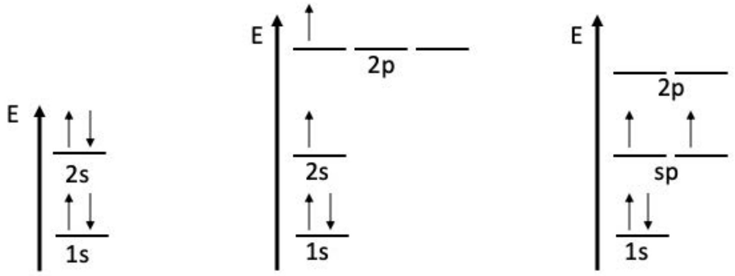
1 Hybridization and atomic orbitals

Lewis dot diagrams and VSEPR are powerful tools to think about electronic configuration and molecular shape, but neither tool offers a way to predict bond stability. The strength of a covalent bond is proportional to the amount of overlap between electronic orbitals.

Consider BeH_2: beryllium contributes 2 valence electrons, and each of the two hydrogen atoms contribute one valence electron.

H—Be—H

As a reminder, the electronic configuration of hydrogen is $1s^1$, while the electronic configuration of beryllium is $1s^2 2s^2$. The valence shell of Be ($2s^2$) is full: it has two electrons, the maximum that can live in an s-orbital. There aren't any singly-occupied orbitals available to form bonds with hydrogen, even though we predict from the Lewis dot diagram above that there should be single bonds between each H and the Be. We can draw the electronic occupation of energy states in the Be atom as a function of energy, and then apply the principle of hybridization:



energy levels of Be atom → promotion → sp hybridization

To get around the issue of the full 2s shell, an electron could be promoted to the 2s subshell, leaving two electrons that are ready to form bonds. However, the 2s and 2p electrons aren't equal: if this were the case, the two H-Be bonds would be unequal, which has no physical basis. Instead, consider the third picture: by combining the 2s orbital with one of the 2p subshells, an intermediate sp-hybridized energy level is created. This sp orbital has two equal-energy subshells that allow for two equal energy bonds to be formed with the Be atom. This is not unique to BeH_2: sp hybridization occurs any time a 2p subshell combines with the 2s subshell. Further, if there are more electrons available to participate in bonding, sp^2 hybridization (3 equal bonds), sp^3 hybridization (4 equal bonds), or higher order hybridization involving d-orbitals can take place.

Hybridization directly correlates to molecular geometry! The following table shows the equivalence:

Molecular geometry	Hybridization
linear	sp
trigonal	sp^2
tetrahedral	sp^3
trigonal bipyramidal	sp^3d
octahedral	sp^3d^2

2 Molecular orbital (MO) theory

We can use molecular orbital theory to gain a better understanding of how electrons form bonds and to predict properties such as bond stability and magnetic character. In 3.091, we'll apply MO theory to dimers. Recall that all electrons are negatively charged: in free space, electrons would feel a repulsive force from other nearby electrons. However, there are additional forces within an atom that create an environment that allows for the concentration of electron density into *bonds*. When considering how two electrons in a solid may interact, it is useful to think about wave nature of electrons. Two electrons can constructively interfere to form a *bonding* MO, or destructively interfere to form an *antibonding* MO.

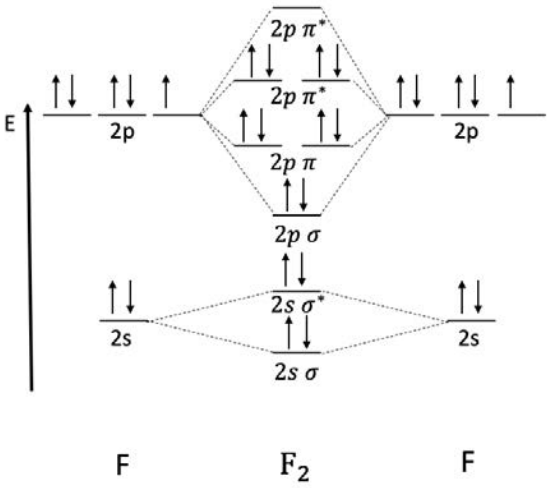
MO diagrams are a convenient tool to keep track of the bonding and antibonding orbitals, and therefore the bond strength. We can quantify the bond strength by calculating *bond order*:

$$\text{Bond order } = \frac{1}{2}\big(\text{\# electrons in bonding orbitals - \# electrons in antibonding orbitals}\big)$$

If the bond order is greater then zero, a stable dimer forms.

If a dimer has any unpaired electrons, it is *paramagnetic*: these unpaired electrons align with applied magnetic fields and are weakly attracted to the applied field. If all the electrons are paired, the dimers are repelled by applied magnetic fields, and the dimers are called *diamagnetic*.

Example: Draw a molecular orbital diagram for the F_2 dimer. Calculate the bond order, and determine whether it is paramagnetic or diamagnetic.



We start here by drawing the AO diagrams of the valence electrons of each F involved in the F_2 dimer. Recall that F (Group VII) has 7 valence electrons. Then, we populate the σ bonding and σ^* antibonding orbitals associated with the 2s valence shell. Then, we draw the 2p σ bonding, π bonding, π^* antibonding, and σ^* antibonding orbitals. Populating from the lowest energy to the highest energy, there are enough electrons to fill the 2p π^* antibonding orbitals.

We can calculate the bond order using the formula from above. There are eight electrons in bonding orbitals and six electrons in antibonding orbitals:

$$\text{bond order} = \frac{1}{2}(8-6) = 1$$

All of the electrons are paired, so the F_2 dimer is diamagnetic.

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