

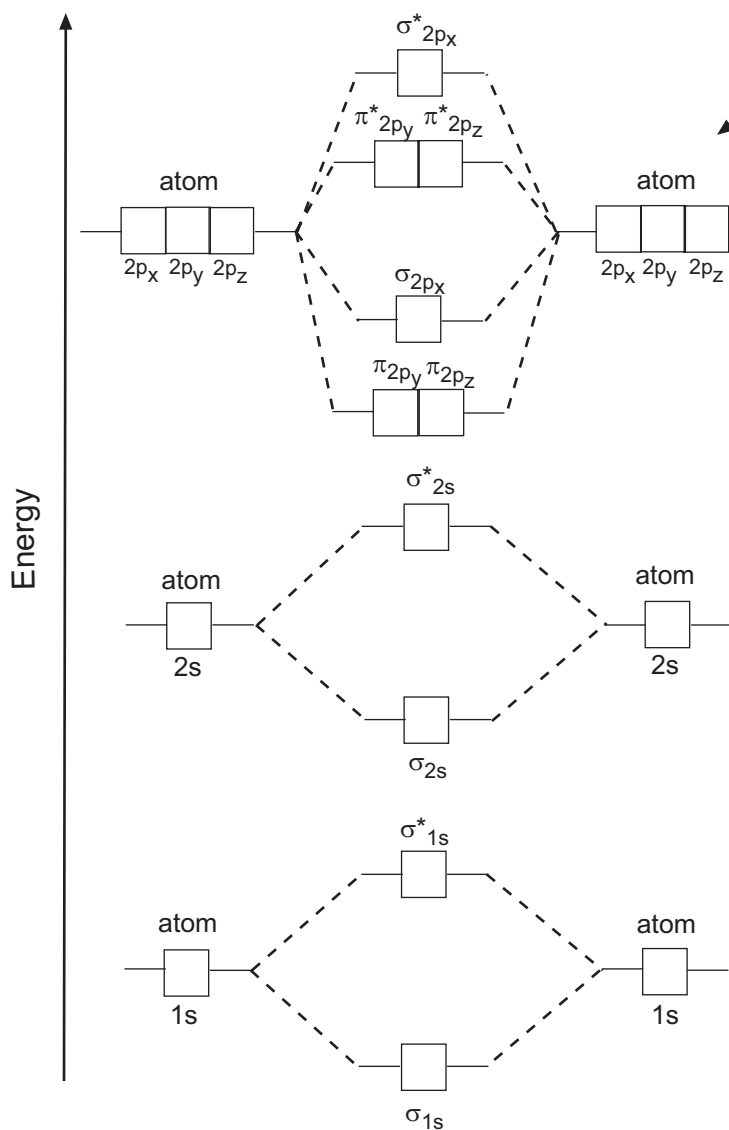
Molecules: Covalent Bonding--Molecular Orbital Theory: Student Review Notes

How do you tell if a molecule is paramagnetic or diamagnetic?

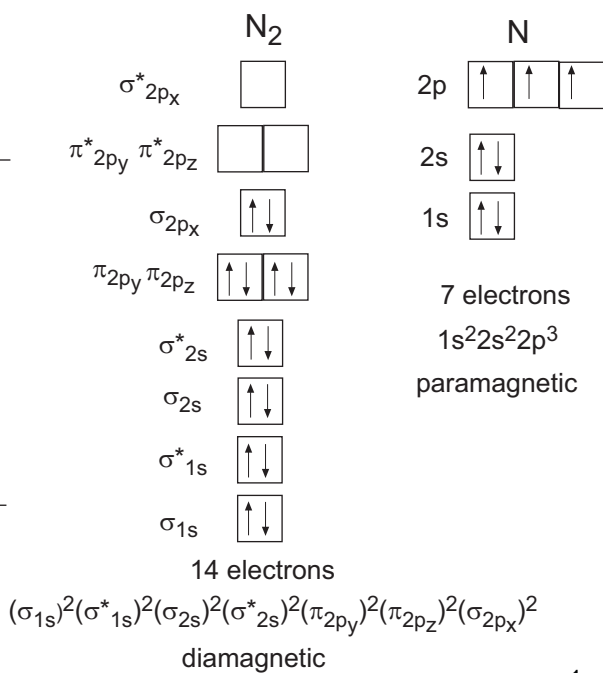
How do you tell if a molecule is possible?

In some cases, valence bond theory cannot account for the observed properties of a molecule. Take diatomic oxygen for example. According to VB theory, each oxygen atom has 3 sp^2 hybrid orbitals, there is one sigma-bond formed by the overlap of a pair of sp^2 hybrid orbitals from each atom, one pi-bond formed by the overlap of atomic p-orbitals and each oxygen atom has 2 non-bonding pairs in 2 sp^2 hybrid orbitals. From this picture, it appears that all of electrons in the molecule are paired up and therefore the molecule should be diamagnetic. It turns out that molecular oxygen is paramagnetic. VB theory is not complex enough to account for this physical property and here is where molecular orbital theory comes in. The other thing that MO theory is useful for at this level of chemistry, is to predict whether or not a molecule will actually form. This is done via a calculation of the bond order based on an MO diagram.

Molecular orbital theory describes the energy levels of bonding and non-bonding electrons in terms of molecular orbitals that result from the interaction of the atomic orbitals of the bonding atoms. Take a look, you need to understand this picture. It is the **general molecular orbital energy-level diagram for the first two energy levels**. In terms of using it, you just need to now how to make an MO diagram--this is analogous to an atomic orbital diagram, and fill in electrons.



Atomic orbitals combine to yield molecular bonding and antibonding orbitals (the ones with the *). The bonding orbitals represent the space shared by the bonding atoms in which electrons can be located. The antibonding orbitals (*) represent the space that is available to the electrons that is not shared by the two atoms in the bond. It is useful to see the analogy between an MO electron configuration and an atomic electron configuration. Take a look at the MO diagram and electron configuration for molecular N_2 and atomic N.



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Rules for writing the MO diagram for a molecule

1. The number of molecular orbitals formed is equal to the number of atomic orbitals combined.
2. Filling electrons in the MOs occurs from lowest energy to highest energy.
3. Pauli Exclusion Principle still holds--two electrons per MO.
4. Hund's Rule still holds--use maximum spin multiplicity when filling MOs.
5. The number of electrons in MOs is equal to the sum of all electrons for the bonding atoms.

Okay, so you've seen an example of how to write out an MO diagram to examine the magnetic properties of a molecule. The second place where MO theory is useful to general chemistry is in determining if a molecule will form. At this level of chemistry, you'll typically only see MO questions that deal with diatomic species--i.e. for which it is easy to write out the MO diagram. The stability of a species can be examined by looking at the **Bond Order** of the molecule. Here is the formula,

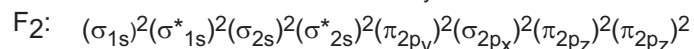
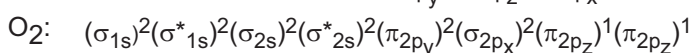
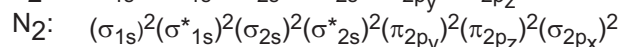
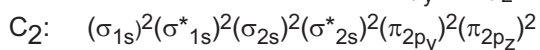
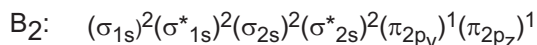
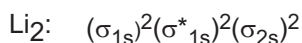
$$\text{Bond Order} = \frac{1}{2} \left[\text{the sum of electrons in bonding MOs} - \text{the sum of electrons in antibonding MOs} \right]$$

1. A bond order of 0 (zero) means that the molecule cannot exist.
2. You can have fractional bond orders but integer values are more stable.
3. A single bond has order 1, a double bond has order 2, a triple bond has order 3.

Know how to examine the properties of diatomic molecules of the second period elements using MO Theory.

	Li ₂	B ₂	C ₂	N ₂	O ₂	F ₂
σ* _{2p_x}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
π* _{2p_y} π* _{2p_z}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
σ _{2p_x}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
π _{2p_y} π _{2p_z}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
σ* _{2s}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
σ _{2s}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
σ* _{1s}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
σ _{1s}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
No. electrons	6	10	12	14	16	18
Bond Order	1	2	2	3	2	1
Magnetic Props	diamagnetic	paramagnetic	diamagnetic	diamagnetic	paramagnetic	diamagnetic

Electron Configurations:



for O₂ and F₂, σ_{2p_x} is lower in energy than π_{2p_y} and π_{2p_z}

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The previous example shows how to use MO diagrams to determine the magnetic properties of simple molecules. It also shows that the bond order calculation substantiates the formation of diatomic species.

Take a look at this example and how MO diagrams & bond order calculation can be used to examine the stability of some proposed molecules.

Rank the following pairs of molecules in terms of stability:

	H_2^+	H_2		He_2^+	He_2
σ^*_{1s}	<div style="border: 1px solid black; width: 20px; height: 20px; display: inline-block;"></div>	<div style="border: 1px solid black; width: 20px; height: 20px; display: inline-block;"></div>	σ^*_{1s}	<div style="border: 1px solid black; width: 20px; height: 20px; display: inline-block; text-align: center;">↑</div>	<div style="border: 1px solid black; width: 20px; height: 20px; display: inline-block; text-align: center;">↑↓</div>
σ_{1s}	<div style="border: 1px solid black; width: 20px; height: 20px; display: inline-block; text-align: center;">↑</div>	<div style="border: 1px solid black; width: 20px; height: 20px; display: inline-block; text-align: center;">↑↓</div>	σ_{1s}	<div style="border: 1px solid black; width: 20px; height: 20px; display: inline-block; text-align: center;">↑↓</div>	<div style="border: 1px solid black; width: 20px; height: 20px; display: inline-block; text-align: center;">↑↓</div>
No. electrons	1	2	No. electrons	3	4
Bond Order	$\frac{1}{2}$	1	Bond Order	$\frac{1}{2}$	0

H_2^+ less stable than H_2

He_2 less stable than He_2^+

↑
Bond Order of 0 (zero)
indicates that this molecule
will not form