

AP* Chemistry

COVALENT BONDING: ORBITALS

The localized electron model views a molecule as a collection of atoms bound together by sharing electrons between their atomic orbitals. The arrangement of valence electrons is represented by the Lewis structure and the molecular geometry can be predicted from the VSEPR model. There are 2 problems with this.

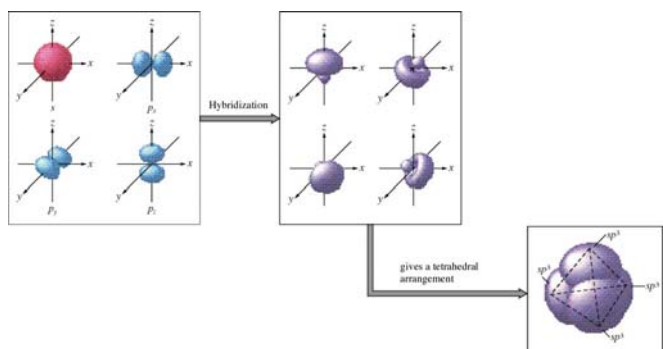
- Using the $2p$ and the $2s$ orbitals from carbon in methane would result in 2 different types of bonds when they overlap with the $1s$ from Hydrogen. [three $2p/1s$ bonds and one $2s/2p$ bond] However, experiments show that methane has FOUR IDENTICAL bonds. Uh, oh....we need to modify the model!
- Since the $3p$ orbitals occupy the x , y and z -axes, you would expect those overlaps of *atomic* orbitals to be at bond angles of 90° . Darn those experiments! All 4 angles are 109.5° .

It's not that the localized electron model is wrong; it's just that carbon adopts a *set* of orbitals rather than its "native" $2s$ & $2p$. THIS IS WHY THESE ARE MODELS/THEORIES rather than LAWS!!

VALENCE BOND THEORY—an extension of the LE model—it's all about hybridization!

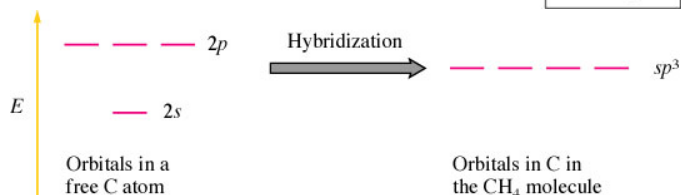
Two atoms form a bond when *both* of the following conditions occur:

- There is orbital overlap between two atoms.
- A maximum of two electrons, of opposite spin, can be present in the overlapping orbitals.
 - Because of orbital overlap, the *pair* of electrons is found within a region influenced by both nuclei. Both electrons are attracted to both atomic nuclei and this leads to bonding.
 - As the extent of overlap increases, the strength of the bond increases. The electronic energy drops as the atoms approach each other but, increases when they become too close. This means there is an optimum distance, the observed bond distance, at which the total energy is at a minimum.
 - sigma (σ) bond**--overlap of two s orbitals or an s and a p orbital or head-to-head p orbitals. Electron density of a sigma bond is greatest *along the axis* of the bond.
 - maximum overlap**: forms the strongest possible bond, two atoms are arranged to give the greatest possible orbital overlap. Tricky with p orbitals since they are directional.
 - hybrid orbitals**-- a blending of atomic orbitals to create orbitals of intermediate energy. Methane: all of the C-H bonds are 109.5° apart while p orbitals are only 90° apart. Pauling explained:

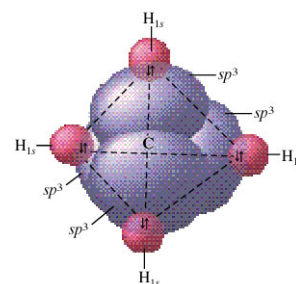


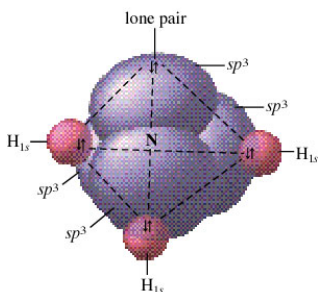
The orbitals on the left are for a carbon atom [no bonding]

Once the carbon atom begins to bond with say, H to keep it simple, the atomic orbitals **HYBRIDIZE** which changes their shape considerably! There's an energy payoff, else they wouldn't behave this way!



leads to →





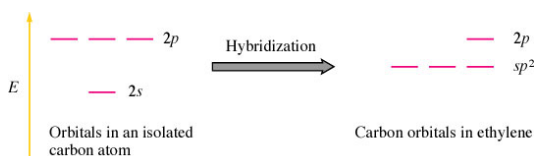
Ammonia also has sp^3 hybridization even though it has a lone pair.

I find it helpful to think of electron pairs as “sites” of electron density that can be occupied by *either* a lone pair or a shared pair. If there are 4 “sites” then 4 orbitals need to hybridize so use one s and three p 's to make FOUR equivalent orbitals named sp^3 or sp^3 orbitals. [1 s + 3 p = 4 sp^3 orbitals]

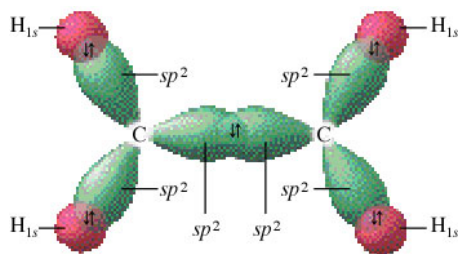
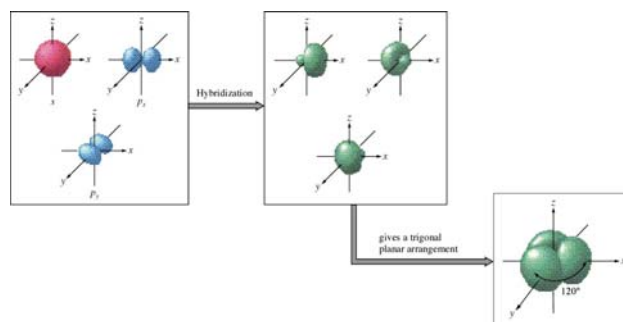
MULTIPLE BONDING—lowers the number of hybridizing orbitals since Unhybridized orbitals are necessary to form the pi bonds

Pi (π) bonds--come from the sideways overlap of p atomic orbitals; the region above and below the internuclear axis. *NEVER* occur **without** a sigma bond first!

- may form **only** if unhybridized p orbitals remain on the bonded atoms
- occur when sp or sp^2 hybridization is present on central atom NOT sp^3 hybridization.
- Carbon often does this with N, O, P, and S since they have p orbitals (remember CNOPS?)
- This is the formation of an sp^2 set of orbitals [3 orbitals formed, 3 sites, 3 letters!]. This molecule would contain a double bond like ethene. The molecule reserves a set of p 's to form the π bond.

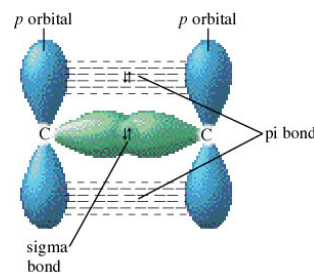


leads to →

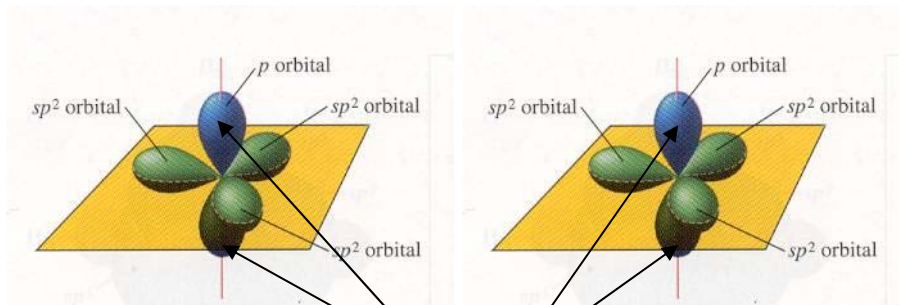
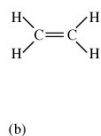
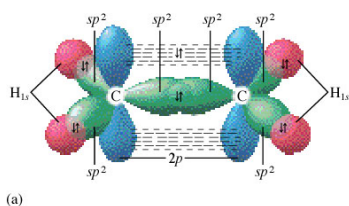


The set of p 's that are UNhybridized are not pictured here at left, they are hovering above and below this very page.

A different view, without the hydrogens, centering on the C atoms shows the unhybridized p orbitals that are making the sideways overlap necessary to create the double (π) bond.



Here's the whole mess altogether:

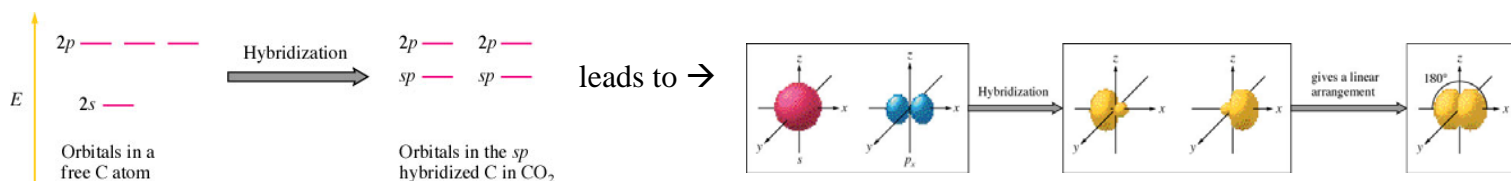


Carbon #1

Carbon #2

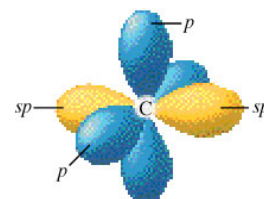
OVERLAPPING UNhybridized p -orbitals that form pi bond.

- This is the formation of an sp set of orbitals [2 orbitals formed, 2 sites, 2 letters!]. This molecule would contain a triple bond like ethyne or the double-double arrangement in carbon dioxide.

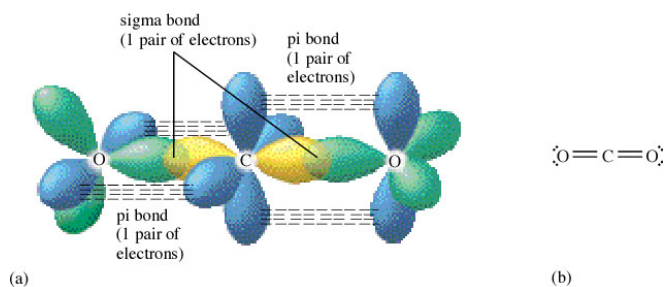


The molecule reserves TWO sets of UNhybridized p 's to form the 2π -bonds.

At right, is a picture of the 2 unhybridized p 's on the C atom that is about to make a triple bond. The one labeled at the top is in the plane of this page, the other plain p is in a plane perpendicular to this page. (No typo—just appropriate use of homonyms; plain vs. plane!)

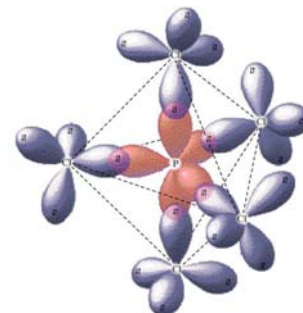
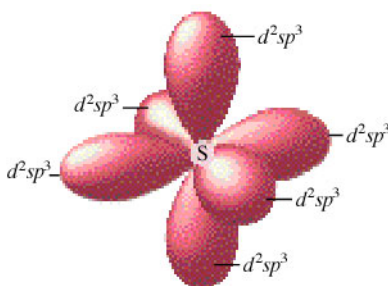
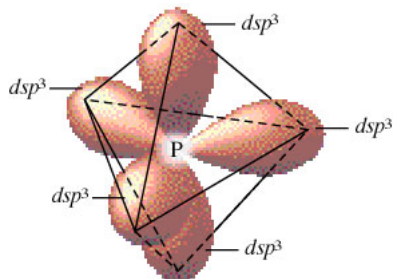


Look at the CO_2 Lewis diagram. The carbon has 2 sites of electron density, each occupied by a double bond, and is therefore sp [2 sites, 2 letters] hybridized while the oxygens have 3 sites [2 lone pairs and a double bond]. The oxygen's have sp^2 hybridization [3 sites, 3 letters].



This should help:

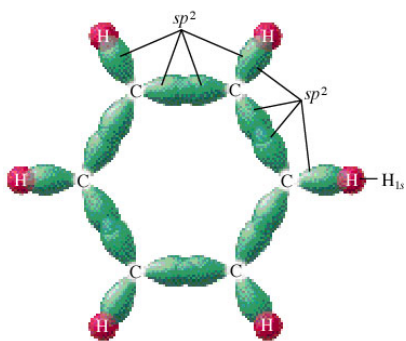
HYBRIDIZATION	# OF HYBRID ORBITALS	GEOMETRY	EXAMPLE
sp	2	Linear	
sp^2	3	Trigonal planar	
sp^3	4	Tetrahedral	
dsp^3	5	Trigonal bipyramidal	
d^2sp^3	6	Octahedral	



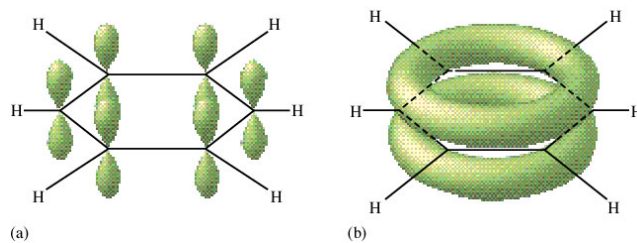
Number of Effective Pairs	Arrangement of Pairs		Hybridization Required	
2		Linear	sp	
3		Trigonal planar	sp^2	
4		Tetrahedral	sp^3	
5		Trigonal bipyramidal	dsp^3	
6		Octahedral	d^2sp^3	

Check out Benzene

The sigma bond formations



The pi bond formations



Draw the Lewis structure for benzene:

Exercise 5**The Localized Electron Model V**

For each of the following molecules or ions, predict the hybridization of each atom, and describe the molecular structure.

a. CO

b. BF_4^- c. XeF_2

A: linear, sp hybridized
 B: tetrahedral, sp^3 hybridized
 C: trigonal bipyramidal e⁻ pair,
 Xe dsp^3 , linear

THE MOLECULAR ORBITAL MODEL

Though the molecular orbital model will not be covered on the AP exam, I feel that students should be exposed to a little of this theory for several reasons.

1. Electrons are not always localized as in the VSEPR theory; therefore resonance must be added and explained as best possible.
2. Molecules containing unpaired electrons are not easily dealt with using the localized model.
3. Magnetism is easily described for molecules using the MO theory. (Oxygen is paramagnetic which is unexplained by the localized electron model.)
4. Bond energies are not easily related using the localized model.

TERMS TO KNOW:

Bonding molecular orbital - an orbital lower in energy than the atomic orbitals from which it is composed. (favors formation of molecule)

Antibonding molecular orbital - an orbital *higher* in energy than the atomic orbitals from which it is composed. (favors separated atoms) represented by a * [The diagram at the top of the next page uses A for antibonding and B for bonding—I prefer the *, it has more personality!]

Bond order - the difference between the number of bonding electrons and the number of antibonding electrons divided by two. Indicates bond strength.

Homonuclear diatomic molecules - those composed of two *identical* atoms.

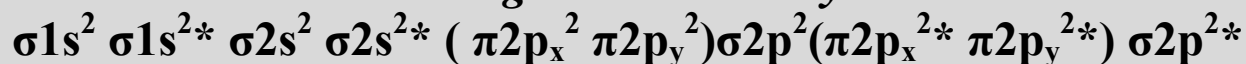
Heteronuclear diatomic molecules - those composed of two *different* atoms

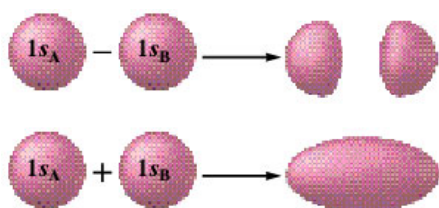
Paramagnetism - causes the substance to be drawn into a magnetic field; associated with unpaired electrons.

Diamagnetic - causes the substance to be repelled by the magnetic field; associated with paired electrons.

General Energy Level Sequence for Filling Orbitals

Using the MO Theory





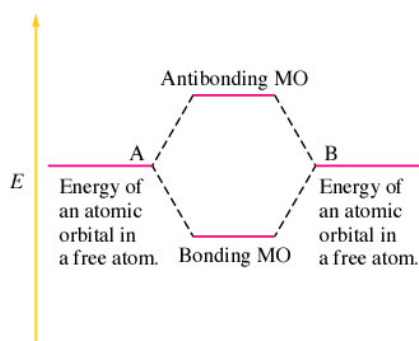
If we assume that the molecular orbitals can be constructed from the atomic orbitals, the quantum mechanical equations result in two molecular orbitals

$$\text{MO}_1 = 1s_A + 1s_B \quad \text{and}$$

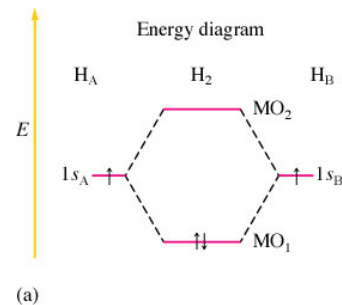
$$\text{MO}_2 = 1s_A - 1s_B$$

Let's start simple. 2 Hydrogen atoms.

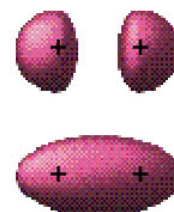
Where $1s_A$ and $1s_B$ represent the $1s$ orbitals from the two separated hydrogen atoms.



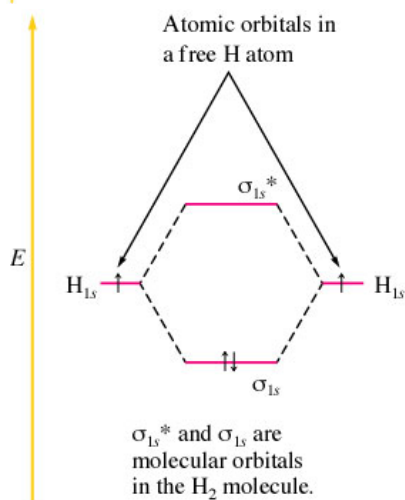
This is actually a simple model to follow. Look at the diagram on the right, each H entered with its lone $1s$ electron. As they approach each other, their atomic orbitals [two of them] blend to form molecular orbitals [two of them—no magic here]. One MO is of high energy and one MO is of low energy. Which will the electrons choose? The LOW, of course! The electrons occupy the lower energy level and thus a bond is formed.



Electron probability distribution

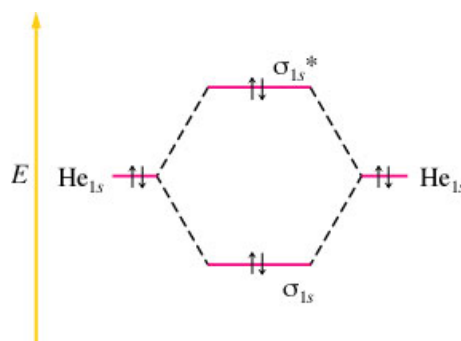


(b)



The diagram at left uses the symbols we want to use.

Try this again with He:



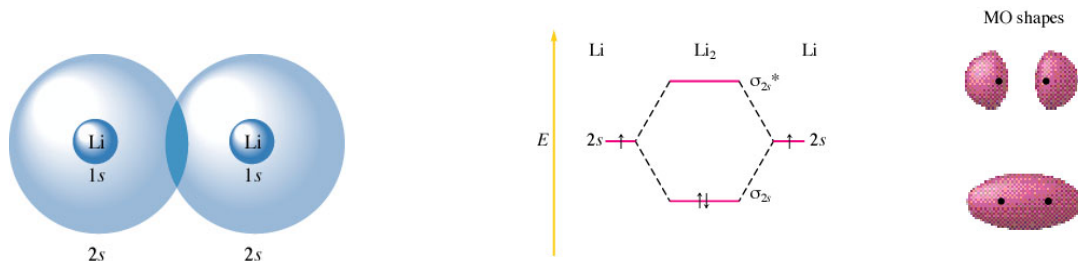
Since 4 electrons are involved, the first 2 get to be lazy and go to the low E state, the other 2 must occupy the higher energy state and thus cancel out the bond, therefore He_2 DOES NOT EXIST!!

Now **bond order** can be redefined in this theory:

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

If the bond order is zero \rightarrow no bond!

Shall we predict if Li_2 is possible? Li has its valence electrons in the 2s sublevel.



Yes! It may also exist. What is its bond order?

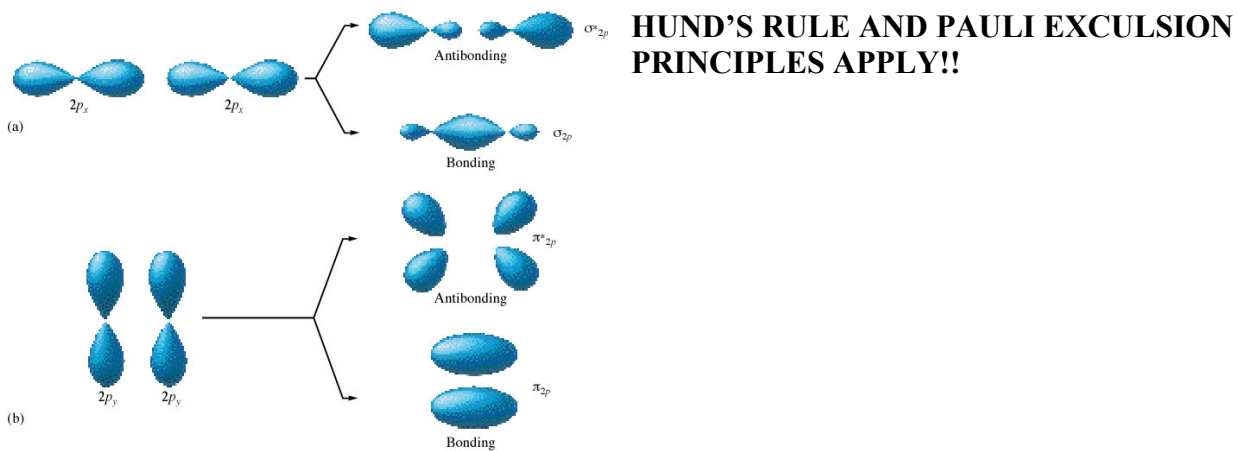
Can Be_2 exist?

Things get slightly more complicated when we leave Be and move to 2p...

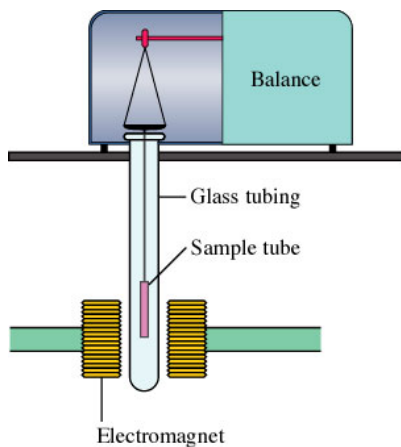
**General Energy Level Sequence for Filling Orbitals
Using the MO Theory**

$\sigma 1s^2 \sigma 1s^{2*} \sigma 2s^2 \sigma 2s^{2*} (\pi 2p_x^2 \pi 2p_y^2) \sigma 2p^2 (\pi 2p_x^{2*} \pi 2p_y^{2*}) \sigma 2p^{2*}$

The filling order for p's is pi, pi, sigma all bonding, followed by pi, pi, sigma all antibonding.



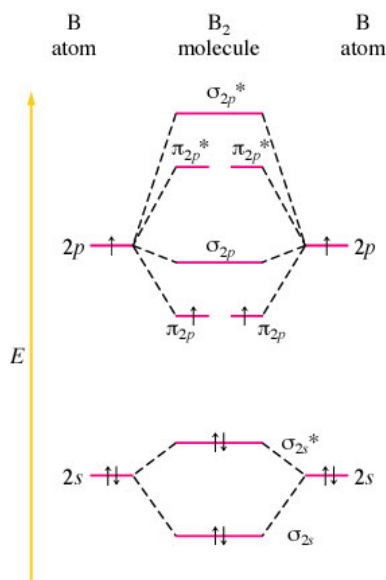
Try to predict the configuration of B_2



One of the most useful parts of this model is its ability to accurately predict para- and diamagnetism as well as bond order.

This device is used to test the paramagnetism of homonuclear samples. When the electromagnet is on, a paramagnetic substance is drawn down into it and appears heavier on the balance.

B_2 is paramagnetic! That means that the pi orbitals are of LOWER energy than the sigma's and Hund's rule demands that the 2 electrons fill the 2 bonding pi orbitals singly first before pairing.



Will C_2 exist? Will it be para- or diamagnetic?

Exercise: Write the appropriate energy diagram using the MO theory for the nitrogen molecule. Find the bond order for the molecule and indicate whether this substance is paramagnetic or diamagnetic.

	B ₂	C ₂	N ₂	O ₂	F ₂
σ_{2p}^*	—	—	—	σ_{2p}^* —	—
π_{2p}^*	— —	— —	— —	π_{2p}^* \uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$
σ_{2p}	—	—	$\uparrow\downarrow$	π_{2p} $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
π_{2p}	\uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	σ_{2p} $\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}^*	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ_{2s}^* $\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ_{2s} $\uparrow\downarrow$	$\uparrow\downarrow$
Magnetism	Para-magnetic	Dia-magnetic	Dia-magnetic	Para-magnetic	Dia-magnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

If you use the usual models to examine the paramagnetism of oxygen, you'd say it was diamagnetic. The truth is that it is paramagnetic. If you pour liquid oxygen into the space between the poles of a strong horseshoe magnet, it stays there until it boils away in the warm room!



Exercise 6

For the species O_2 , O_2^+ , O_2^- , give the electron configuration and the bond order for each. Which has the strongest bond?

Exercise 7

Use the molecular orbital model to predict the bond order and magnetism of each of the following molecules.

- a) Ne_2
- b) P_2

This model also works in heteronuclear molecules.

Exercise 8

Use the MO Model to predict the magnetism and bond order of the NO^+ and CN^- ions.

