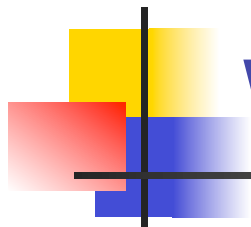


Struttura delle molecole:

Teoria degli Orbitali Molecolari



Why Do Bonds Form?

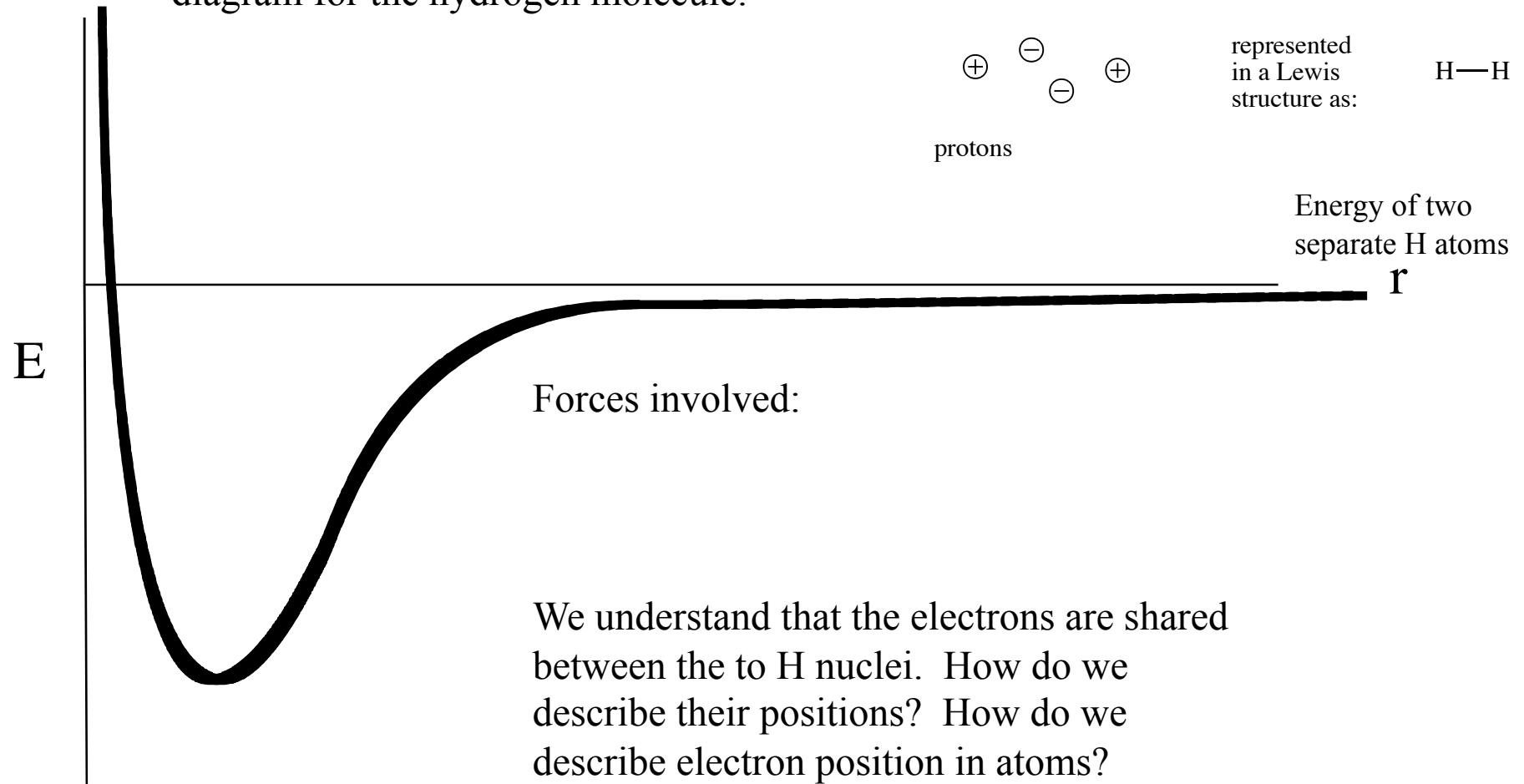
- An energy diagram shows that a bond forms between two atoms if the overall energy of the system is lowered when the two atoms approach closely enough that the valence electrons experience attraction to both nuclei:
- It is important to consider both the attractive and repulsive forces involved!
- Also, remember that atoms are in constant motion above 0 K. Bonds are NOT rigid!

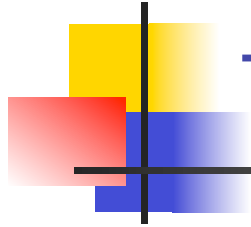
Why do bonds form?

Chemical bonds...

... result from the sharing of electrons between atoms.

Lennard-Jones potential energy diagram for the hydrogen molecule.





The Quantum Mechanics of H_2^+

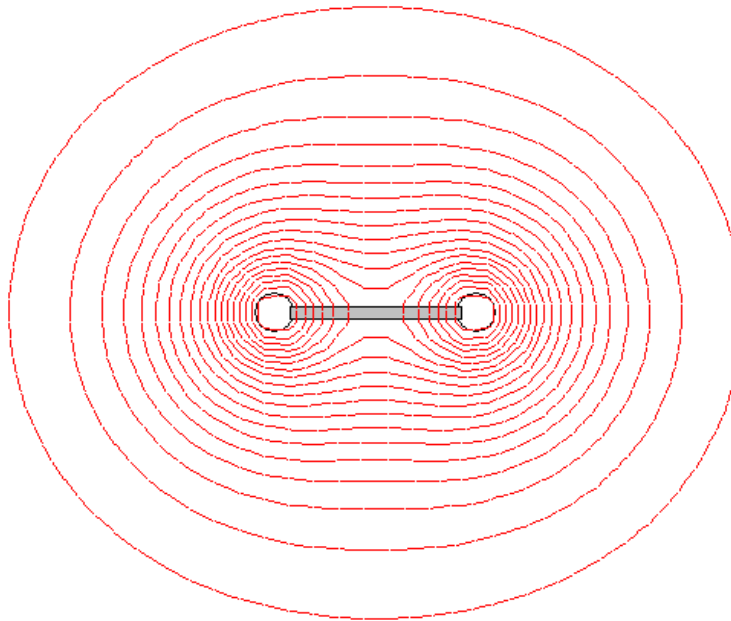
- To get a better understanding of bonding, it's best to start with the simplest possible molecule, H_2^+ .
- What forces do we need to consider?
- This is a three-body problem, so there is no exact solution.
- The nuclei are much more massive than the electrons (1 u for a proton; 0.0005u for an electron). To simplify the problem, we use the **Born-Oppenheimer approximation**. We assume that the motion of the nuclei is negligible compared to the motion of the electrons and treat the nuclei as though they were immobile.

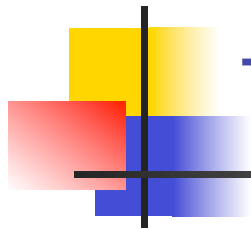
The Quantum Mechanics of H_2^+

- If we set the internuclear distance to R , we are then able to solve for the wavefunction of the electron in H_2^+ and its energy:

Electron energy = kinetic energy + electron-nuclear attraction

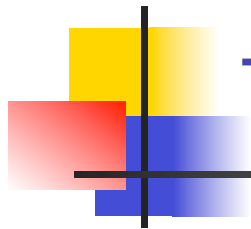
- This is possible because H_2^+ has only one electron and simple (cylindrically symmetric) geometry. The resulting ground-state orbital looks like this:





The Quantum Mechanics of H_2^+

- The energy of this ground state orbital depends on R .
- If we calculate the potential energy of the system (both the electron and the internuclear repulsion) at different values of R , we arrive at an energy diagram just like the one on the first slide of this lecture.
- Important Points to Note:
 - In H_2^+ , the electron doesn't belong to either atom.
 - In H_2^+ , the electron is in an orbital which spans the molecule – a **molecular orbital**!
 - Just as atoms have many atomic orbitals ($1s$, $2s$, $2p$, etc.), molecules can have many molecular orbitals. In H_2^+ , the higher energy molecular orbitals are all empty.
 - The energy of a molecular orbital depends in part on the relative positions of the nuclei.



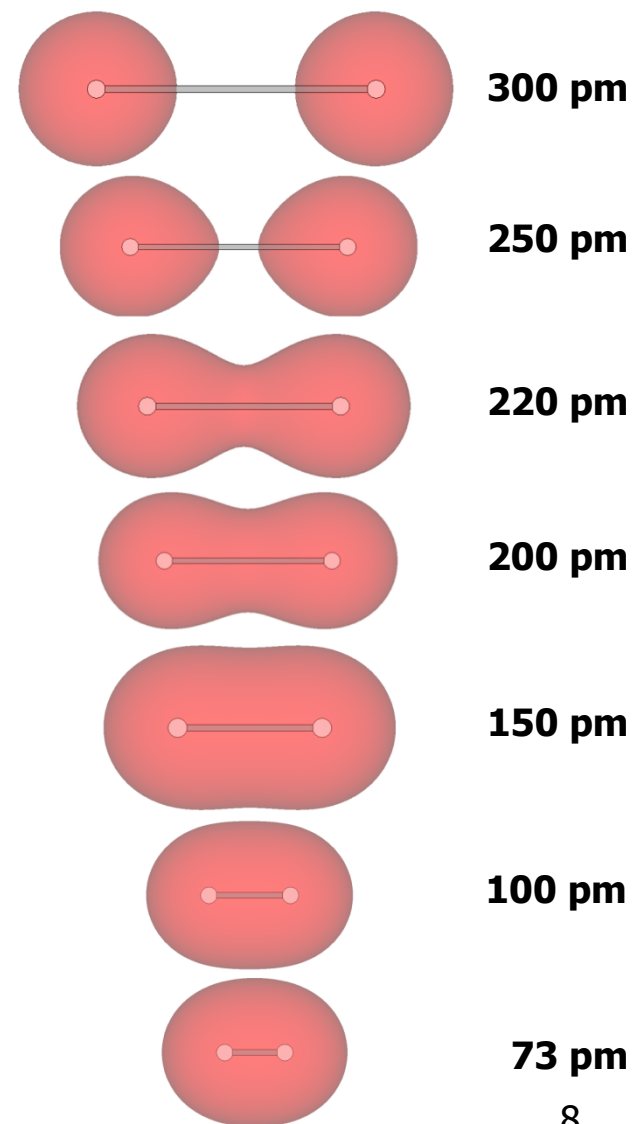
The Molecular Orbitals of H_2

- It was possible to solve the Schrödinger equation exactly for a hydrogen atom, but a helium atom had too many electrons. We encounter the same problem with H_2 . While H_2^+ can be solved, as soon as a second electron is introduced, there are too many moving bodies and the wavefunction cannot be solved exactly. This does not mean we're finished with quantum mechanics! Instead, we make more approximations...
- So, what's a reasonable approximation? We know that, when two hydrogen atoms are far apart (i.e. R is large), they behave like two free hydrogen atoms.

If we were able to bring them together such that the nuclei overlapped (i.e. $R = 0$ pm), we would have :

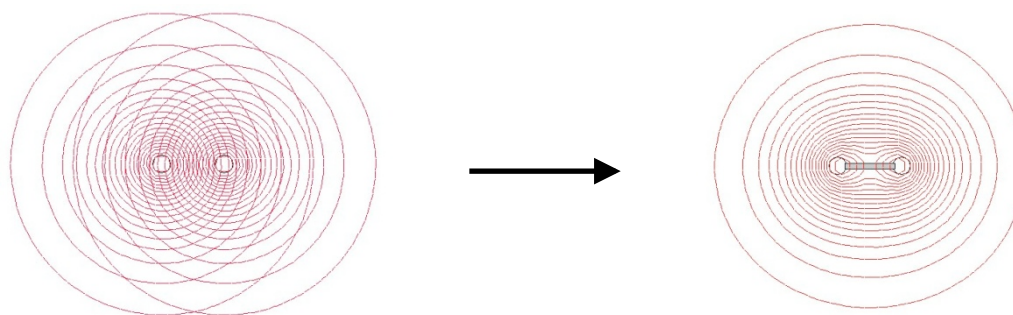
The Molecular Orbitals of H₂

- If we imagine the initially separate hydrogen atoms approaching each other (as in the diagram at the right), we see the electrons begin to “lean in” to begin making the H-H bond. What is responsible for this behaviour?

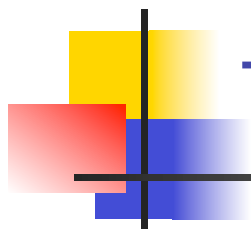


The Molecular Orbitals of H₂

- The orbitals of a hydrogen molecule ($R = \sim 74 \text{ pm}$) must be somewhere between those two extremes. We often approximate molecular orbitals by describing them as combinations of atomic orbitals. This is termed **Linear Combination of Atomic Orbitals** (LCAO) and gives an LCAO-MO such as that below:

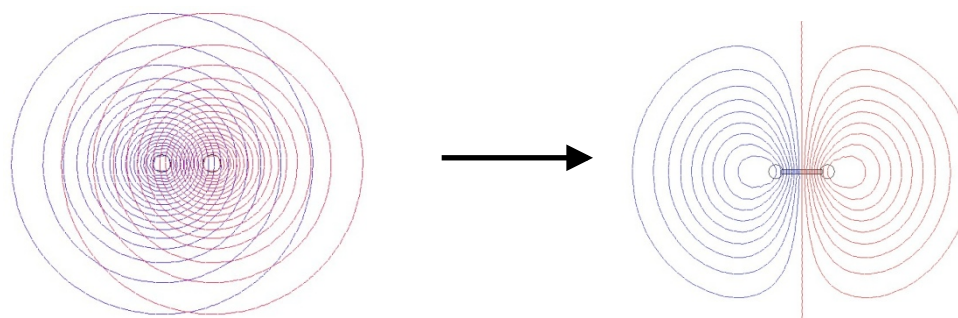


- By adding the two atomic orbitals, we obtain a **sigma bonding orbital** (σ).
 - **Bonding:** lots of electron density between the two nuclei
 - **Sigma symmetry:** high electron density along the axis connecting the nuclei



The Molecular Orbitals of H₂

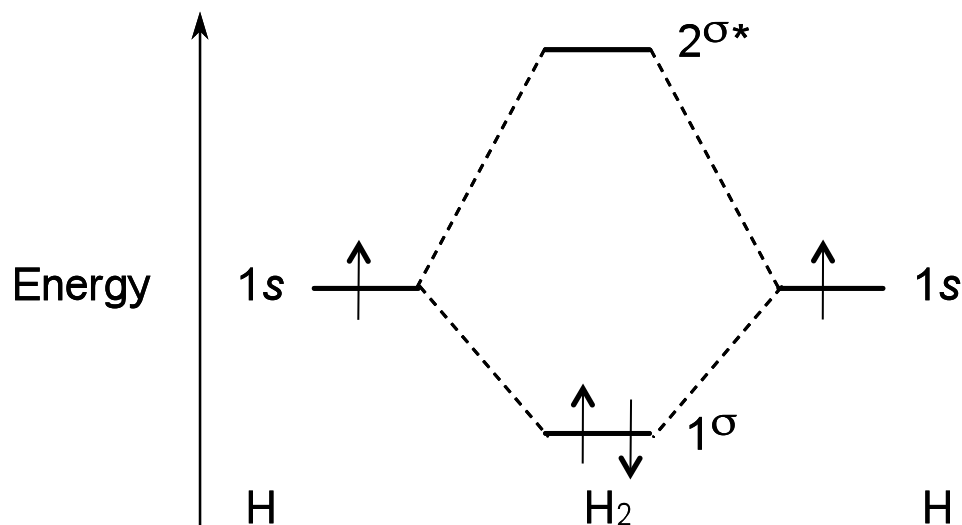
- We can also subtract the two atomic orbitals (*equivalent to adding them after inverting the phase of one – just as subtracting 5 is equivalent to adding -5*):



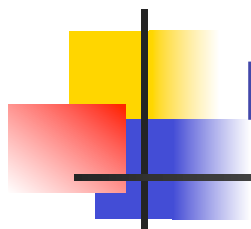
- This is a **sigma antibonding orbital** (σ^*).
 - **Antibonding:** depleted electron density between the two nuclei (*look for a node perpendicular to the axis connecting the nuclei*)
 - **Sigma symmetry:** high electron density along the axis connecting the nuclei

Molecular Orbital Diagram for H₂

- We can draw an energy level diagram showing molecular orbitals and the atomic orbitals from which they were derived. This is referred to as a molecular orbital diagram (**MO diagram**).



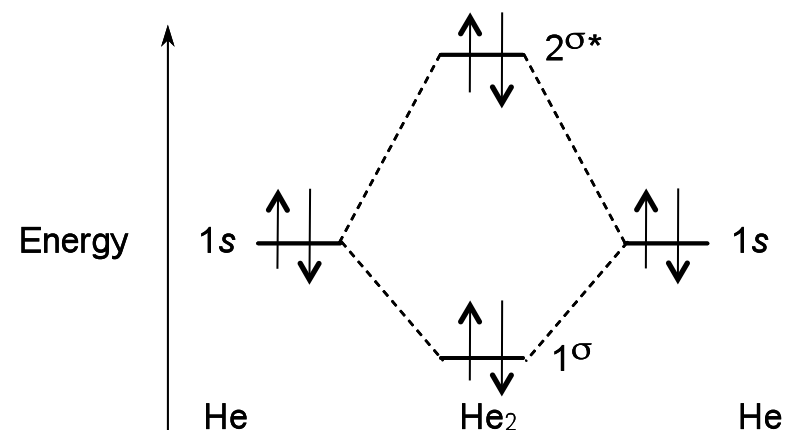
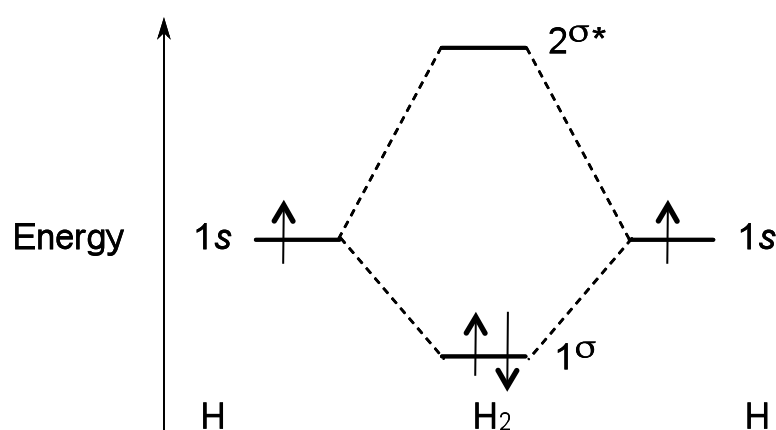
Note that the energy difference is larger between the atomic orbitals and the antibonding orbital than between the atomic orbitals and the bonding orbital.



Molecular Orbital Diagram for H₂

- **MO diagrams** relate the energies of molecular orbitals to the atomic orbitals from which they were derived. If the total energy of the electrons is lower using molecular orbitals (*the middle column*), the molecule forms. If the total energy of the electrons is lower using atomic orbitals (*the two outside columns*), no molecule is formed.
- To fill a molecular orbital diagram with electrons, use the same rules as you would to fill in an atomic orbital diagram:
 - Fill σ first.
 - Pauli's exclusion principle still applies:
 - Hund's rule still applies:

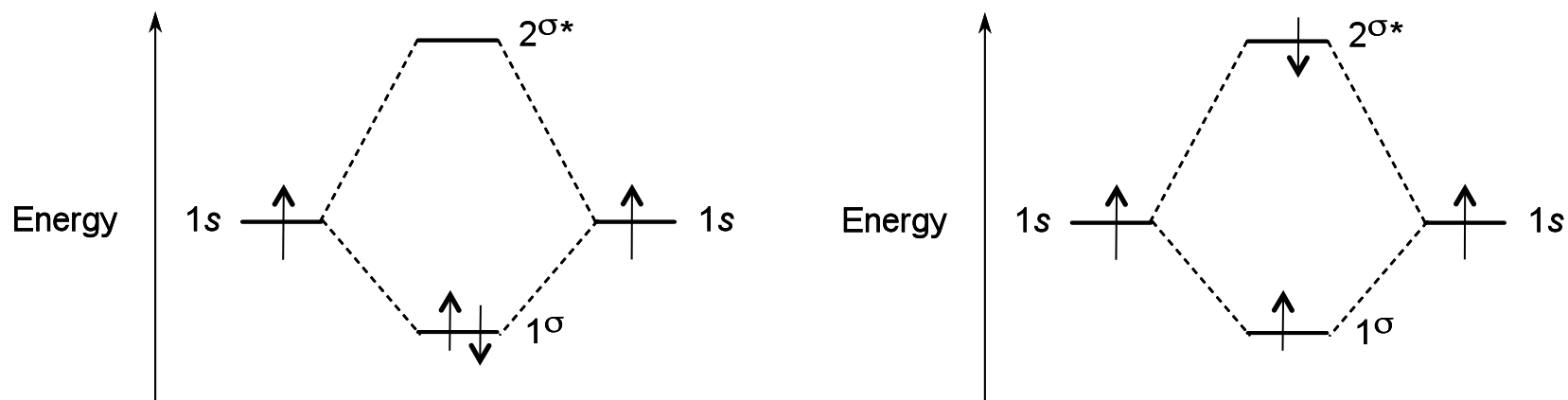
Molecular Orbital Diagram for H₂



- Thus, the orbital occupancy for H₂ in the ground state is and the orbital occupancy for He₂ in the ground state is
- We can calculate bond orders for these two “molecules” from their MO diagrams:

$$\text{bond order} = \frac{1}{2} (\# \text{ bonding } e^- - \# \text{ antibonding } e^-)$$

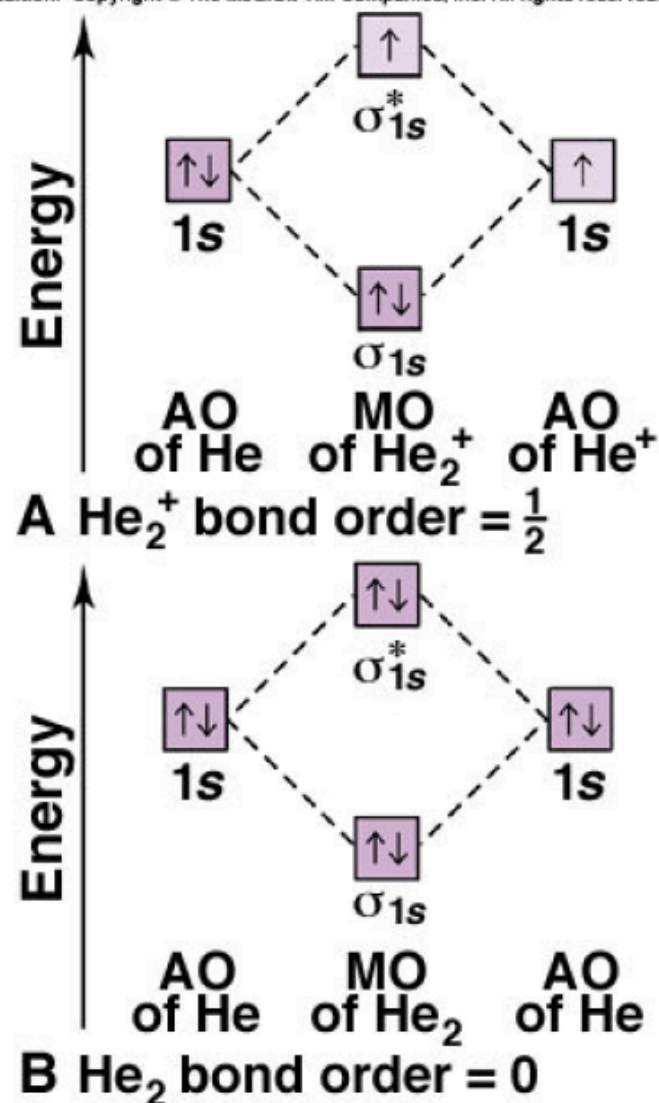
Molecular Orbital Diagram for H₂



- If a molecule of H₂ was irradiated with light, exciting an electron from 1σ to 2σ*, what would happen?
- Should it be possible for H₂⁻ to exist?
- What about He₂⁺?

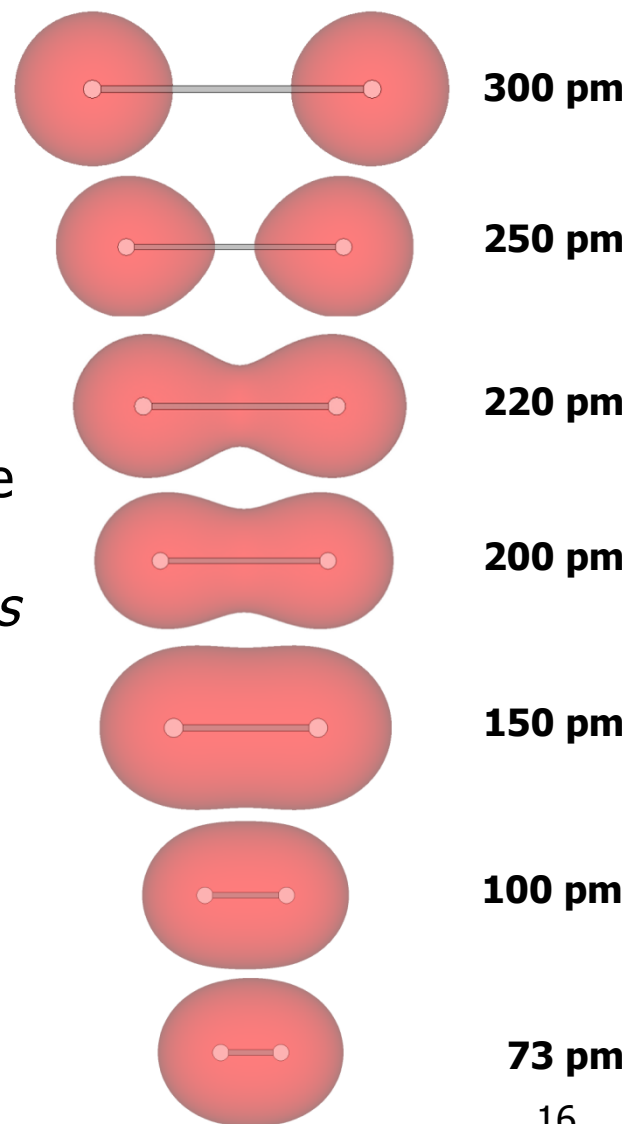
MO Diagrams of He_2^+ and He_2

- Bond order = $\frac{1}{2}$ (#bonding e-
s - #antibonding e-s)
- Bond order = 0 indicates the
species will not exist.



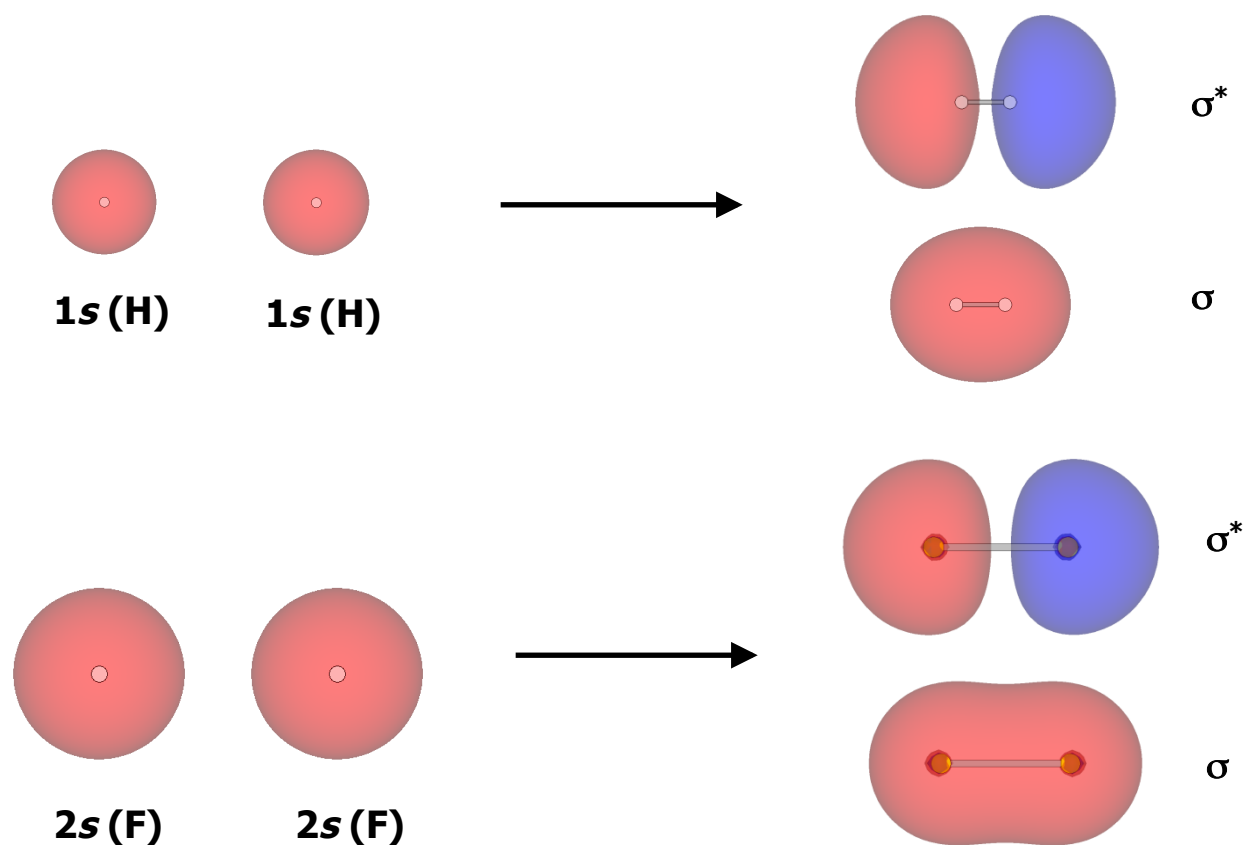
Molecular Orbitals of Homonuclear Diatomics

- As the two hydrogen atoms approach, we can see that the orbitals change from looking like two separate $1s$ orbitals (one per H) to looking like a σ molecular orbital:
- The picture for the “development” of the antibonding σ^* molecular orbital is similar except that, instead of the two $1s$ orbitals appearing to “reach in toward” each other, they appear to “push away from” each other.



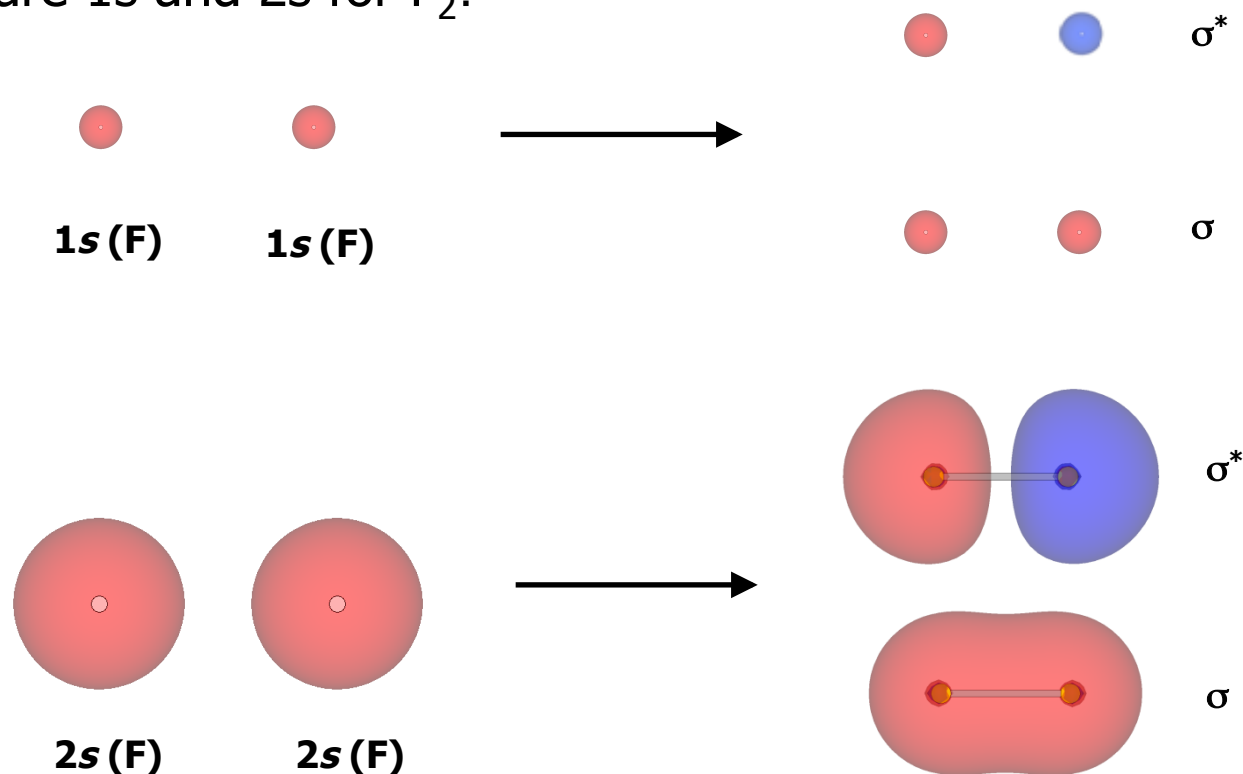
Molecular Orbitals of Homonuclear Diatomics

- We can combine higher energy atomic orbitals in the same way. Compare the σ and σ^* orbitals made from the 2s orbitals in F_2 to the σ and σ^* orbitals made from the 1s orbitals in H_2 :

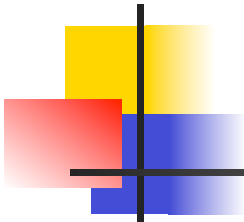


Molecular Orbitals of Homonuclear Diatomics

- Note that as the distance between nuclei increases, the overlap between the 1s orbitals decreases. That's why we can't just compare 1s and 2s for F_2 !

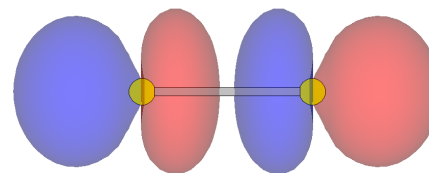
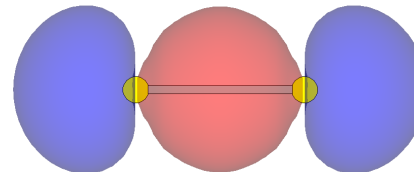
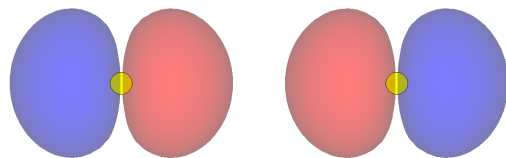


- This is also why, for the most part, we focus on **valence** molecular orbitals. The core MOs look just like core AOs.



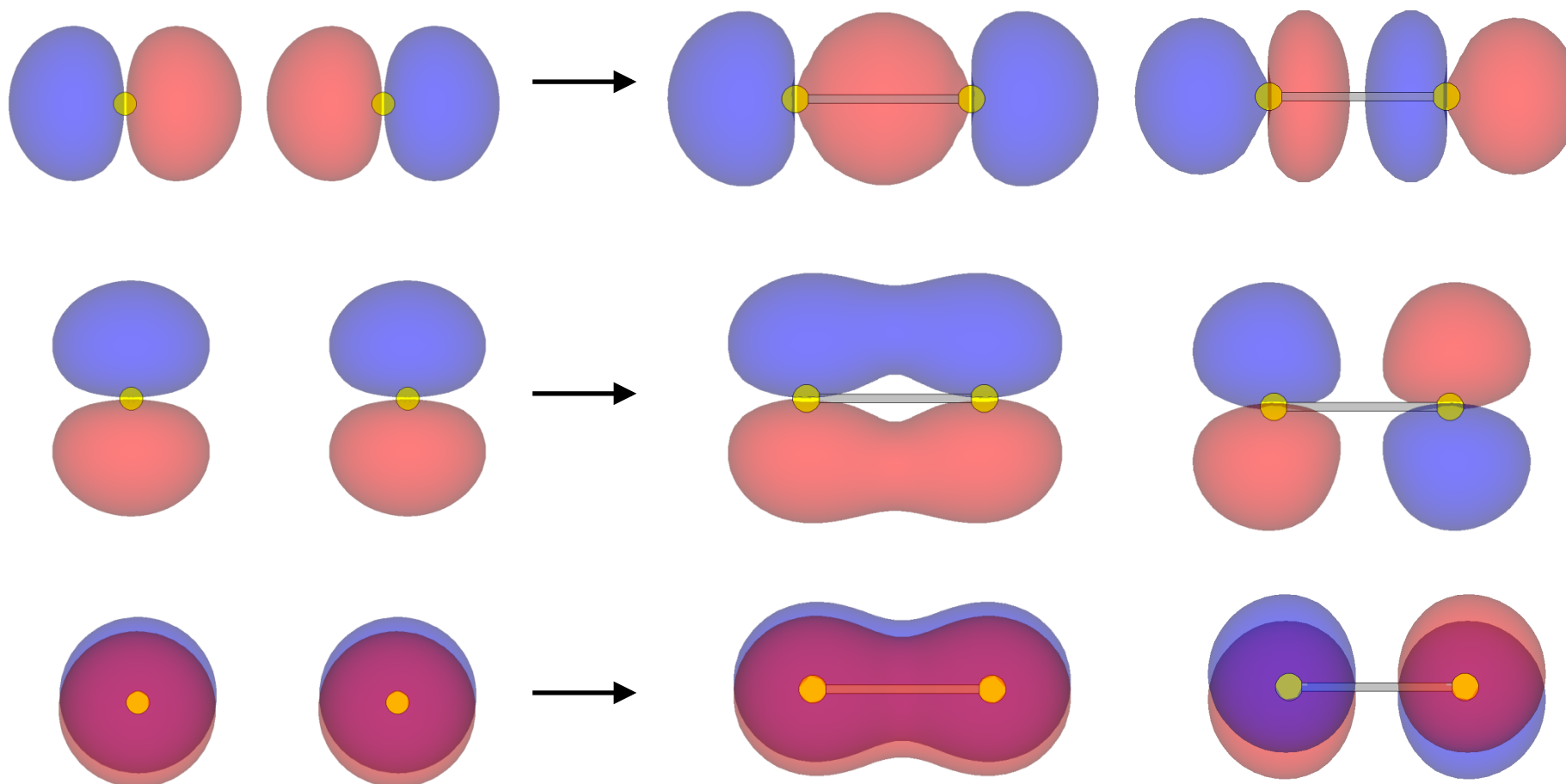
Molecular Orbitals of Homonuclear Diatomics

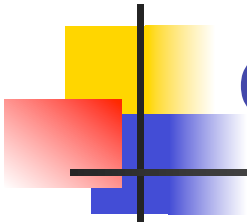
- p orbitals can also be combined to make molecular orbitals. The type of molecular orbital formed will depend on the orientation of the p orbitals.
- p orbitals that overlap head-on (usually defined as the p_z orbitals) give σ molecular orbitals:



Molecular Orbitals of Homonuclear Diatomics

p orbitals that overlap side-on (usually defined as the p_x or p_y orbitals) give π molecular orbitals and here are the pretty computer-generated pictures of those orbitals:

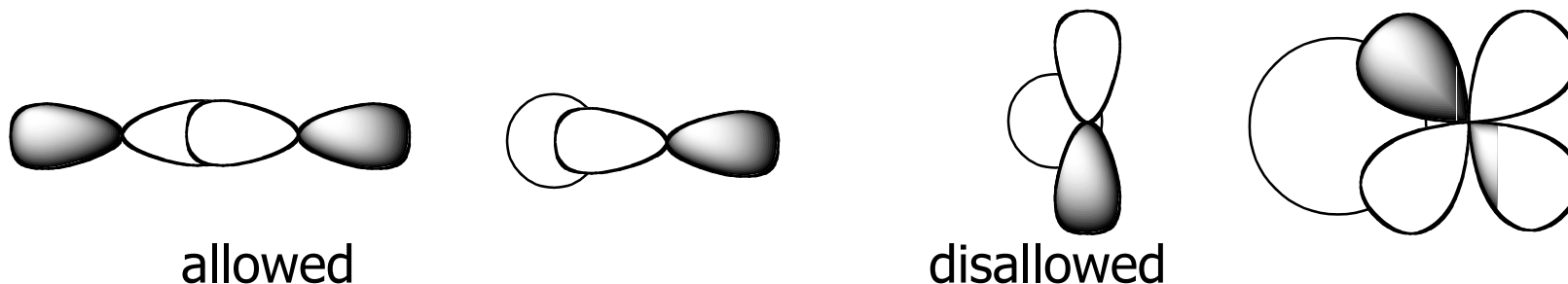




General Rules for LCAO-MOs

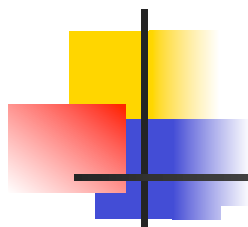
- Linear Combination of Atomic Orbitals (LCAO) can only be used to generate molecular orbitals when the atomic orbitals have compatible symmetry.

e.g. Combination of an *s* orbital and a *p* orbital



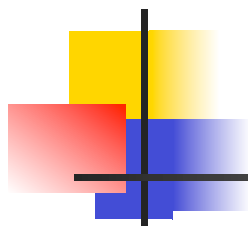
- When atomic orbitals are added in phase (constructive interference), a bonding orbital is made. When added out of phase (destructive interference), an antibonding orbital is made.

THE NUMBER OF MOLECULAR ORBITALS IS **ALWAYS** EQUAL TO THE NUMBER OF ATOMIC ORBITALS INCLUDED IN THE CALCULATION!!!



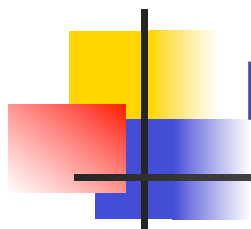
MO Theory: Bonding Types

	AO's	Combinations	Symmetry Label
σ bonds	s and s		σ_s or σ_g σ_s^* or σ_u^*
	s and p_z		σ_{sp} σ_{sp}^*
	p_z and p_z		σ_p or σ_g σ_p^* or σ_u^*
	non-bonding		no overlap no overlap
π bonds	p_x and p_x		π_p or π_u π_p^* or π_g^*



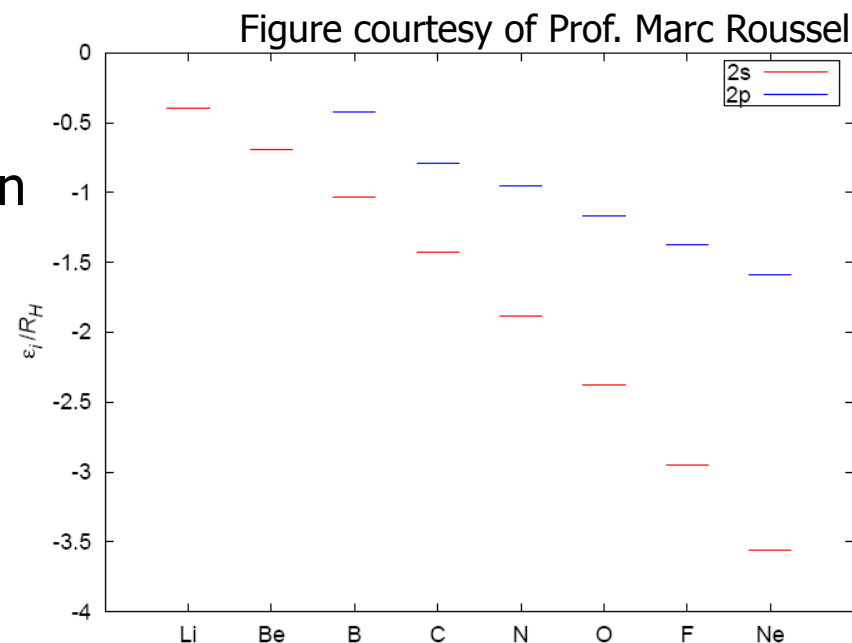
MO Theory: Bonding Types (continued)

	AO's	Combinations	Symmetry Label
π bonds	p_x and d_{xz}		π_{pd}
			π_{pd}^*
	d_{xz} and d_{xz}		π_d
			π_d^*
δ bonds	d_{xy} and d_{xy}		δ_d or δ_g
			δ_d^* or δ_u^*



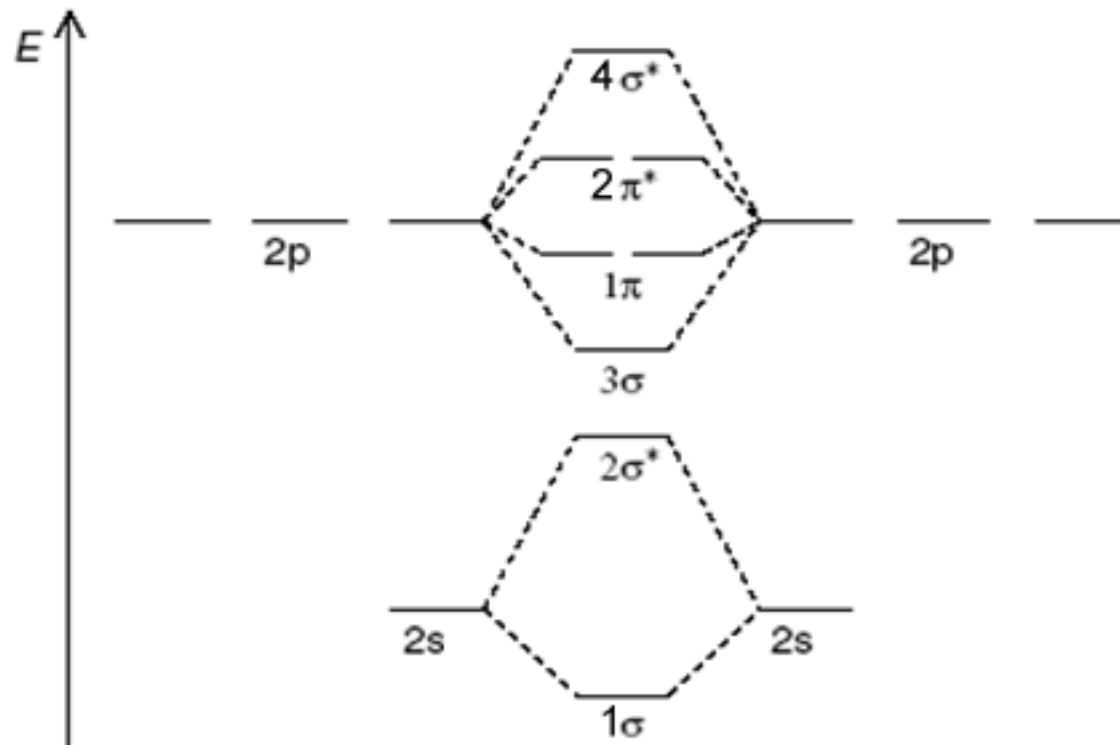
Molecular Orbitals of Homonuclear Diatomics

- Which p orbital combines with which other p orbital is symmetry-determined. Since orthogonal orbitals on different atoms don't combine, you won't see combination of a p_x orbital on one atom and a p_y orbital on its neighbour, for example.
- s orbitals "can" combine with p orbitals when making σ MoS "if" the orbitals are close enough in energy (within $1 \text{ Ry} = 2.179 \times 10^{-18} \text{ J} = R_H$).
- The figure at the right shows $2s$ and $2p$ atomic orbital energies for the elements in period 2. We can see that there will be little mixing between $2s$ and $2p$ orbitals for the heavier elements in period 2.



Molecular Orbitals of Homonuclear Diatomics

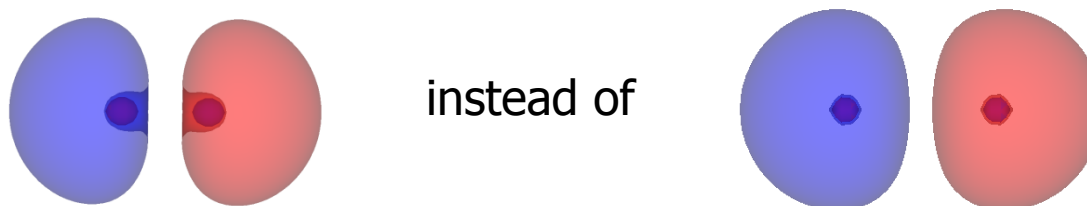
- O, F and Ne have large enough energy gaps between their $2s$ and $2p$ orbitals that they give the “normal” MO diagram:



Molecular Orbitals of Homonuclear Diatomics

- Because Li, Be, B, C and N have smaller energy gaps between their $2s$ and $2p$ orbitals, some mixing is observed when forming the σ and σ^* orbitals, primarily $2\sigma^*$ and 3σ :

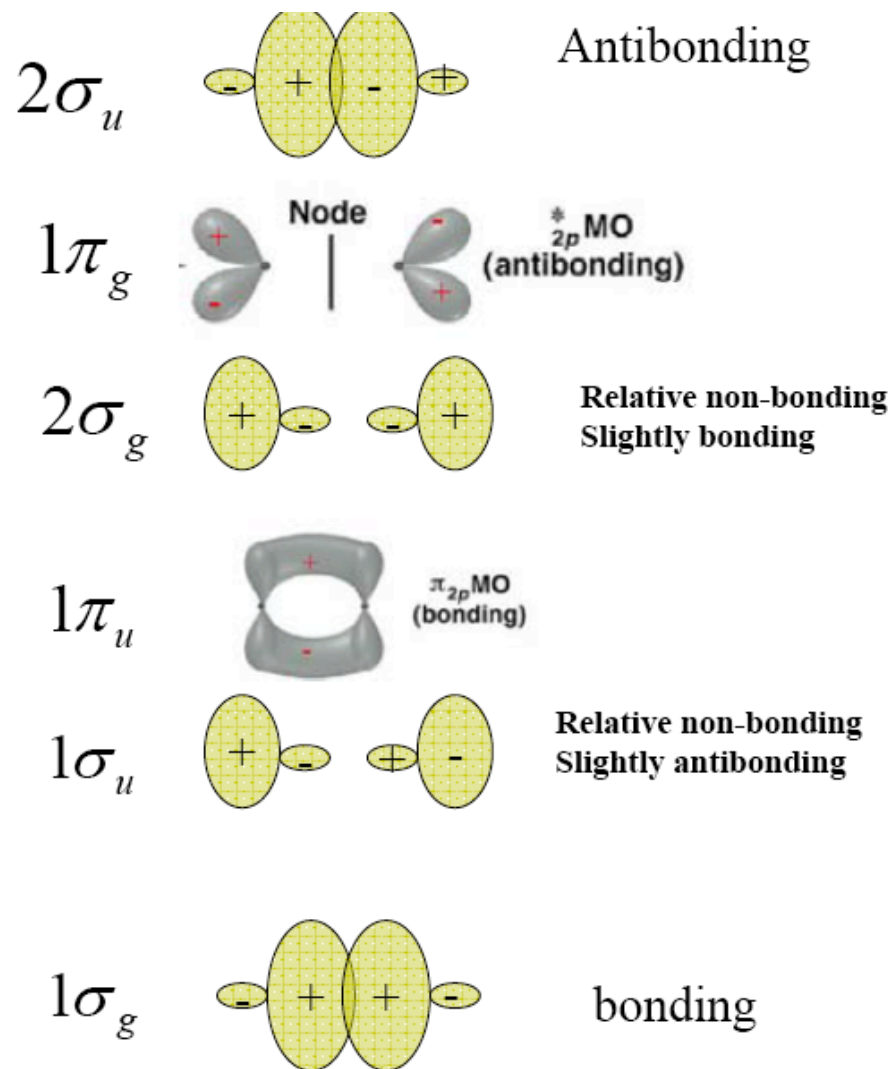
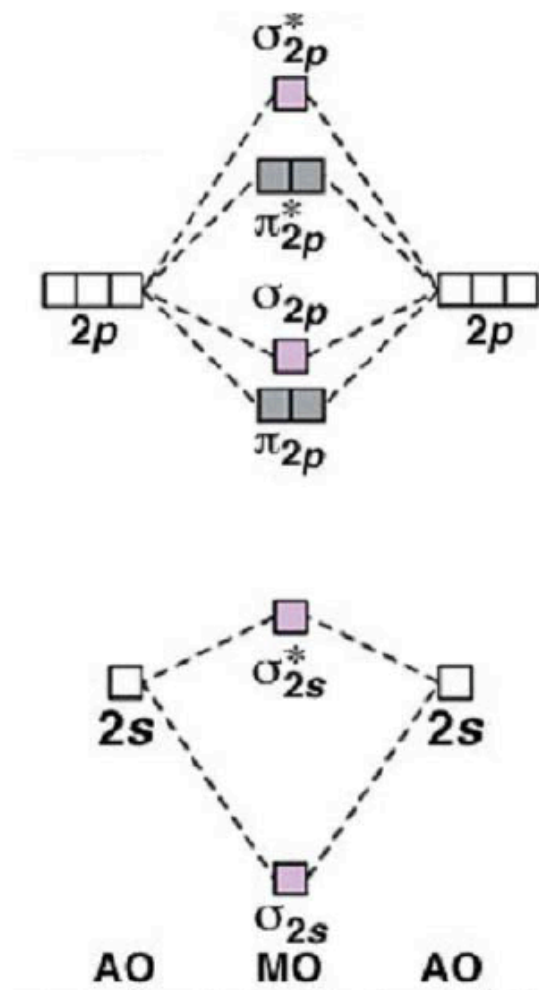
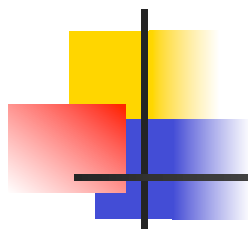
- Mixing in some “ p character” lowers the energy of the $2\sigma^*$ MO

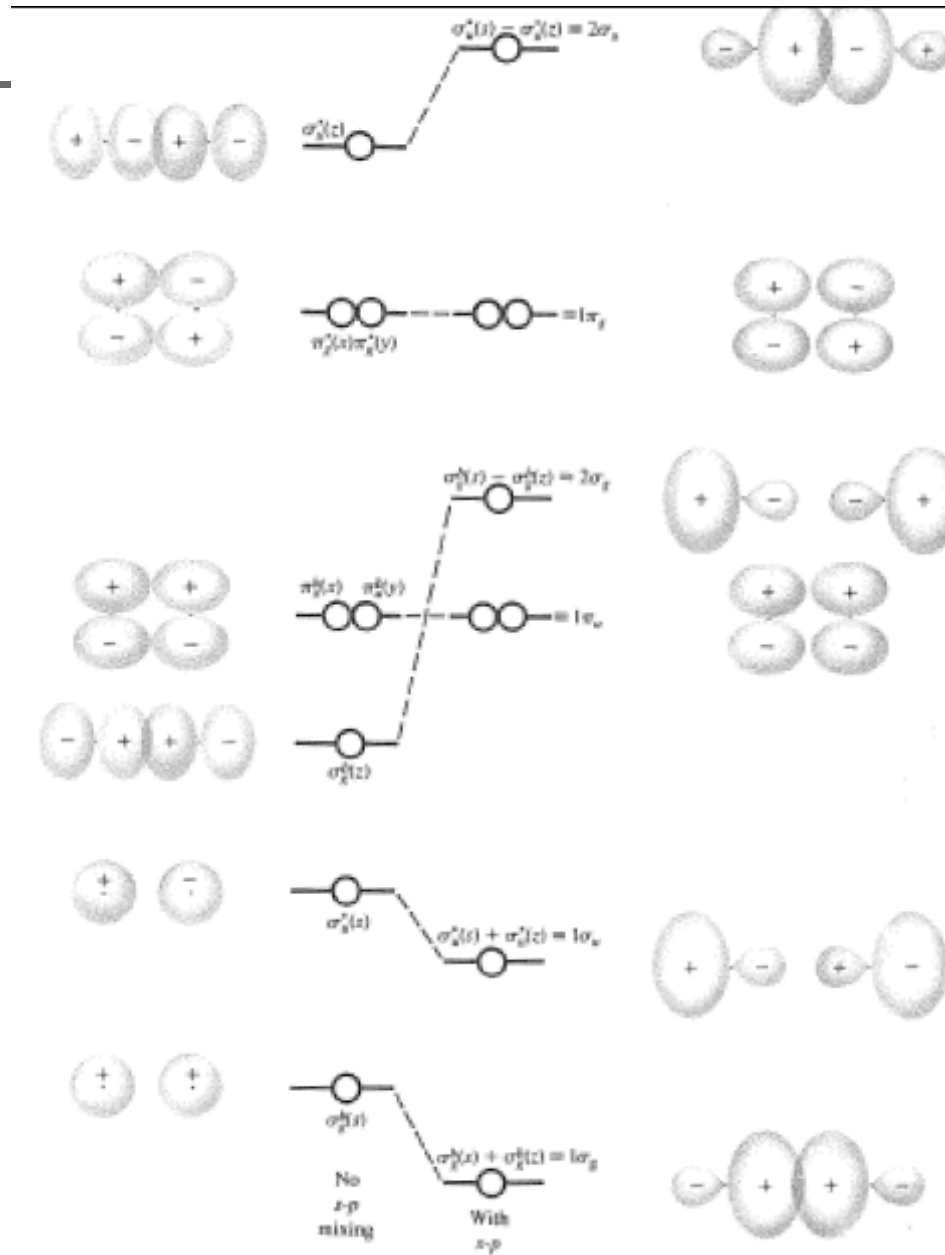
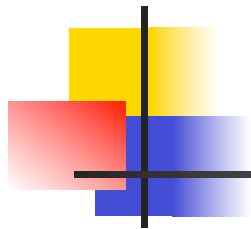


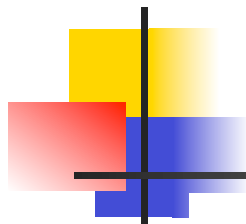
- Mixing in some “ s character” raises the energy of the 3σ MO



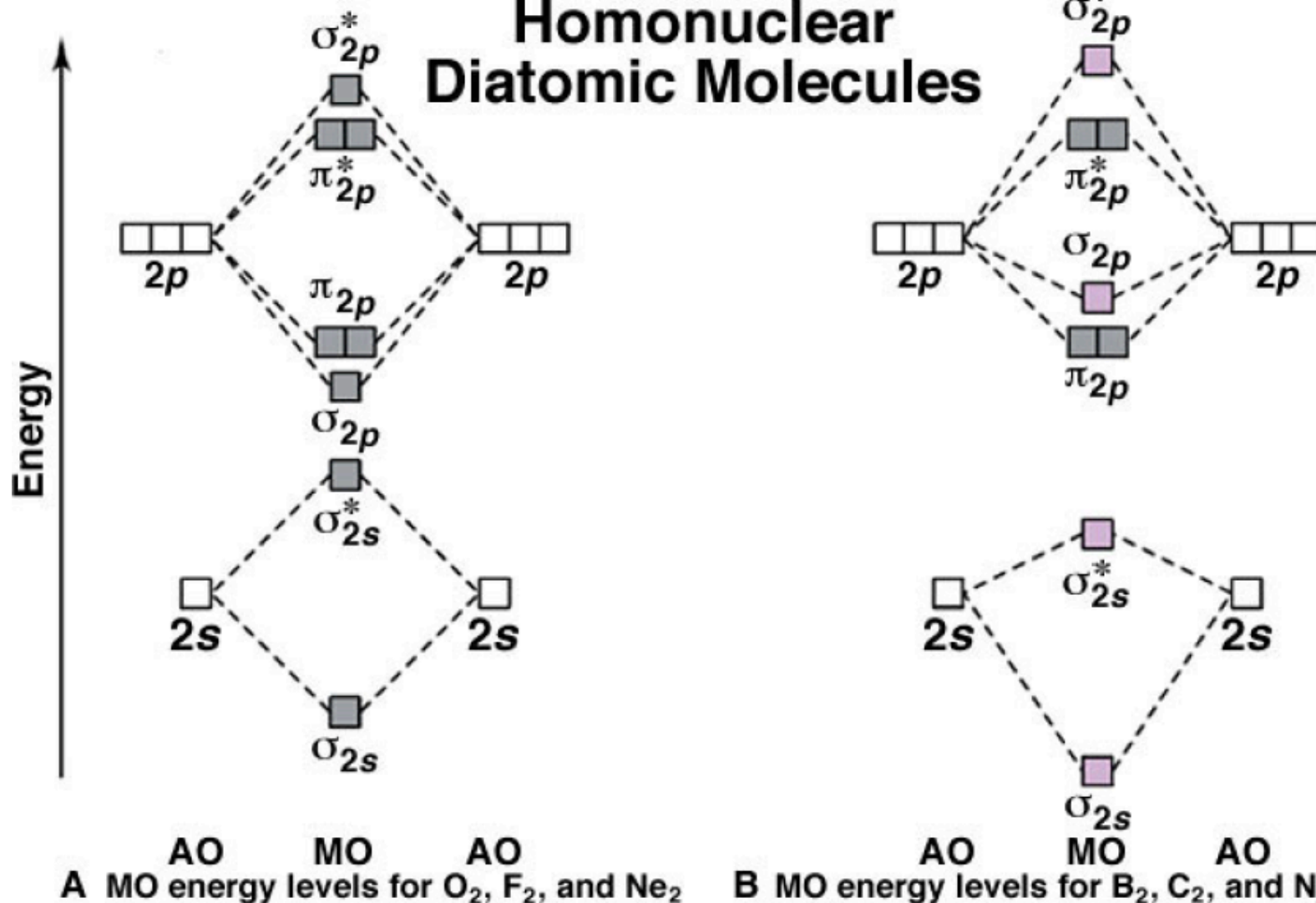
- If this effect is strong enough, the 3σ orbital can end up higher in energy than the 1π orbital, giving the MO diagram on the next page. This is the case in Li_2 , Be_2 , B_2 , C_2 and N_2 .

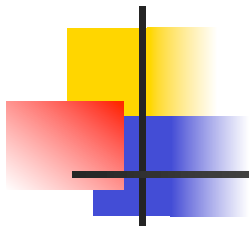




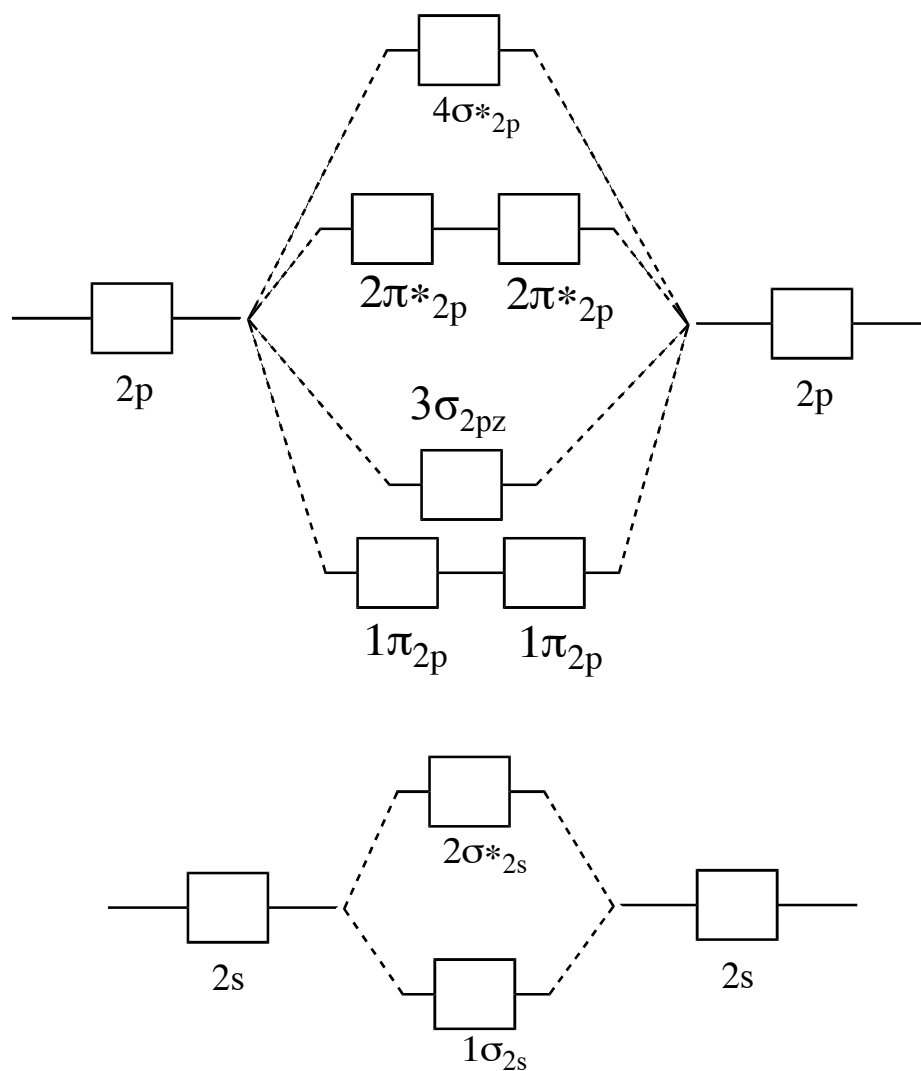


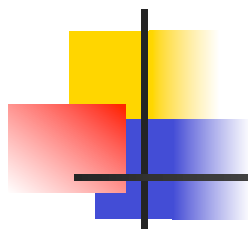
Relative MO Energy Levels for Period 2 Homonuclear Diatomic Molecules





The MO Diagram for $\text{Li}_2\text{-N}_2$





Li₂ and Be₂

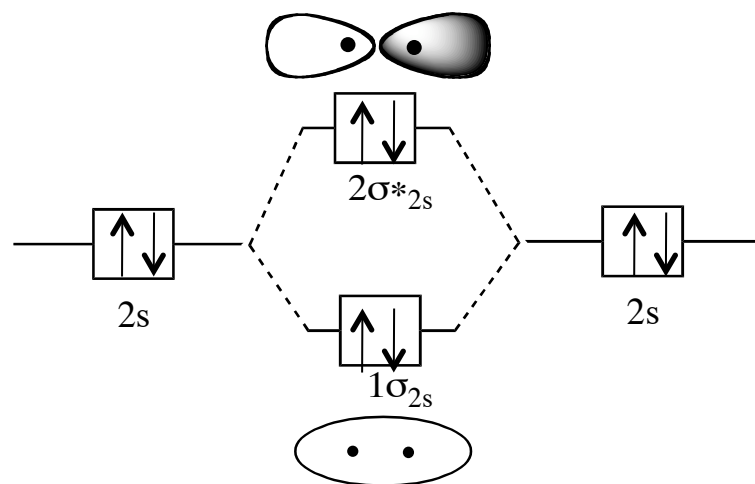
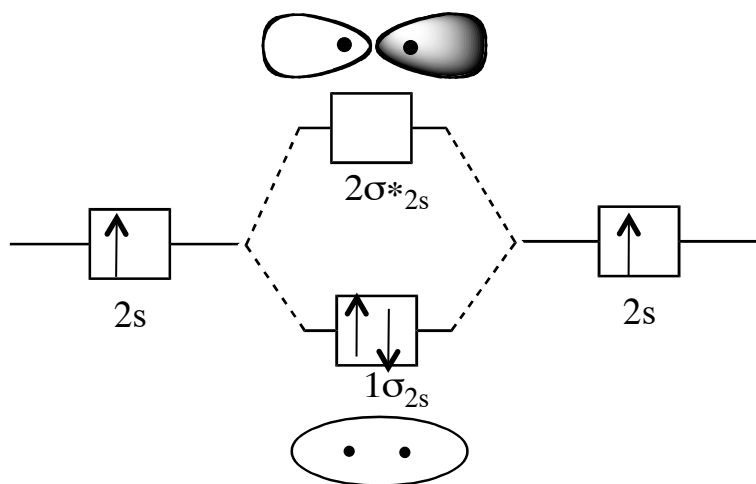
Li₂

Be₂

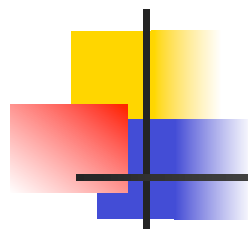
BO:

Bond energy: 106 kJ/mol

BO:



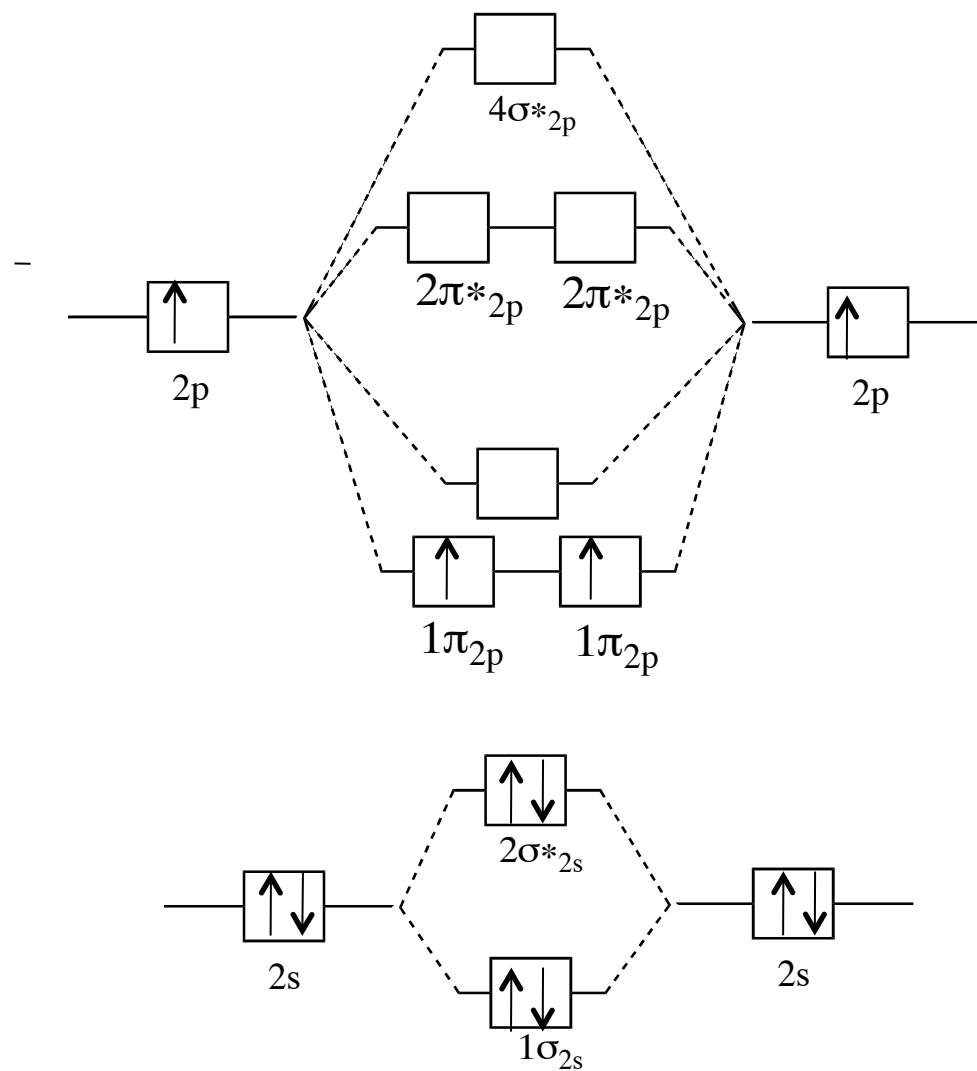
Correlation diagram for homonuclear diatomics, Z up to 7 ($\text{Li}_2\text{-N}_2$)

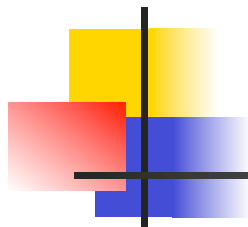


B_2

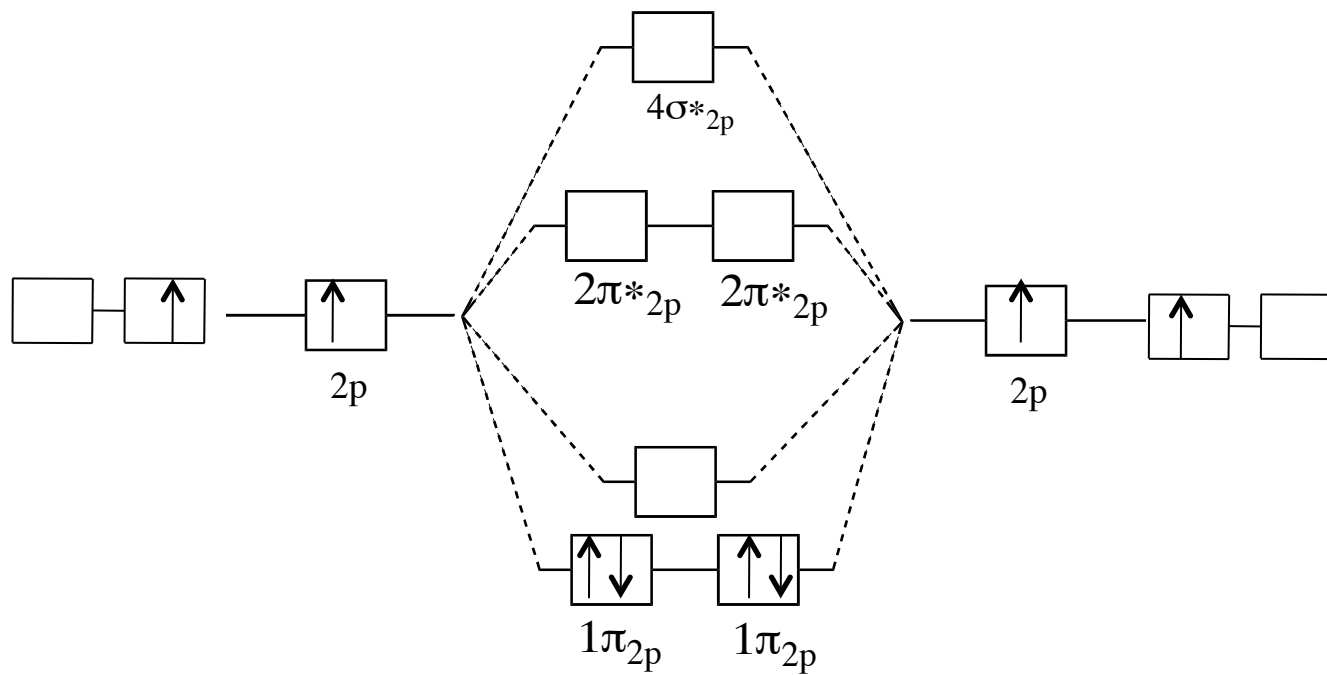
Bond order =

BDE = 290 kJ

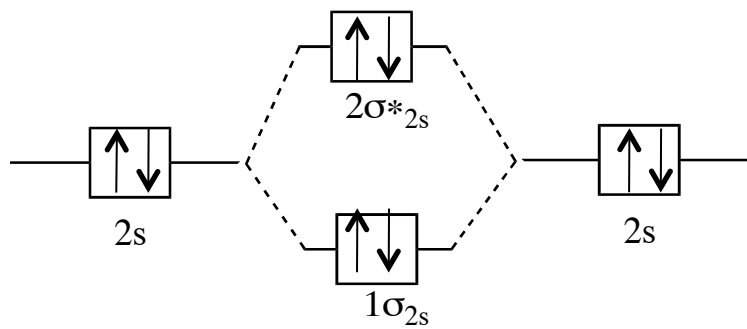


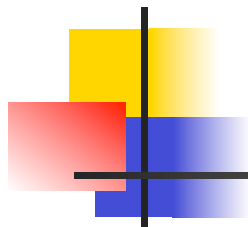


C_2
Bond order
BDE 620 kJ



MOEC:

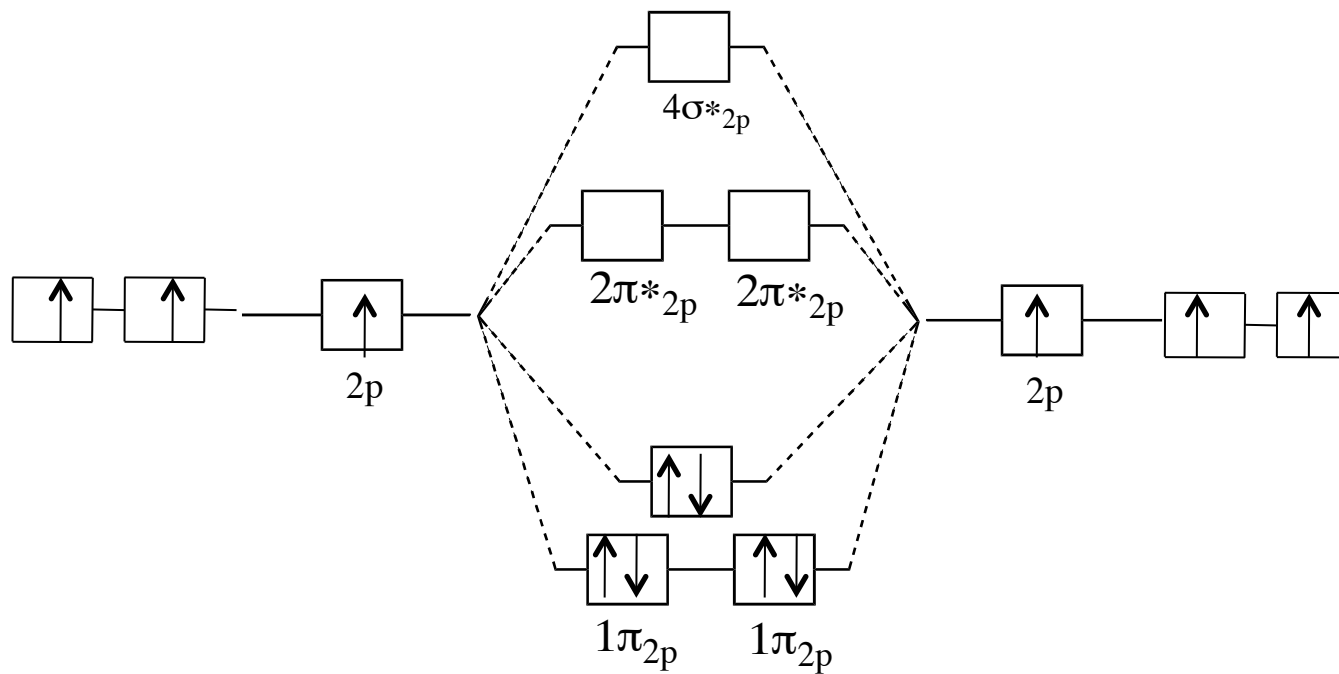




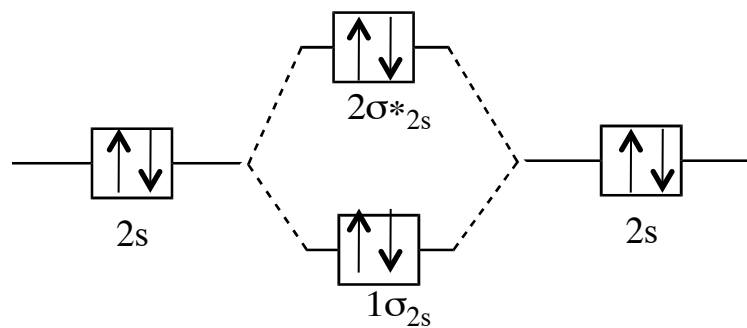
N_2

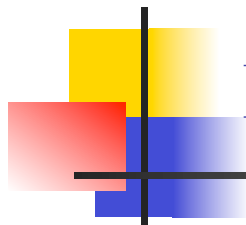
Bond order

BDE 945 kJ



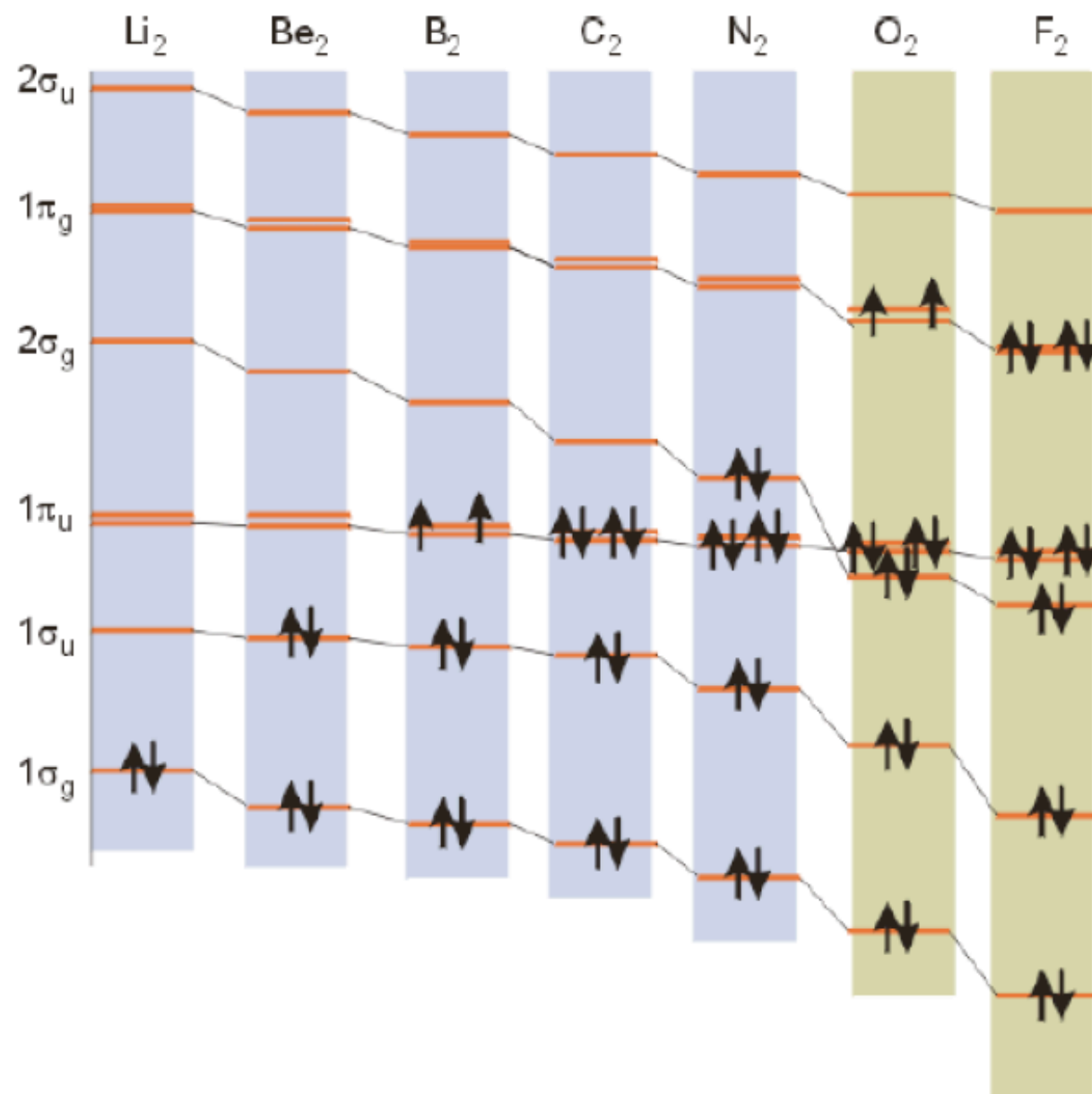
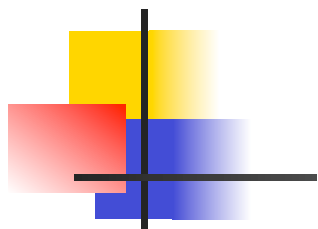
MOEC:





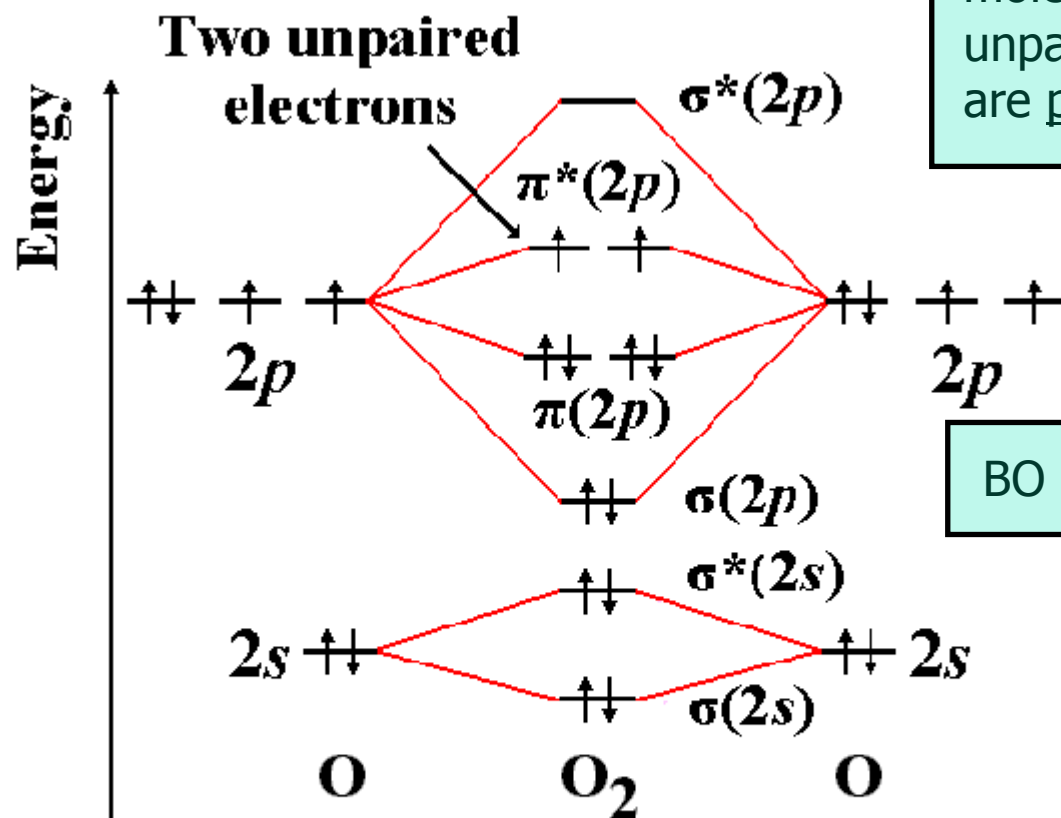
Recap

TABLE 18-2		Molecular Orbitals of Homonuclear Diatomic Molecules			
Species	Number of Valence Electrons	Ground-State Valence-Electron Configuration	Bond Order	Bond Length (Å)	Bond Enthalpy (kJ mol ⁻¹)
H ₂	2	$(\sigma_{2s})^2$	1	0.746	436
He ₂	4	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	Not observed	
Li ₂	2	$(\sigma_{2s})^2$	1	2.67	106
Be ₂	4	$(\sigma_{2s})^2(\sigma_{2s}^*)^2$	0	2.45	9
B ₂	6	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$	1	1.59	297
C ₂	8	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$	2	1.24	607
N ₂	10	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p_z})^2$	3	1.10	945
O ₂	12	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^2$	2	1.21	498
F ₂	14	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^4$	1	1.41	158
Ne ₂	16	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p_z}^*)^2$	0	Not observed	



O₂ molecule, bond order = 2

The ability to predict the number of unpaired electrons in molecules is where MO excels, and Lewis-dot fails.



molecules with unpaired electrons are paramagnetic

$$BO = (6-2)/2 = 2$$

(disregarding overlap of 2s orbitals)

MO diagram for dioxygen (O₂) molecule, showing origin of two unpaired electrons

Magnetism-Background

- Magnetism is a property of matter in which there is a force of repulsion or attraction between like or unlike poles. *Only a few solid materials are naturally magnetic.*
- *Because we can't see magnetism*, a model or mental picture can help us visualize the atoms that make up the solid.
- Electrons in most atoms exist in pairs, with each electron spinning in an opposite direction.

Magnetism-Background

- Each spinning electron causes a magnetic field to form around it. In most materials, the magnetic field of one electron is cancelled by an opposite magnetic field produced by the other electron in the pair.
- The atoms in materials such as iron, cobalt and nickel have unpaired electrons, so they don't cancel the electrons' magnetic fields.
- As a result, **each atom** of these elements acts like a very **small magnet**.

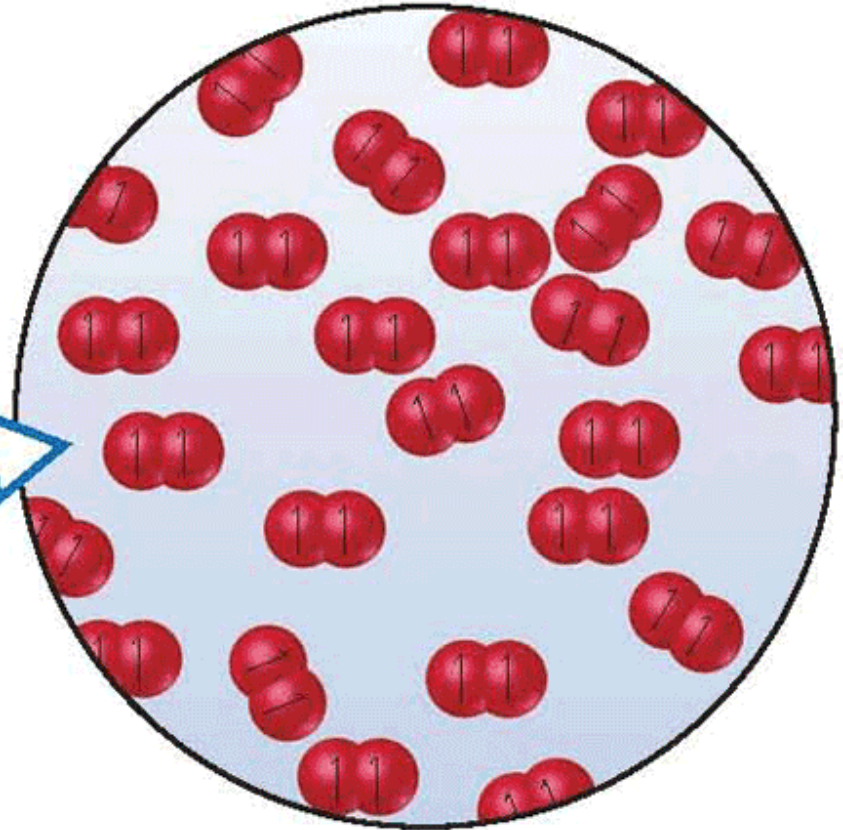
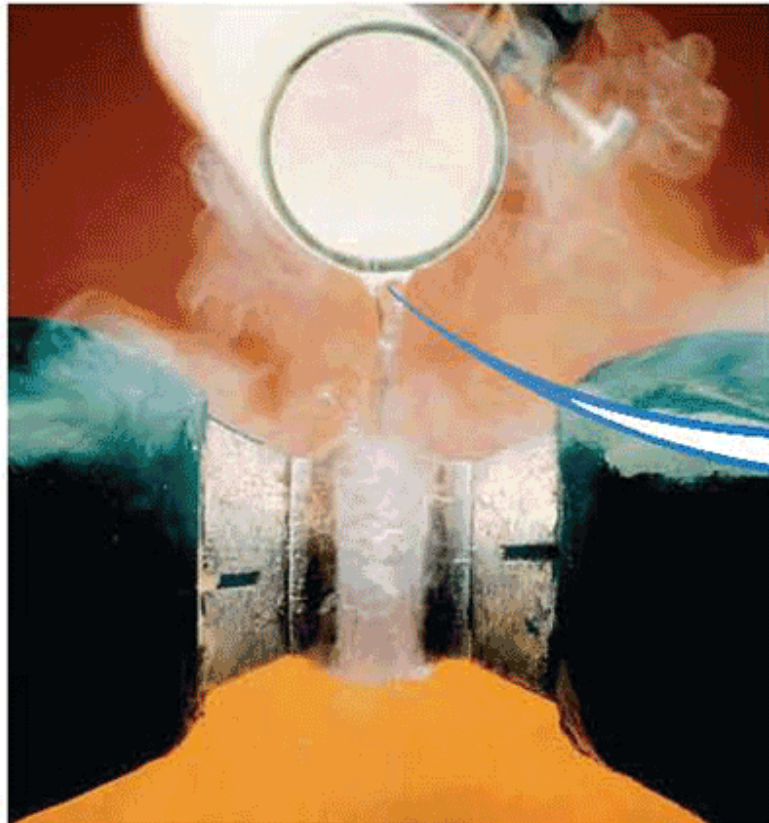
Introduction to Magnetochemistry

- The processes which create magnetic fields in an atom are
 - **Nuclear spin.** Some nuclei, such as a hydrogen atom, have a net spin, which creates a magnetic field.
 - **Electron spin.** An electron has two intrinsic spin states (similar to a top spinning) which we call up and down or alpha and beta.
 - **Electron orbital motion.** There is a magnetic field due to the electron moving around the nucleus.
- Each of these magnetic fields interact with one another and with external magnetic fields. However, some of these interactions are strong and others are negligible.

Magnetic States of Matter

- Diamagnet - A diamagnetic compound has all of its electron spins paired giving a net spin of zero. Diamagnetic compounds are weakly repelled by a magnet.
- Paramagnet - A paramagnetic compound will have some electrons with unpaired spins. Paramagnetic compounds are attracted by a magnet. Paramagnetism derives from the spin and orbital angular momenta of electrons. This type of magnetism occurs only in compounds containing unpaired electrons, as the spin and orbital angular momenta is cancelled out when the electrons exist in pairs.
- Compounds in which the paramagnetic centres are separated by diamagnetic atoms within the sample are said to be magnetically dilute.

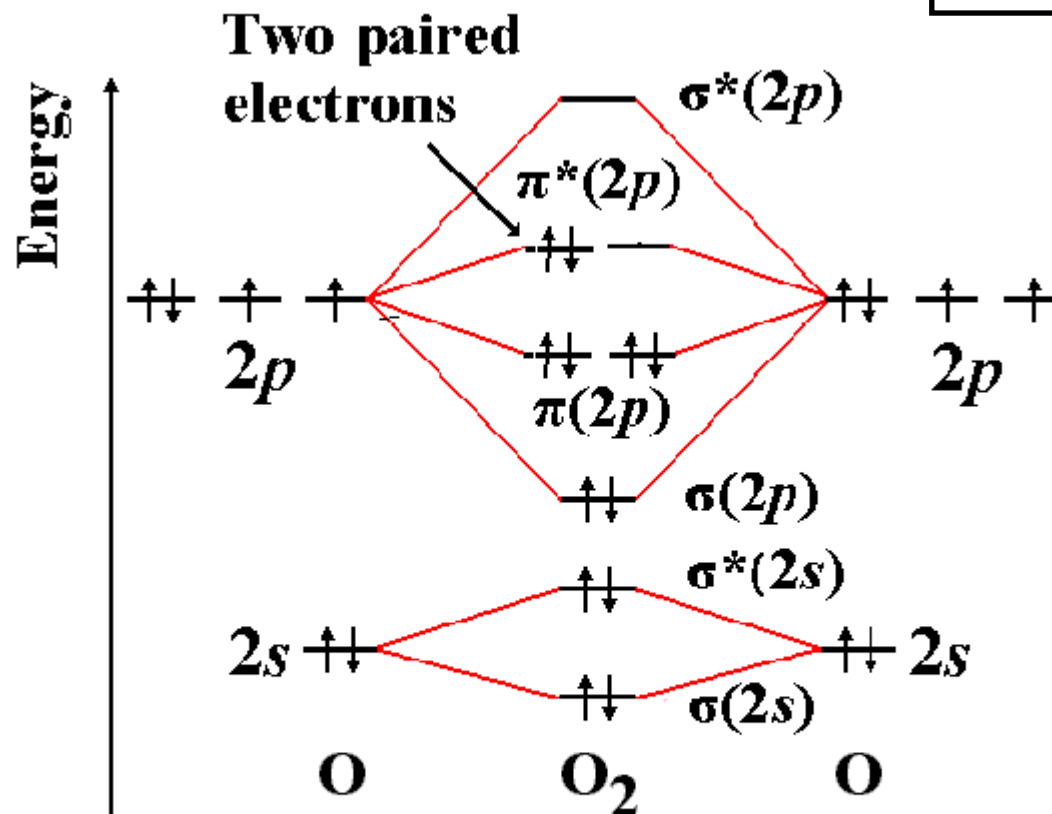
Paramagnetismo ossigeno



Singlet oxygen ($^1\text{O}_2$)

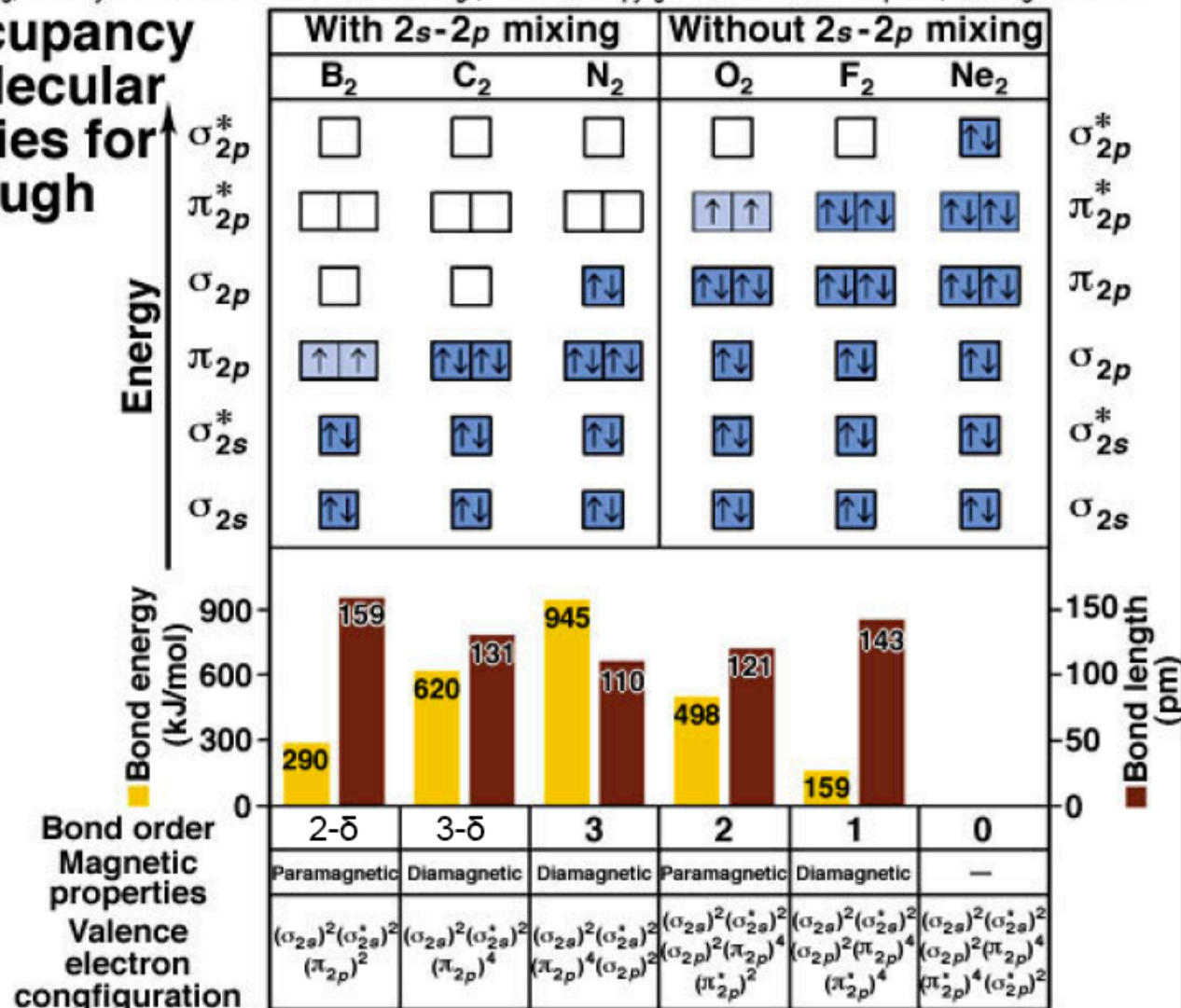
$$\text{BO} = (6-2)/2 = 2$$

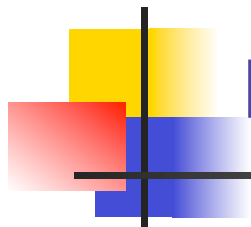
Singlet Oxygen is an excited state of the ground state triplet $^3\text{O}_2$ molecule. It is much more reactive, and will readily attack organic molecules.



The O_2 molecule in its excited singlet state which is 25 kcal/mol in energy above the ground triplet state. Irradiation with IR light causes excitation to the singlet state, which can persist for hours because the spin-selection rule (see later) inhibits transitions that involve a change of spin state.

MO Occupancy and Molecular Properties for B₂ Through Ne₂



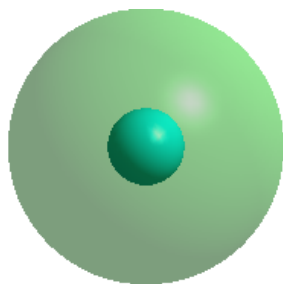


Molecular Orbitals of Heteronuclear Diatomics

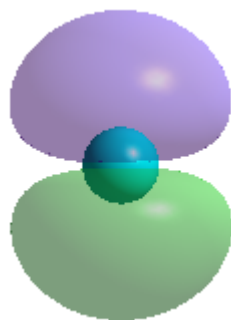
- The molecular orbitals of heteronuclear diatomics (HF, CO, CN⁻, etc.) can be predicted using the same principles that we used to construct the molecular orbitals of homonuclear diatomics:
 - Ignore the core electrons
 - Total number of MOs = Total number of AOs
 - Only AOs of **similar energy** combine to make LCAO-MOs
 - Only AOs of **compatible symmetry** combine to make LCAO-MOs:
 - σ -type AOs (s and p_z orbitals) make σ MOs
 - π -type AOs (p_x and p_y orbitals) make π MOs

Orbital parity – gerade (g) and ungerade (u)

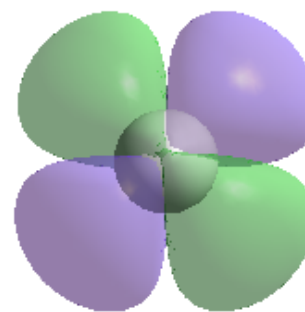
Symmetry of orbitals and molecules is of great importance, and we should be able to determine whether orbitals are *gerade* (g) or *ungerade* (u) (from German for even or odd). This is because in the spectra of inorganic compounds whether absorption of a photon to produce an electronic transition can occur is determined by whether the two orbitals involved are g or u . According to the Laporte selection rules, transitions from $g \rightarrow u$ and $u \rightarrow g$ are allowed, but $g \rightarrow g$ and $u \rightarrow u$ are forbidden. An orbital is g if it has a center of inversion, and u if it does not. So looking at atomic orbitals, we see that s and d are g , while p orbitals are u : (see next page for definition of center of sym.)



s -orbital
gerade (g)



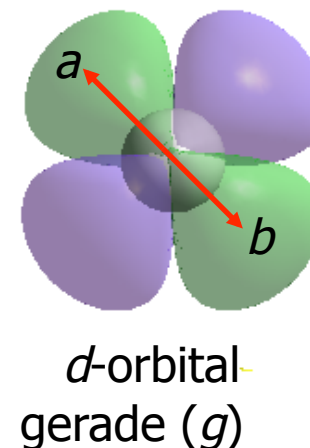
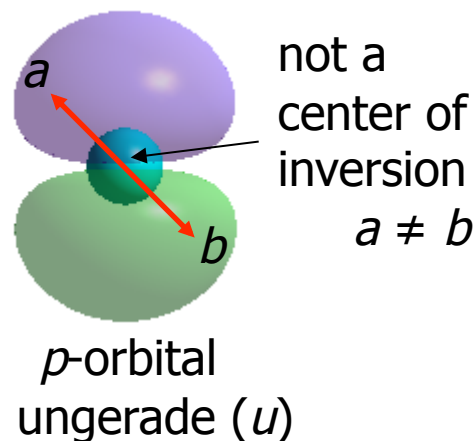
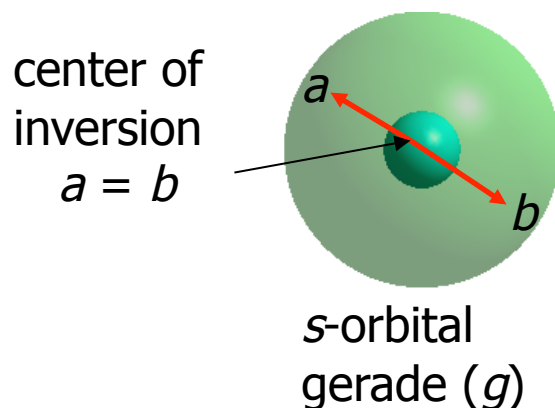
p -orbital
ungerade (u)



d -orbital
gerade (g)

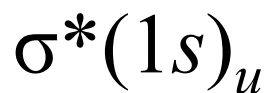
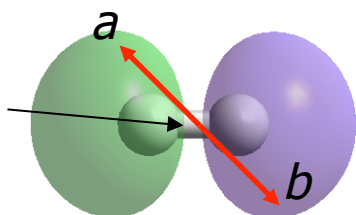
Orbital parity – gerade (*g*) and ungerade (*u*)

Symmetry of orbitals and molecules is of great importance, and we should be able to determine whether orbitals are *gerade* (*g*) or *ungerade* (*u*) (from German for even or odd). This is because in the spectra of inorganic compounds whether absorption of a photon to produce an electronic transition is determined by whether the two orbitals involved are *g* or *u*. According to the Laporte selection rules, transitions from $g \rightarrow u$ and $u \rightarrow g$ are allowed, but $g \rightarrow g$ and $u \rightarrow u$ are forbidden. An orbital is *g* if it has a center of inversion, and *u* if it does not. So looking at atomic orbitals, we see that *s* and *d* are *g*, while *p* orbitals are *u*: (see next page for definition of center of sym.)

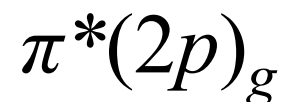
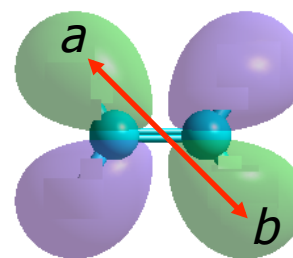


Parity (*g* or *u*) of molecular orbitals:

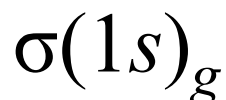
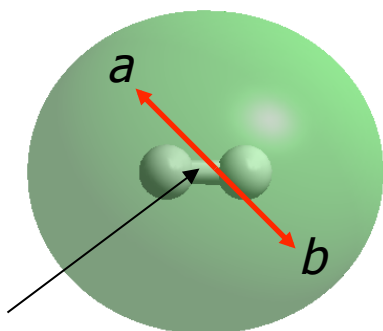
not a center
of inversion
 $a \neq b$
(sign of wave-
function is
opposite)



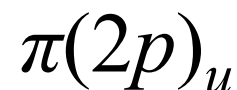
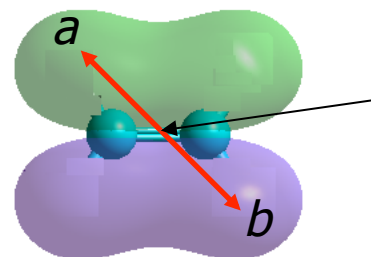
center of
Inversion
 $a = b$



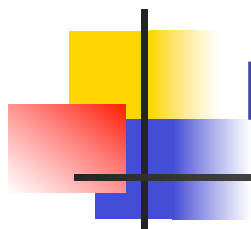
center of
inversion
 $a = b$



not a center of
inversion
 $a \neq b$

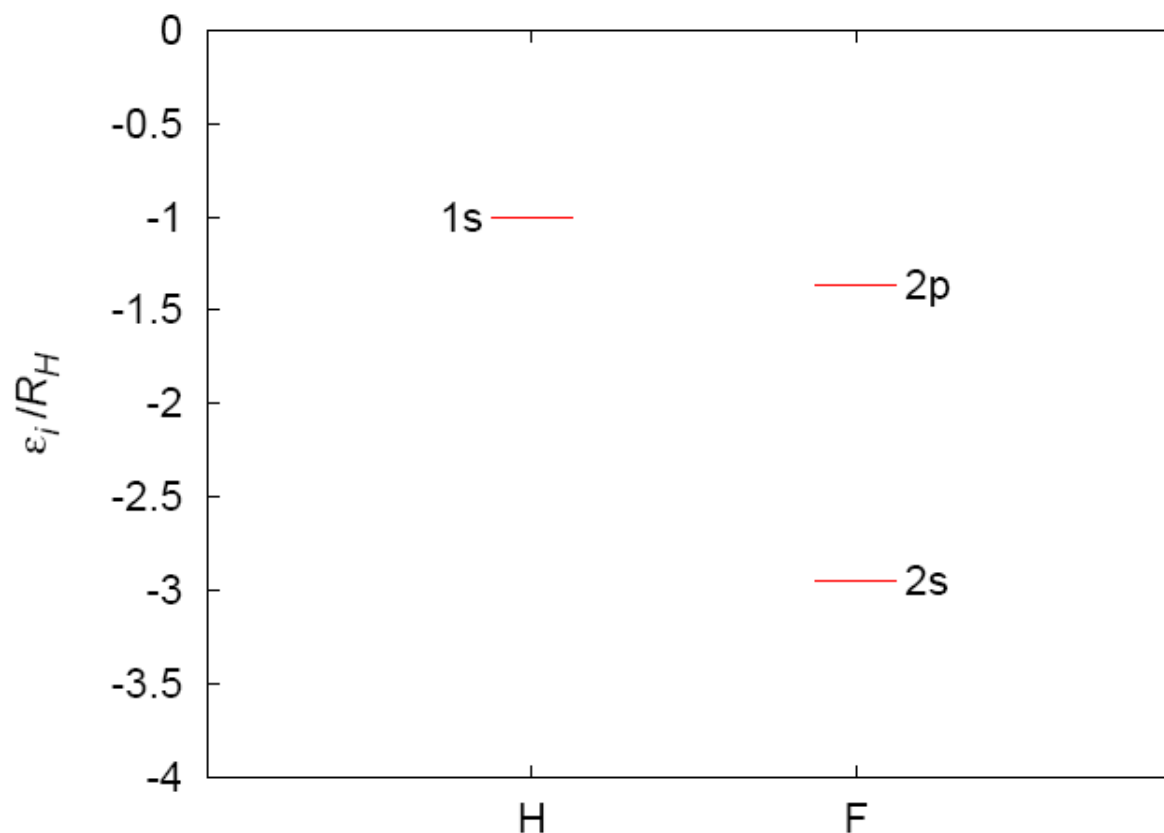


The test for whether an MO is *g* or *u* is to find the possible center of inversion of the MO. If two lines drawn out at 180° to each other from the center, and of equal distances, strike identical points (*a* and *b*), then the orbital is *g*.

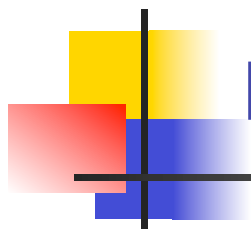


Molecular Orbitals for HF

- Consider the valence atomic orbitals of hydrogen and fluorine:

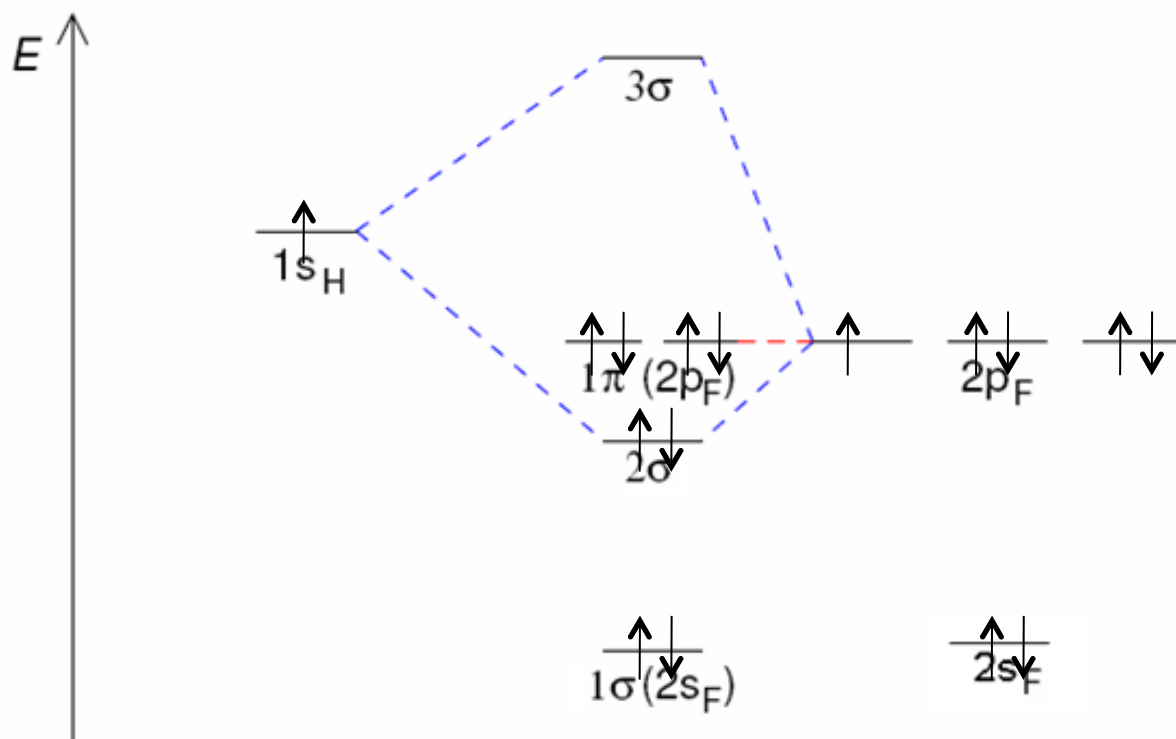


- Which AOs will combine to make MOs?
- Which AOs will not mix (and therefore still look like an AO)?



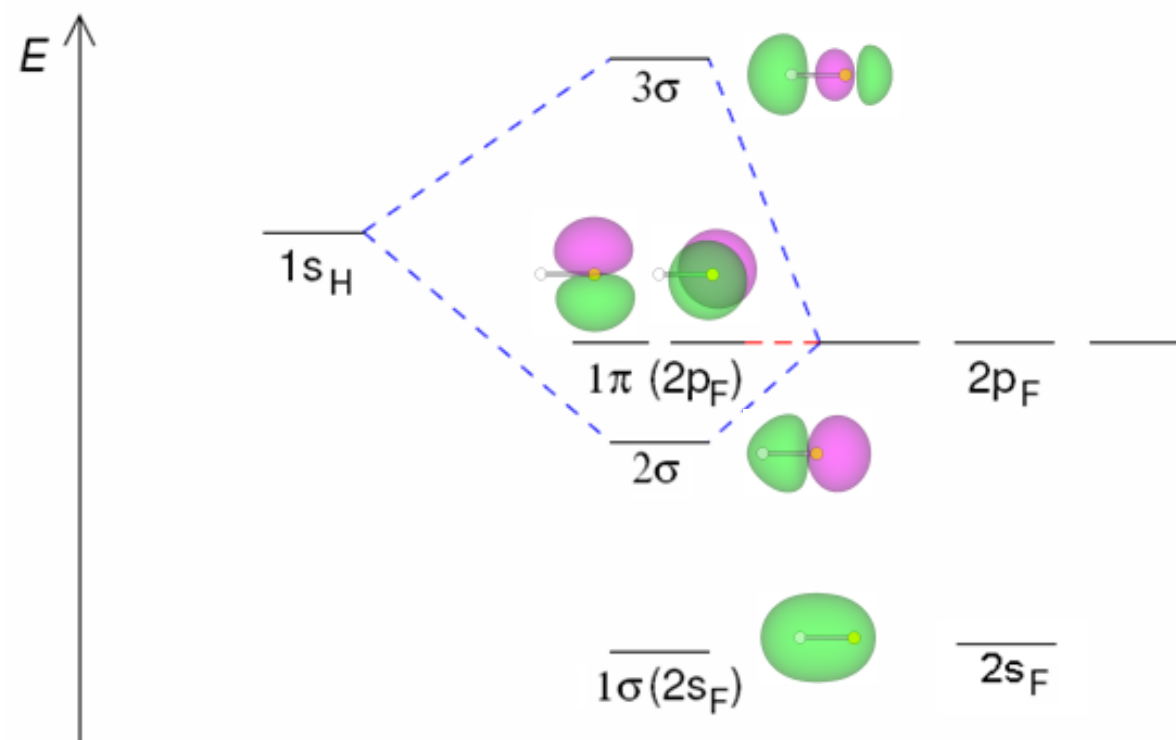
Molecular Orbitals for HF

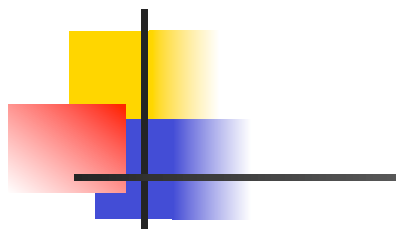
- Using symmetry and energy as our guide, we predict that we will make LCAO-MOs that look something like:



- There will still be orbitals with π symmetry in HF.

Molecular Orbitals for HF

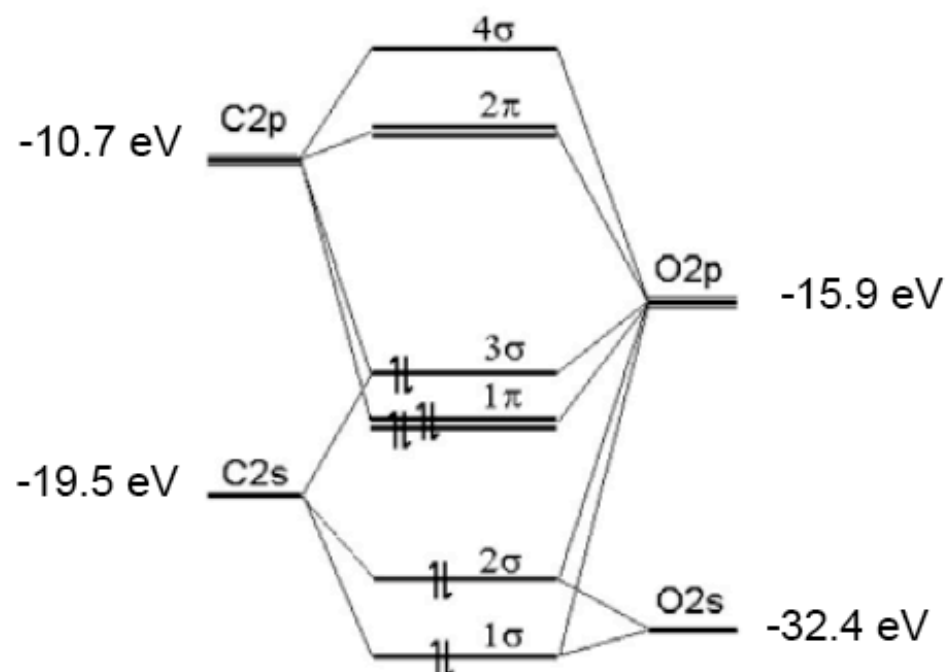




Valence Atomic Orbital Energies

Element	Orbital Potential Energy (eV)						
	1s	2s	2p	3s	3p	4s	4p
H	-13.6						
He	-24.5						
Li		-5.5					
Be		-9.3					
B		-14	-8.3				
C		-19.5	-10.7				
N		-25.5	-13.1				
O		-32.4	-15.9				
F		-40	-18.7				
Ne		-48.5	-21.6				
Na				-5.2			
Mg				-10.7			
Al				-13.1	-6		
Si				-15	-7.8		
P				-18.7	-10		
S				-20.7	-12		
Cl				-25.3	-13.7		
Ar				-29.3	-15.9		
K						-4.3	
Ca						-6.1	
Zn						-9.4	
Ga						-12.6	-6
Ge						-15.6	-7.6
As						-17.6	-9.1
Se						-20.8	-11
Br						-24.1	-12.5
Kr						-27.5	-14.3

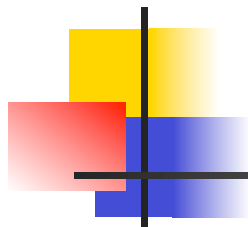
b) CO



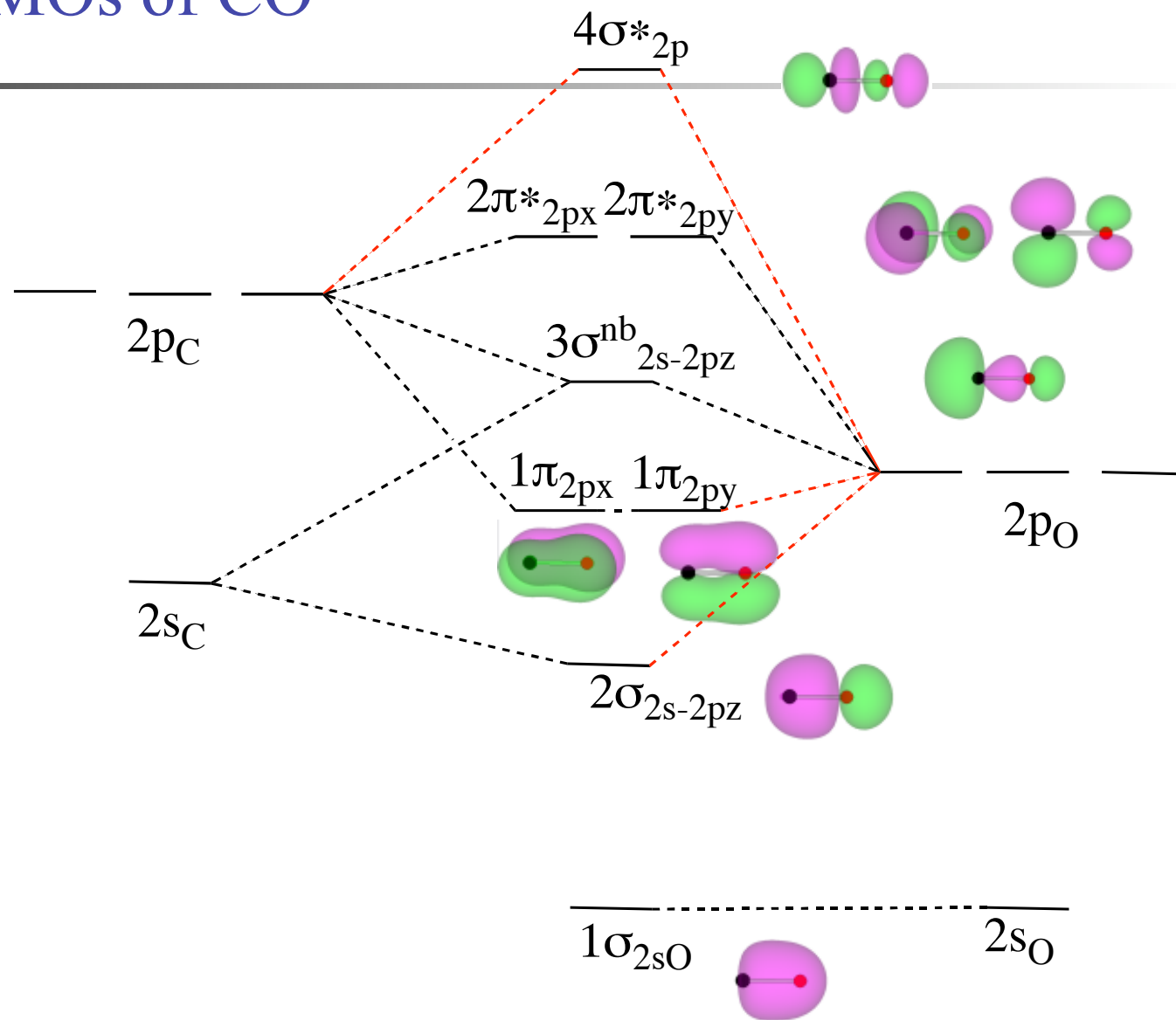
Orbitals: 1σ and 1π are bonding and 4σ and 2π are antibonding. The 2σ and 3σ orbitals are non-bonding.

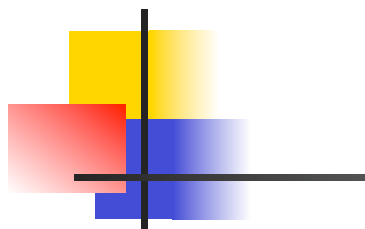
Electronic configuration: $(1\sigma)^2(2\sigma)^2(1\pi)^4(3\sigma)^2$

Bond order: $\frac{1}{2}(6-0) = 3$ [remember electrons in non-bonding orbitals count zero to the calculation].

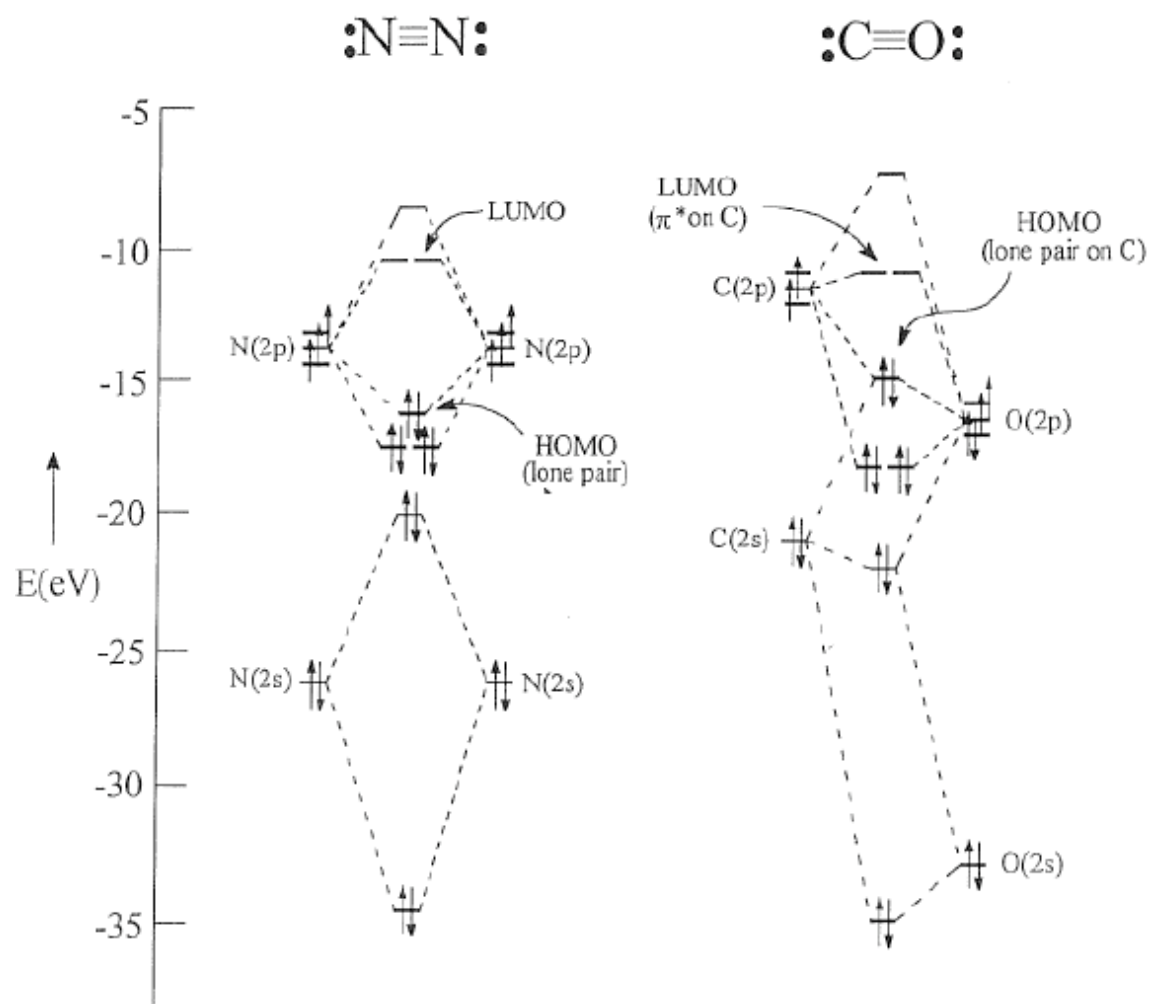


The MOs of CO



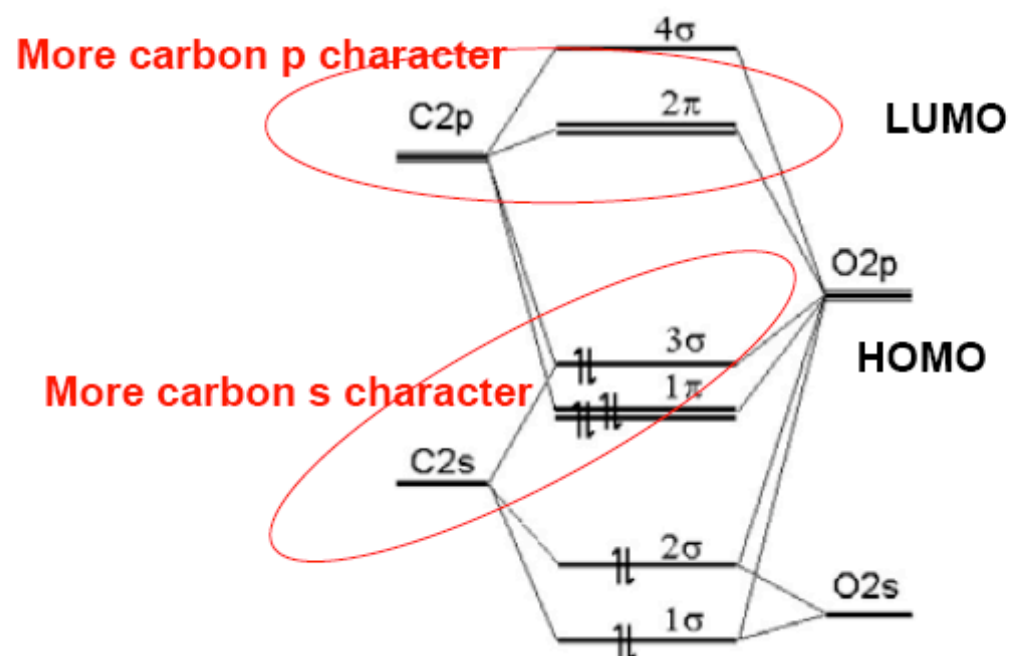


Comparison of A₂ and AB Diatomic Molecules



Frontier Orbitals

b) CO



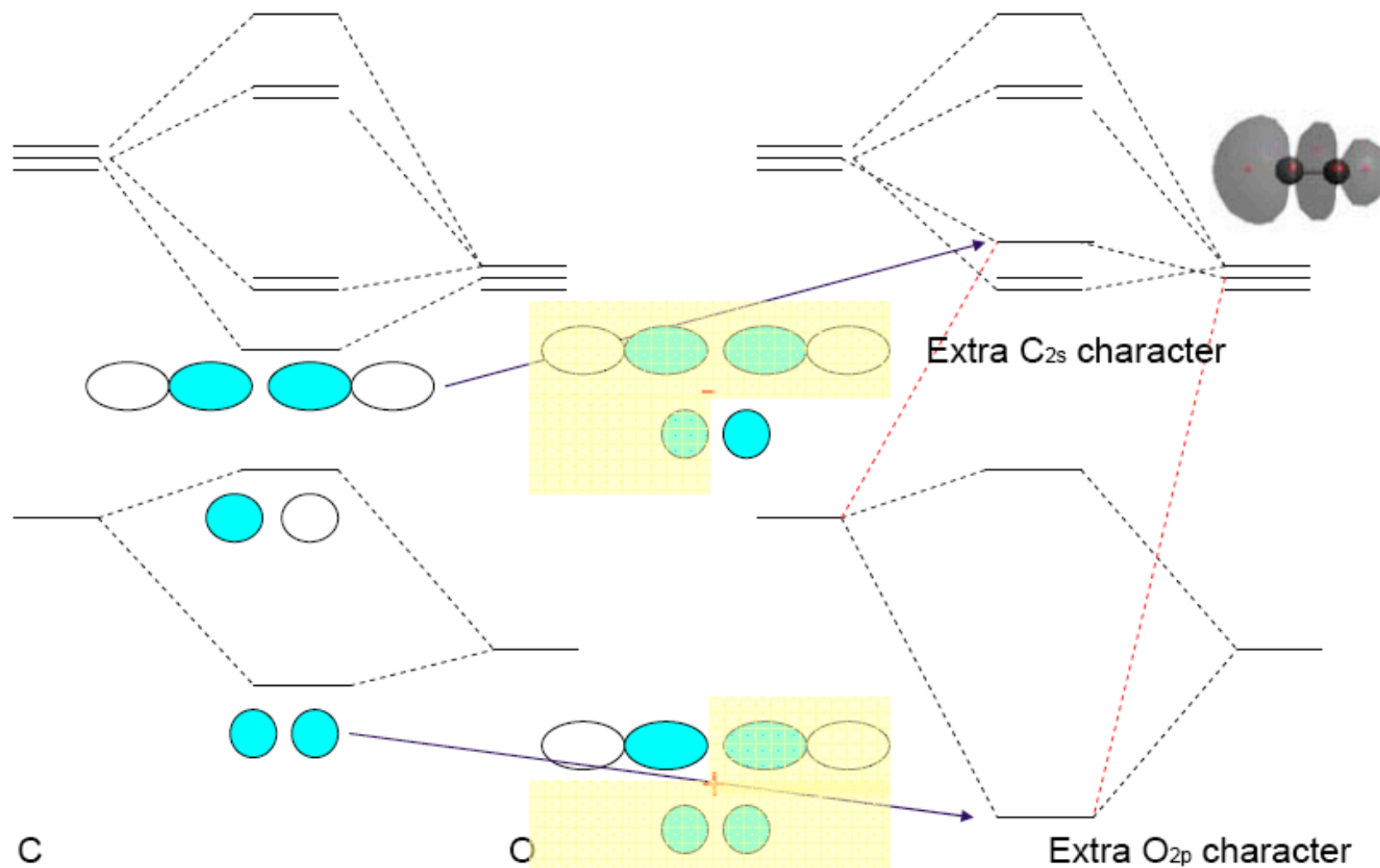
Orbitals: 1σ and 1π are bonding and 4σ and 2π are antibonding. The 2σ and 3σ orbitals are non-bonding.

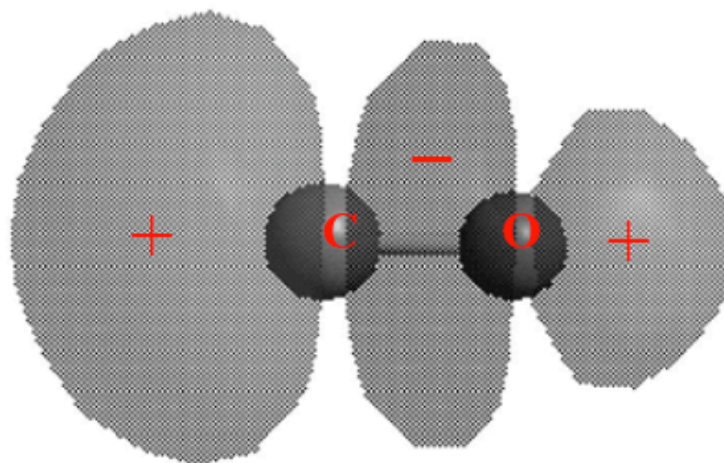
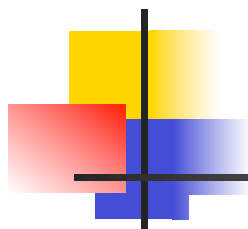
Electronic configuration: $(1\sigma)^2(2\sigma)^2(1\pi)^4(3\sigma)^2$

Bond order: $\frac{1}{2}(6-0) = 3$ [remember electrons in non-bonding orbitals count zero to the calculation].

CO,
without $C_{2s}-O_{2p_z}$ interaction

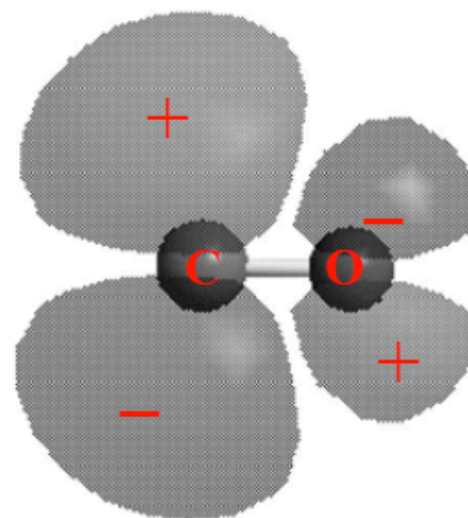
CO,
with $C_{2s}-O_{2p_z}$ interaction





HOMO (3σ)

CO



LUMO $2\pi^*$

N₂

LUMO

$1\pi_g$

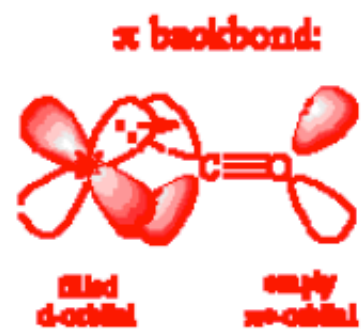
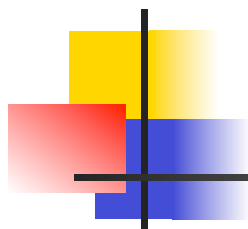


HOMO

$2\sigma_g$



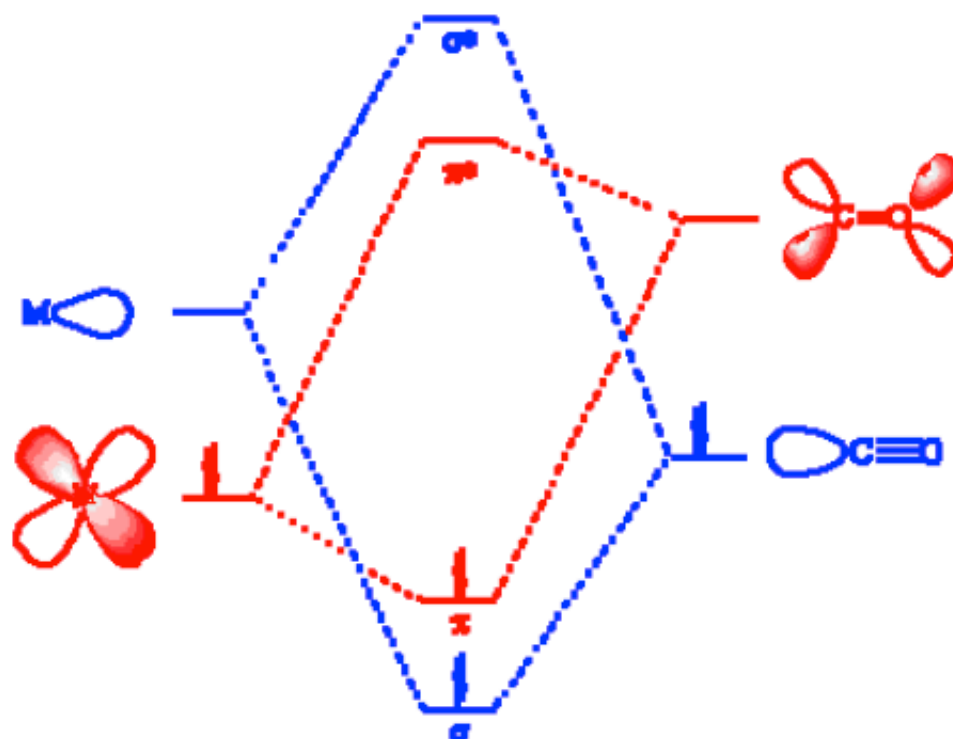
Relative non-bonding
Slightly bonding

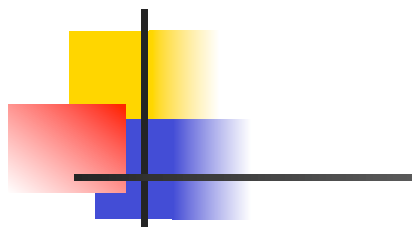


L_nM

$L_nM(CO)$

CO





Free $\text{C}\equiv\text{O}$

$d_{\text{CO}} = 1.128 \text{ \AA}$

$\nu_{\text{CO}} = 2143 \text{ cm}^{-1}$

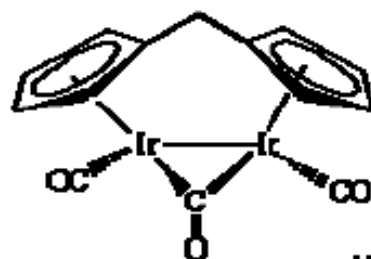
Terminal carbonyls $d_{\text{CO}} = 1.12\text{-}1.18 \text{ \AA}$

Ni(CO)_4 $\nu_{\text{CO}} = 2057 \text{ cm}^{-1}$

$(\text{PR}_3)_3\text{ClIr(CO)}$ $\nu_{\text{CO}} = 1960 \text{ cm}^{-1}$

Co(CO)_4^- $\nu_{\text{CO}} = 1886 \text{ cm}^{-1}$

μ_2 -Bridging carbonyls $d_{\text{CO}} = 1.17\text{-}1.22 \text{ \AA}$



$\nu_{\text{CO}} = 2002(\text{s}), 1959(\text{w}), \text{ and } 1776(\text{m}) \text{ cm}^{-1}$

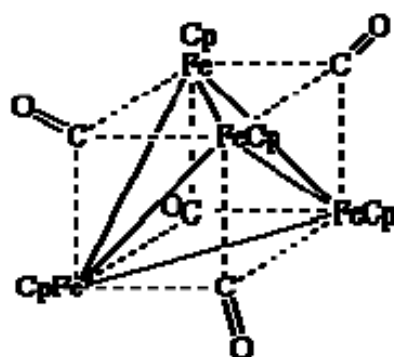
$d_{\text{CO}}(\text{bridge}) = 1.207(58) \text{ \AA}$

$d_{\text{CO}}(\text{terminal}) = 1.177(59) \text{ \AA}$

^{13}C : δ 203.4 (terminal), 171.40 (bridge)

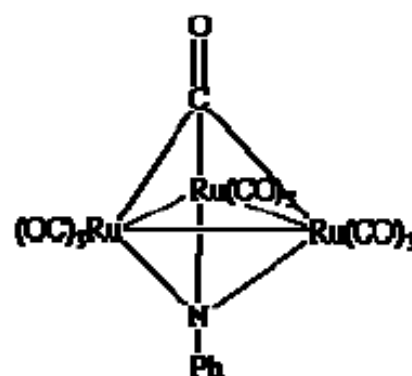
Notice that the $\text{C}=\text{O}$ bond is $\perp$ to the M-M bond

μ_3 -Bridging carbonyls $d_{\text{CO}} = 1.17\text{-}1.22 \text{ \AA}$



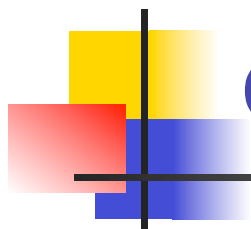
$\nu_{\text{CO}} = 1620 \text{ cm}^{-1}$

$d_{\text{CO}} = 1.197(7) - 1.209(7) \text{ \AA}$



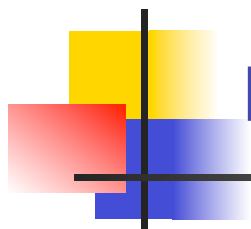
$\nu_{\text{CO}} = 2104(\text{m}), 2070(\text{s}), 2032(\text{vs})$

$2011(\text{s}), 1978(\text{w}), 1743 \text{ cm}^{-1}$



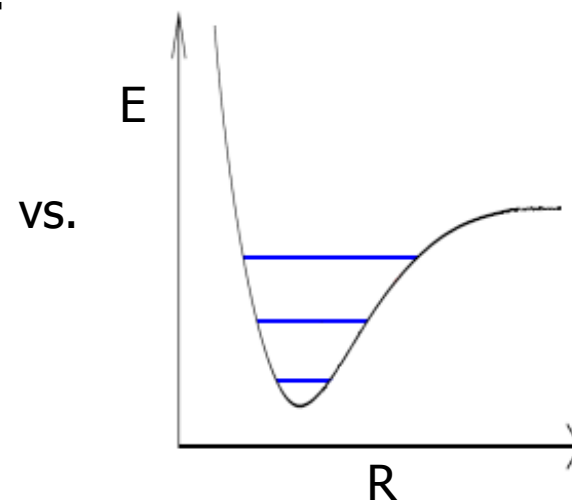
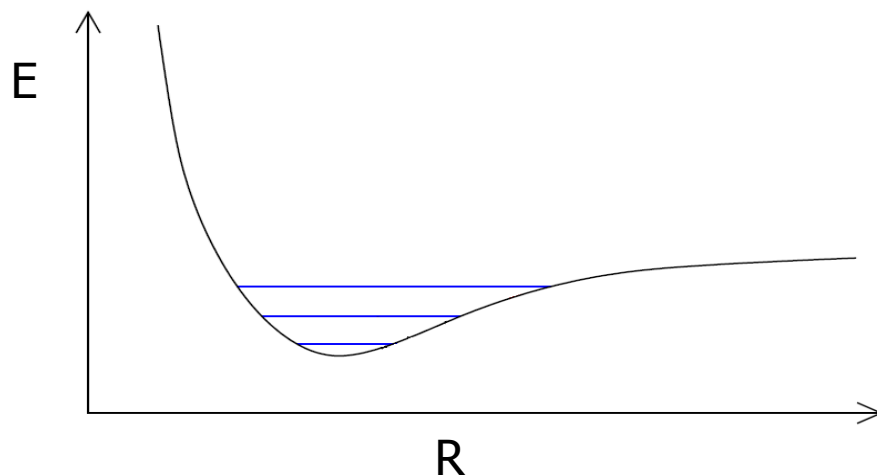
Computational Methods to Predict MOs

- Two computational techniques used to predict molecular orbitals are ***ab initio*** and **semi-empirical**:
 - *Ab initio* means “from the beginning” and refers to calculations made from first principles. (i.e. no simplifications). *Ab initio* calculations consider all electrons in a molecule.
 - Semi-empirical calculations only consider the valence electrons, replacing the nucleus and core electrons with a “core potential” which represents their effect on the valence electrons. These calculations tend to be much faster than the corresponding *ab initio* calculations and generally give relatively good molecular geometries. The MO diagrams that they predict are less accurate than those from an *ab initio* calculation, but generally have the MOs in the right order with roughly the right separations.
- The molecular geometries predicted by these techniques can be verified by X-ray crystallography and other analyses of the molecules themselves. The energies can be verified by spectroscopy.



Experimental Evidence for MO Predictions

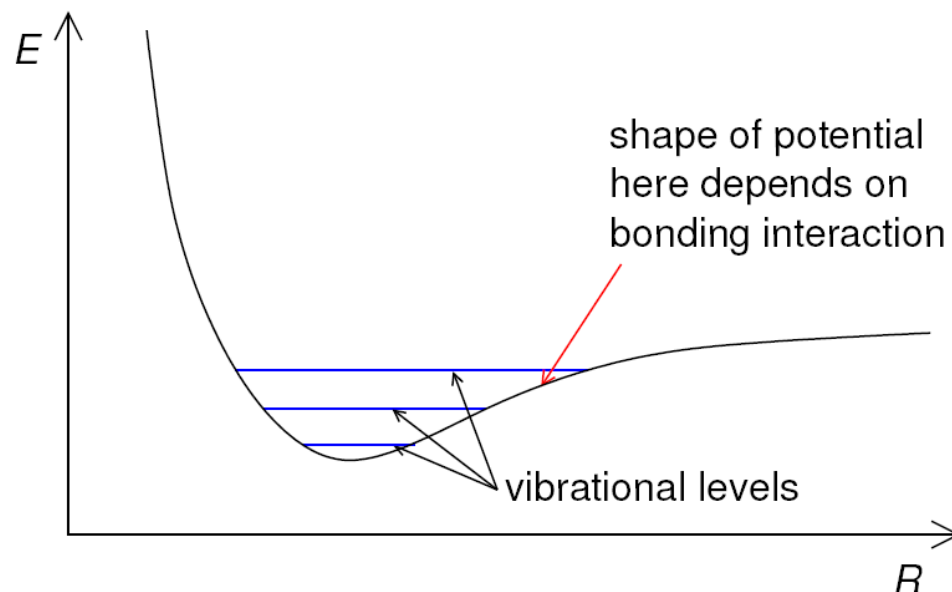
- Every possible electron configuration for a molecule gives a different potential energy curve. Why is this?
- The shape of a particular potential energy curve dictates the spacing between the different vibrational energy levels for the molecule. Compare a potential energy diagram for with a shallow well to one with a sharp well:



Which diagram corresponds to a more rigid bond?

Experimental Evidence for MO Predictions (IR)

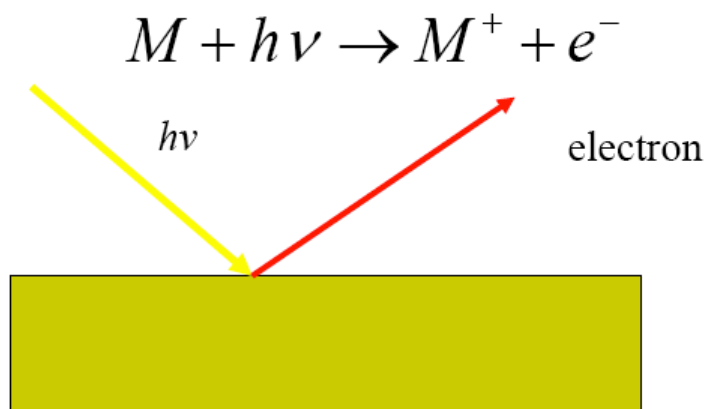
- We can study the shape of a potential energy diagram using vibrational spectroscopy in which photons of infrared light are absorbed by the molecule, exciting it from one vibrational state to another. This is also known as infrared spectroscopy, or IR.



- In practical terms, IR is used to identify the strength and rigidity of bonds. e.g. It readily discriminates between C-O and H-O bonds or between C-O and C=O bonds.

Experimental Evidence for MO Predictions (PES)

- Another form of spectroscopy can be used to corroborate the orbital occupancies predicted by MO theory – **photoelectron spectroscopy** (PES).
- The principles behind photoelectron spectroscopy are the same as those behind the photoelectric effect:

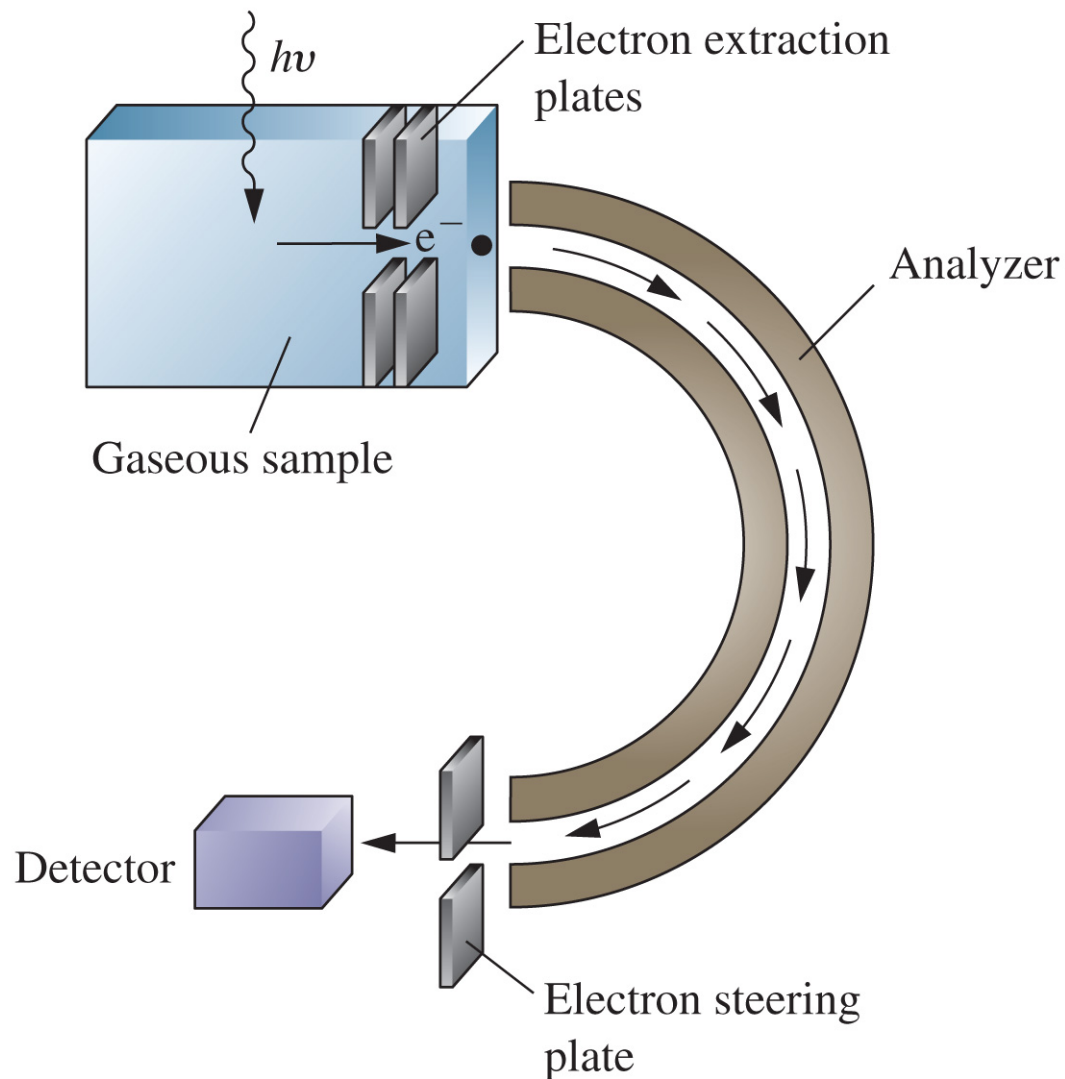


Photoelectric effect (Einstein)

$$h\nu = IE_M + \frac{1}{2}mv_e^2$$

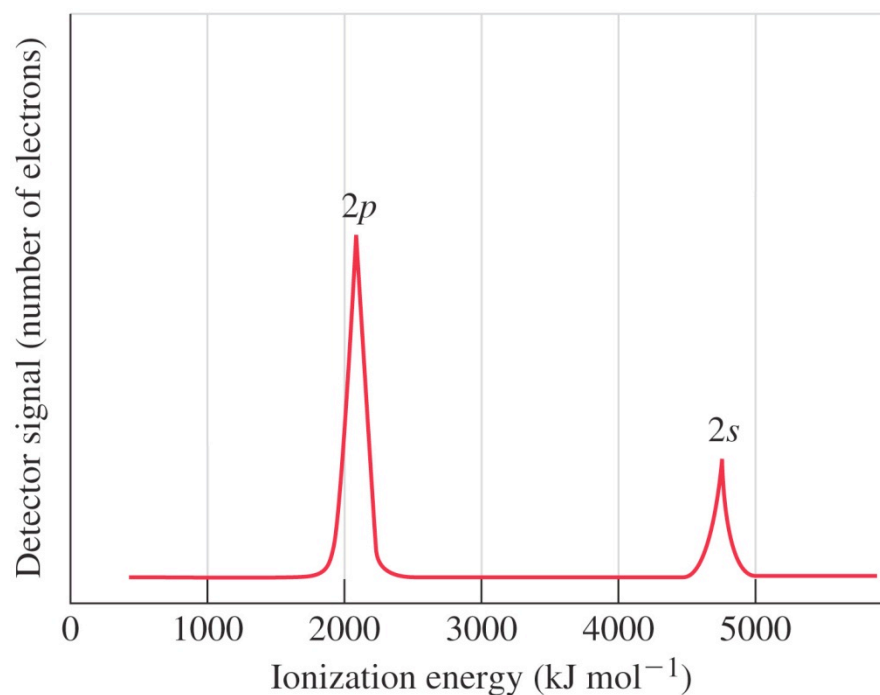
Experimental Evidence for MO Predictions (PES)

- A spectrometer is the instrument used for photoelectron spectroscopy.
- Since the energies being measured typically correspond to the energy of ultraviolet light, this is also called a UPES (ultraviolet photoelectron spectroscopy) spectrometer.



Experimental Evidence for MO Predictions (PES)

- The spectrum below is the result of performing photoelectron spectroscopy on a sample of neon gas (Ne):

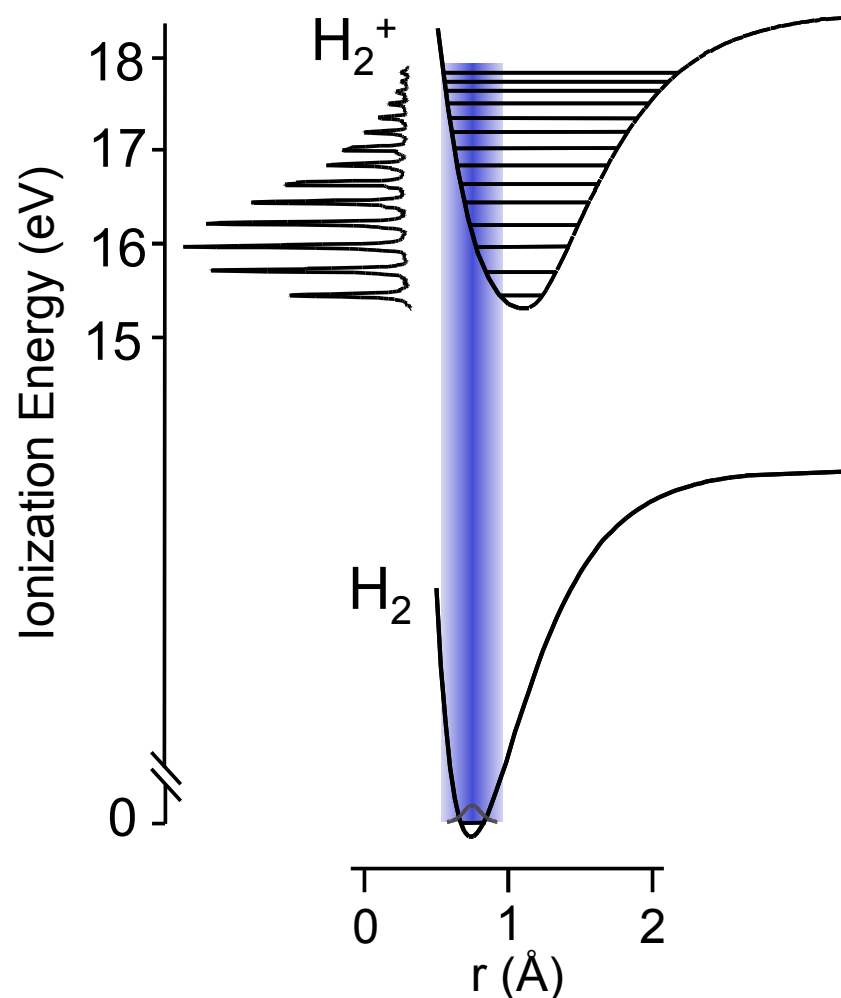


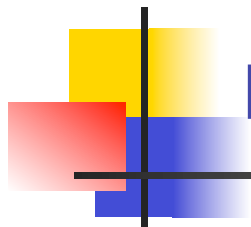
Copyright © 2007 Pearson Prentice Hall, Inc.

- This particular spectrum is very simple, showing only one line for each orbital, because a single atom of neon has no visible vibrations. Why not?

Experimental Evidence for MO Predictions (PES)

- The spectrum at the right (shown sideways) is more complex because there are vibrational energy levels in H_2 .
- If there were no vibrational energy levels, this would give the energy of an orbital directly (as it did for neon).
- In practice, we must account for the different vibrational energy levels in the cation produced. The photoelectron spectrum will have a band of many lines, each corresponding to the energy difference between a vibrational level of the initial molecule and a vibrational level of the cation:

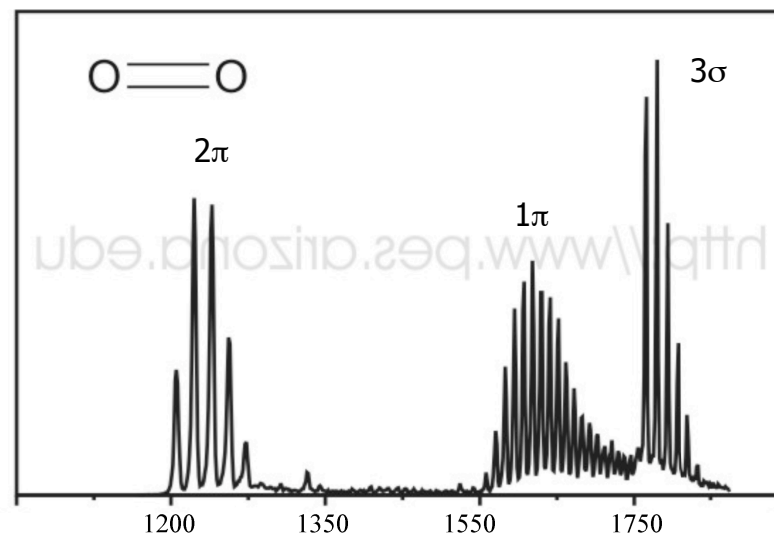
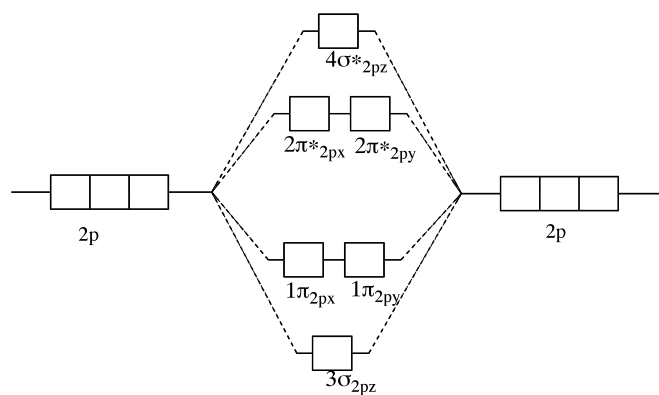
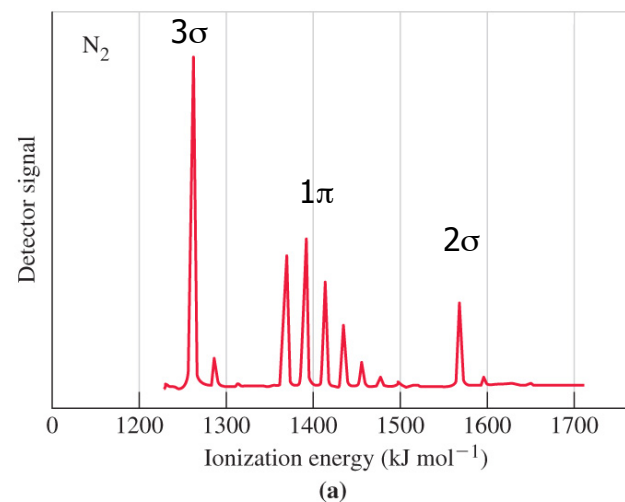
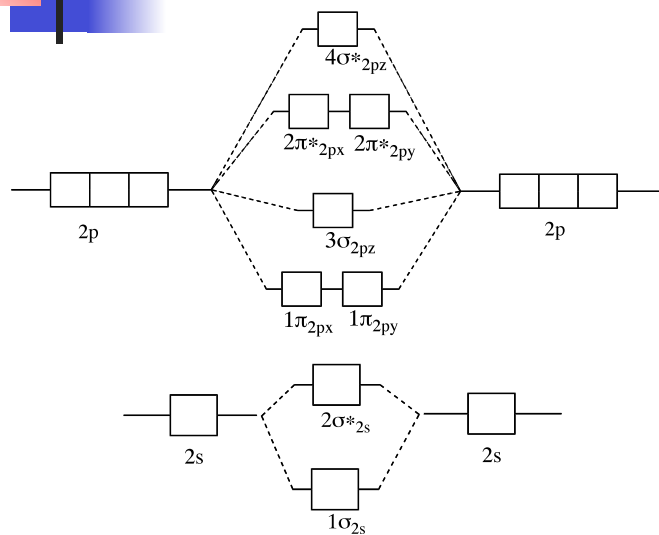




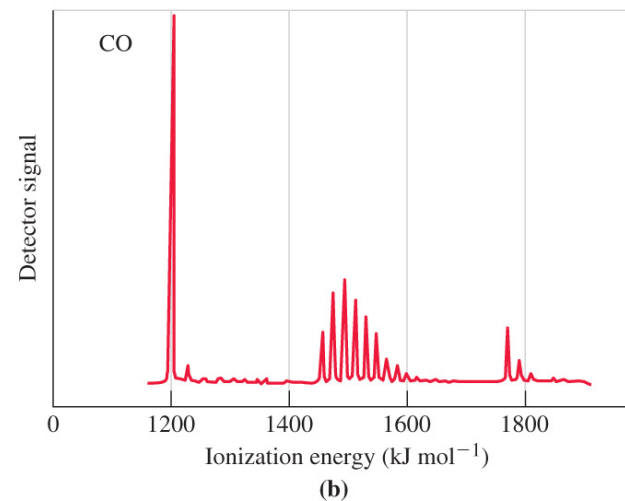
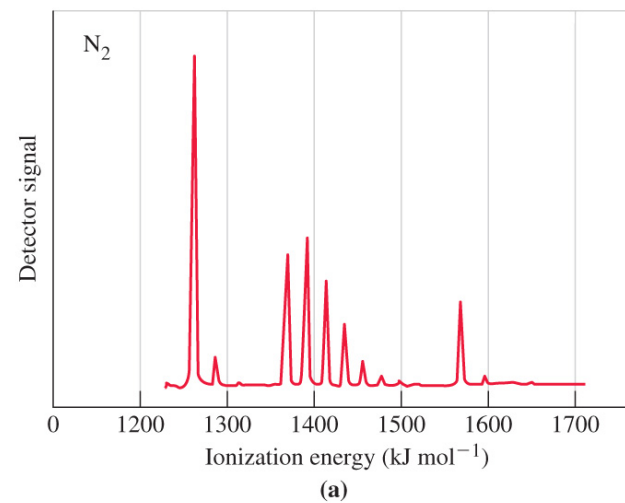
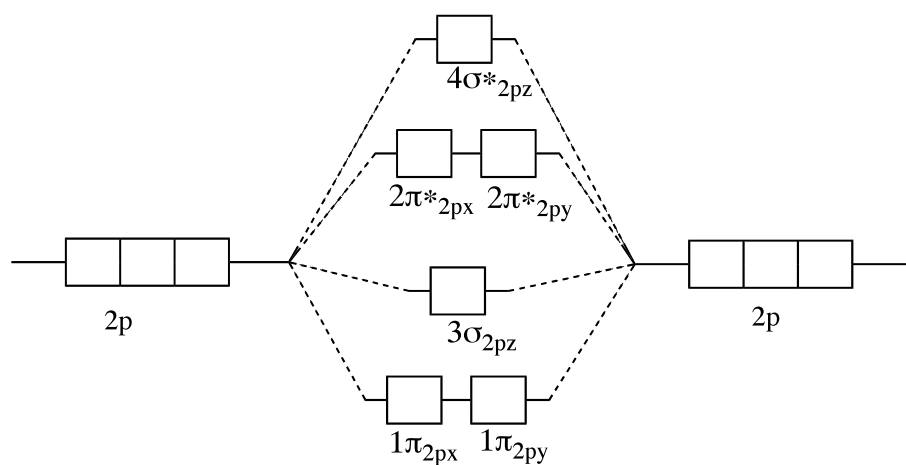
Experimental Evidence for MO Predictions (PES)

- This allows us to indirectly obtain a vibrational spectrum for the cation produced. Comparison of the two vibrational spectra tells us if/how the bond was affected:
 - If a nonbonding electron is removed, the shape of the potential energy diagram for the molecule changes little.
 - If a bonding electron is removed, the shape of the potential energy diagram changes drastically – indicating weakening of the bond.
 - If an antibonding electron is removed, the shape of the potential energy diagram again changes drastically – this time, indicating strengthening of the bond.
- Thus, photoelectron spectroscopy allows us to measure energies of orbitals – as well as confirming behaviour predicted by MO. 69

Experimental Evidence for MO Predictions (PES)



Experimental Evidence for MO Predictions (PES)



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