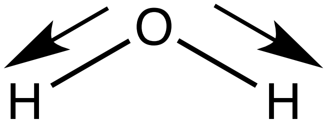
APPLICATIONS OF GROUP THEORY: SELECTED VIBRATIONAL MODES

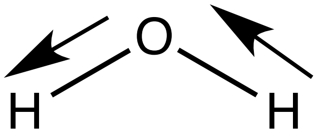
The three vibrational modes of H_2O: symmetry labels

- Symmetric stretch



3700 cm^{-1}, A_1

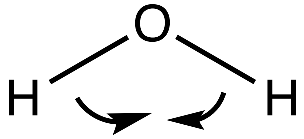
- Asymmetric stretch



3600 cm^{-1}, B_1

A_1 and B_1 describe vibrations in symmetry terms-we derived this!

- Symmetric bend



1600 cm^{-1}, A_1

You are not expected to derive what the vibrational modes look like, however if I give you a picture such as the ones above, you should be able to figure out what irreducible representation it corresponds to, or match vibrations to a given set of irreducible representations

Finding vibrational modes

1) **Find Γ_{3N}** The first step in this process is making a ***reducible representation*** of all possible molecular motions Γ_{3N} (aka Γ_{total})

2) **Use the reduction formula** *to determine irreducible representations that make up reducible representation* Γ_{3N}

3) **Determine which representations represent translational and rotational movements, the remaining are vibrations**

4) **Determine if any of the vibrations are IR or Raman active**

This procedure takes into account ALL of the atoms in a molecule!

Simplified procedure for looking only at selected vibrational modes

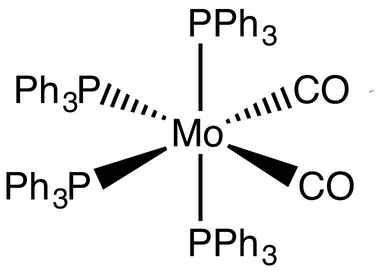
- A shortcut that allows you to look at just the vibration of selected bonds as opposed to all the possible motions of a molecule
- Often used for the study of metal-carbonyl complexes due to the unique stretching frequency of $C\equiv O$

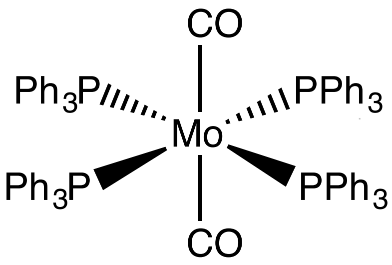
- Instead of analyzing ALL molecular motions (x,y,z for all atoms) , just the $C\equiv O$ units are analyzed to make the reducible representation
  - Can help distinguish between different isomers! See MFT for examples

Application 2: Molecular Vibrations and Vibrational Spectroscopy

- Thus, for these compounds, we don’t have to analyze the motions of all 140 atoms in the molecule, we can simply look at how the COs transform with the different symmetry operations-much simpler!!

IR spectra (CO region) of *cis* vs *trans* $Mo(PPh_3)_4(CO)_2$





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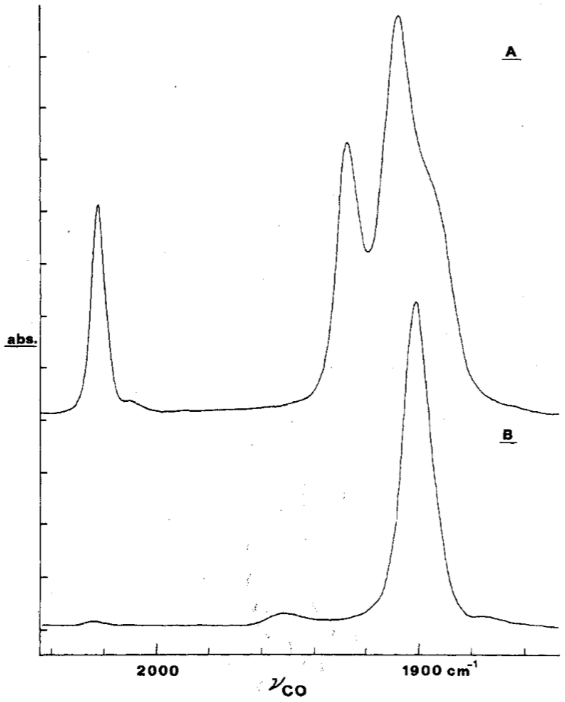


Figure 1. Infrared spectra in the CO stretching region in tetrachloroethylene of $Mo(CO)_4[PPh_3]_2$: A, *cis*-$Mo(CO)_4[PPh_3]_2$; B, *trans*-$Mo(CO)_4[PPh_3]_2$.

Simplified procedure for looking only at selected vibrational modes

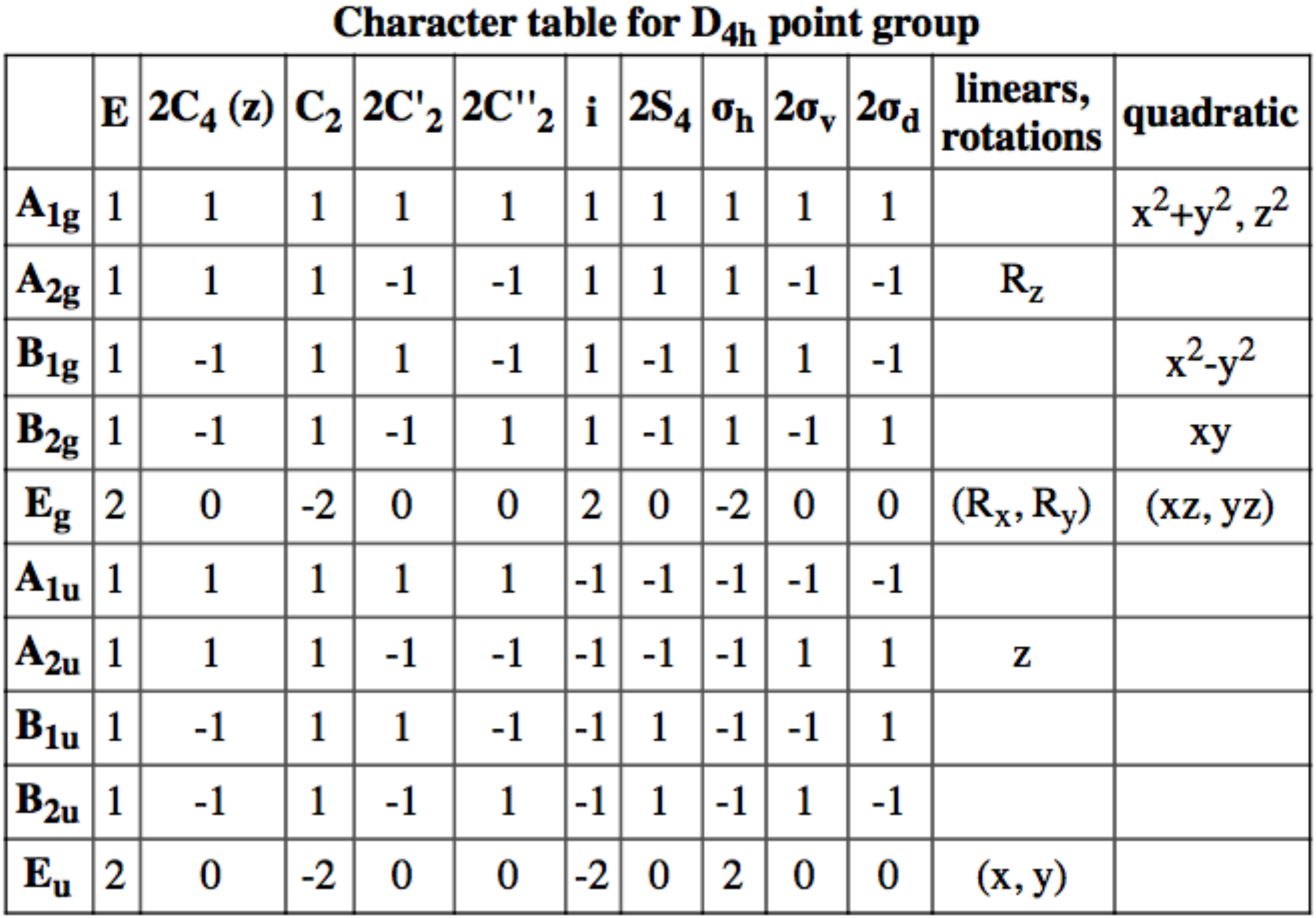
This procedure is much simpler, looks only at specific bonds in a molecule:

1) Determine $\Gamma_{A\text{-}B}$ (how many A-B bonds are unmoved?)

   In the case of CO bonds, we call this Γ_{CO}

2) Use reduction formula to find irreducible representations.

3) Determine how many IR and Raman active stretches there are based off the irreducible representations



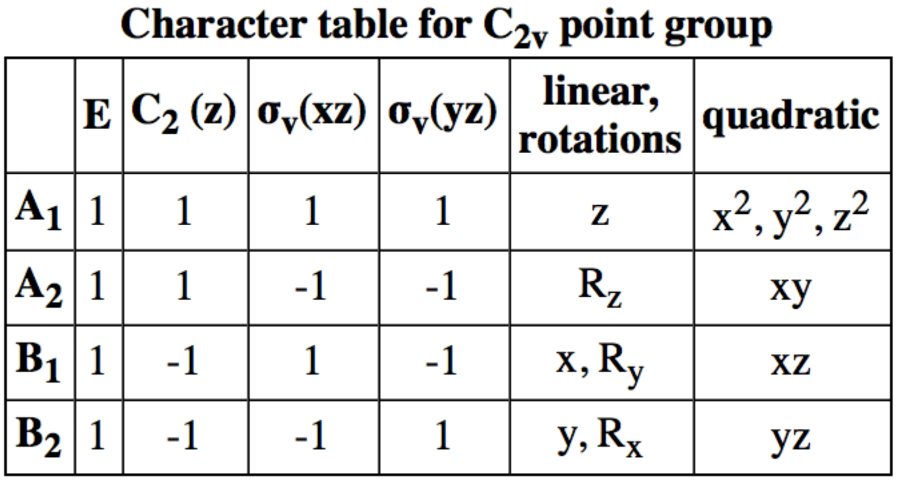
Character table for D_{4h} point group

	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

square planar $M(CO)_4$

Example, square planar $M(CO)_2Cl_2$: cis or trans configuration?
Is it in the C_{2v} point group or D_{2h} point group?

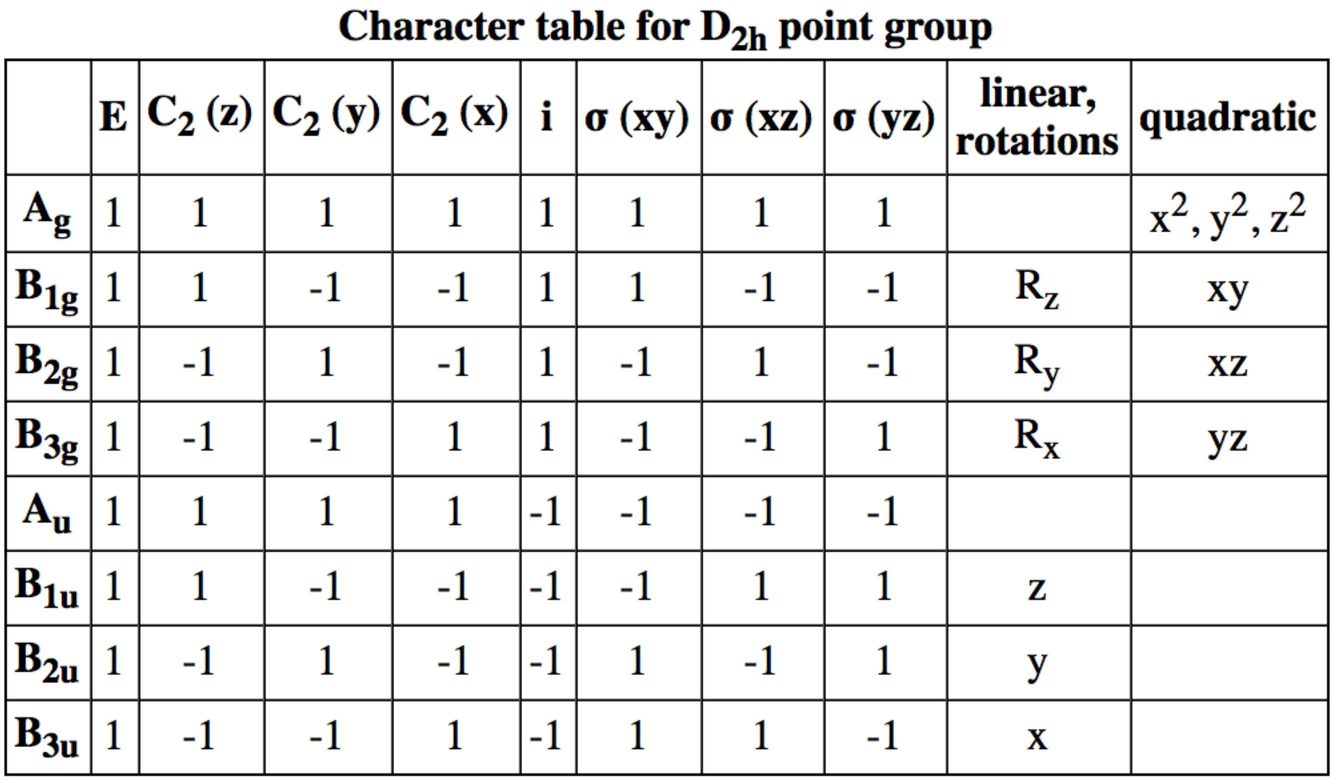
cis-$M(CO)_2Cl_2$



Character table for C_{2v} point group

	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

trans-$M(CO)_2Cl_2$



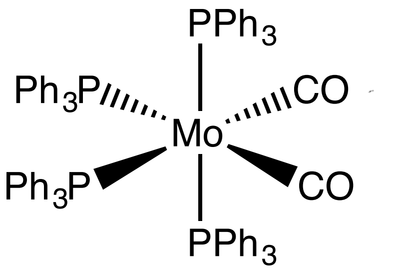
Character table for D_{2h} point group

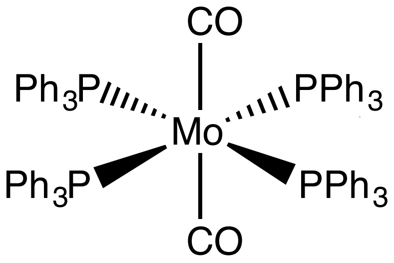
	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

Application 2: Molecular Vibrations and Vibrational Spectroscopy

- You should be able the same procedure to figure out the number of theoretical CO stretches for these two molecules!

IR spectra (CO region) of *cis* vs *trans* $Mo(PPh_3)_4(CO)_2$





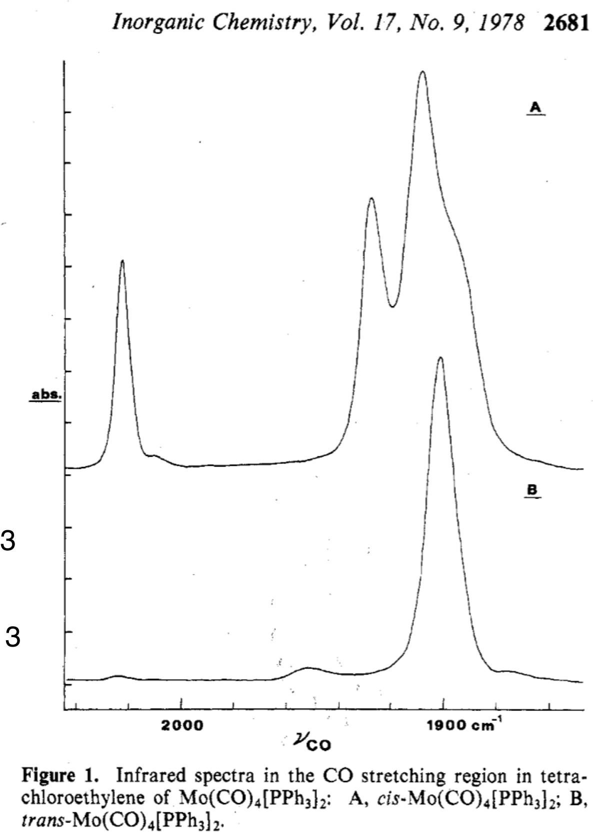

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Figure 1. Infrared spectra in the CO stretching region in tetrachloroethylene of $Mo(CO)_4[PPh_3]_2$: A, *cis*-$Mo(CO)_4[PPh_3]_2$; B, *trans*-$Mo(CO)_4[PPh_3]_2$.

Summary/Outlook

- You should now be able to use the symmetry of a molecule along with its character table to determine the representations for translational, rotational, and vibrational modes.

- MFT has an example for XeF_4 in Section 4.4. Apply the methods we've demonstrated today to determine Γ_{3N}, $\Gamma_{\text{translational}}$, $\Gamma_{\text{rotational}}$, $\Gamma_{\text{vibrational}}$ and which of the vibrations are IR and Raman active.

- There are also examples for selected vibrational modes.
- More practice problems will be posted on Piazza

Next

- Molecular orbitals! (Mos)
- We will use these same symmetry treatments, including finding reducible representations and using the reduction formula, to help derive what MOs look like for molecules with more than 2 atoms

MOLECULAR ORBITALS

MFT Chapter 5

What are molecular orbitals (MOs)?

- Just like the electrons in atoms can be described as wavefunctions (Schrödinger eqn!), the electrons in molecules can be described by wavefunctions as well

- To approximate these molecular wavefunctions, AKA ***molecular orbitals***, we can think of the molecular orbitals as a **linear combination of the atomic orbitals (LCAO)** that belong to each individual atom.

$$\Psi = c_a \Psi_a + c_b \Psi_b$$

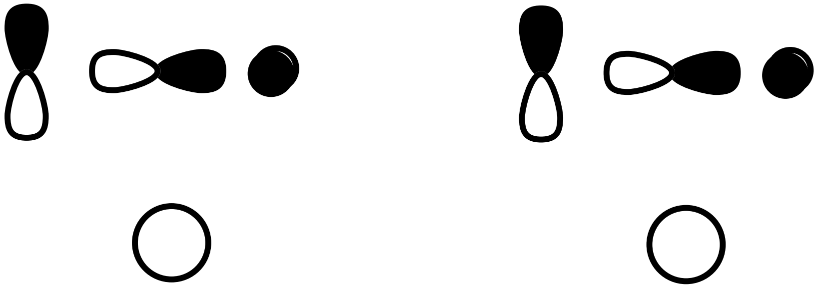
Requirements for forming a MO

In order for an MO to form, there must be sufficient *overlap* between atomic orbitals.

Requirements for overlap

1) The symmetry of the orbitals must be such that regions with the same sign (shaded or not shaded) overlap.
2) The energies of the orbitals must be similar to have significant overlap.
3) The physical distance between the two atoms must be short enough to ensure overlap.

Requirements for forming a MO

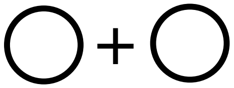


1) The symmetry of the orbitals must be such that regions with the same sign (shaded or not shaded) overlap.

Which of the following atomic orbital combinations satisfy this rule for the generic molecule A_2?

A — A

1



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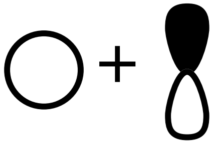

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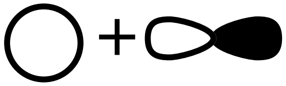

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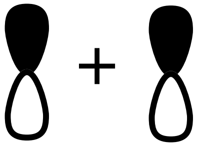

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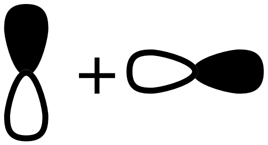
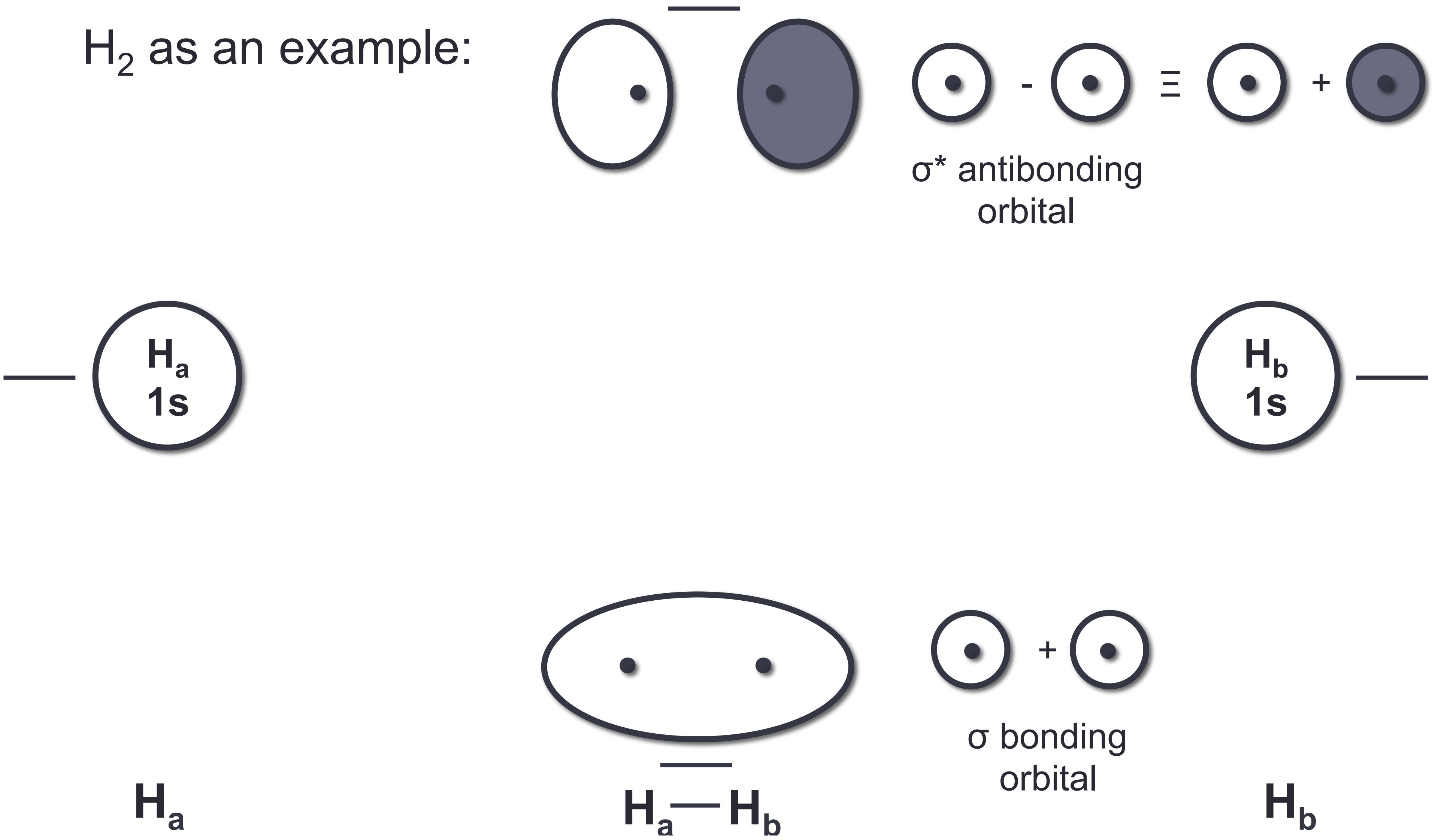


Forming MOs from s orbitals

H_2 as an example:



σ* antibonding orbital

H_a 1s

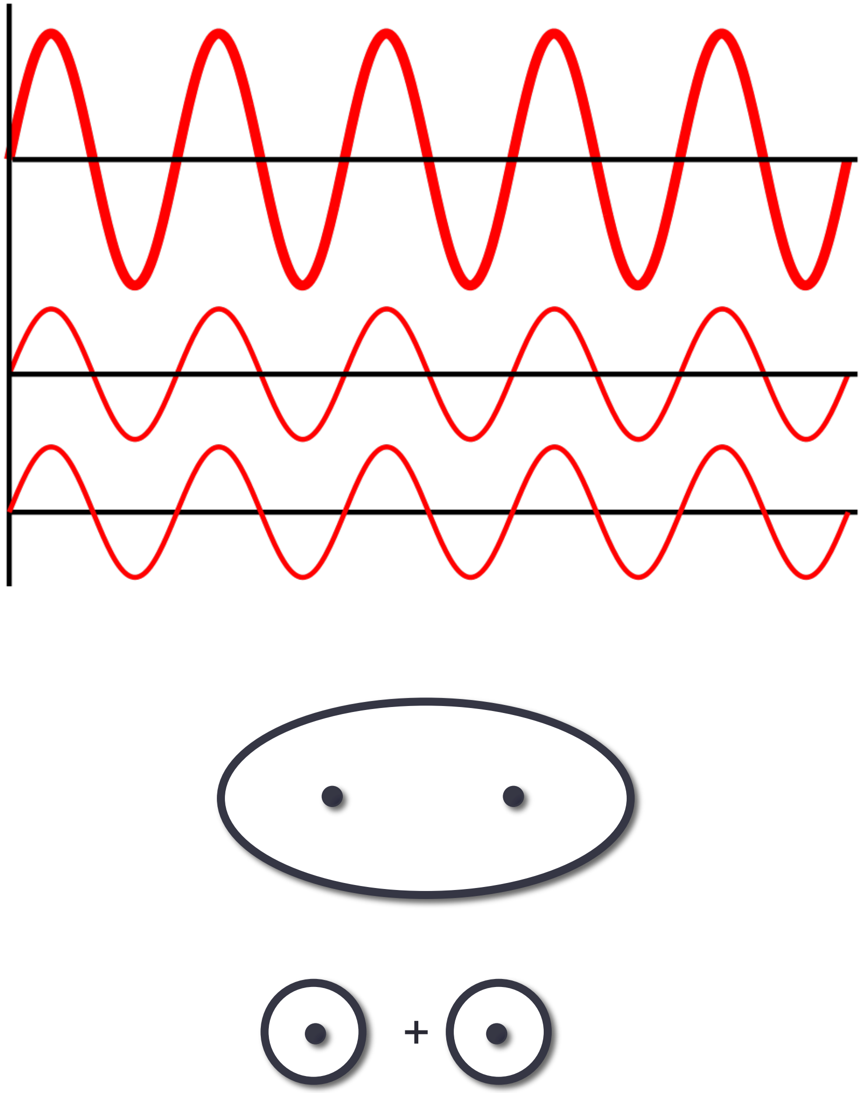
H_b 1s

σ bonding orbital

H_a

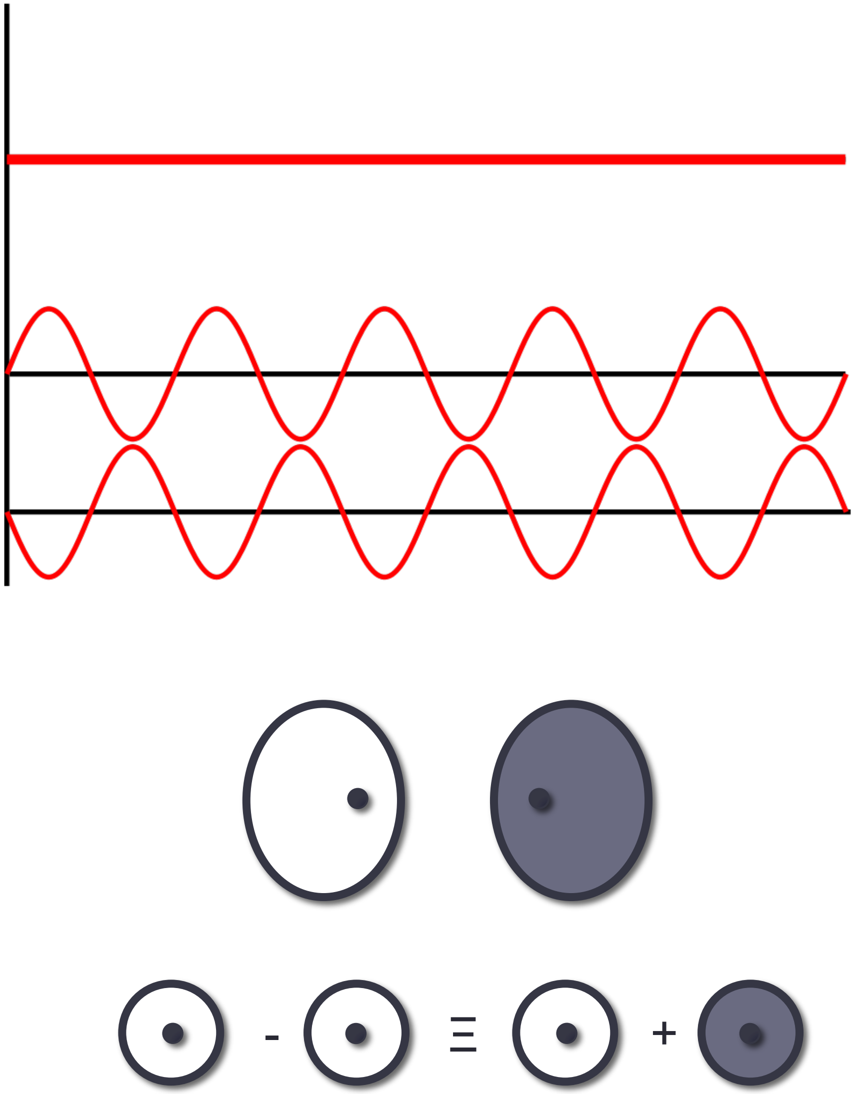
H_a—H_b

H_b



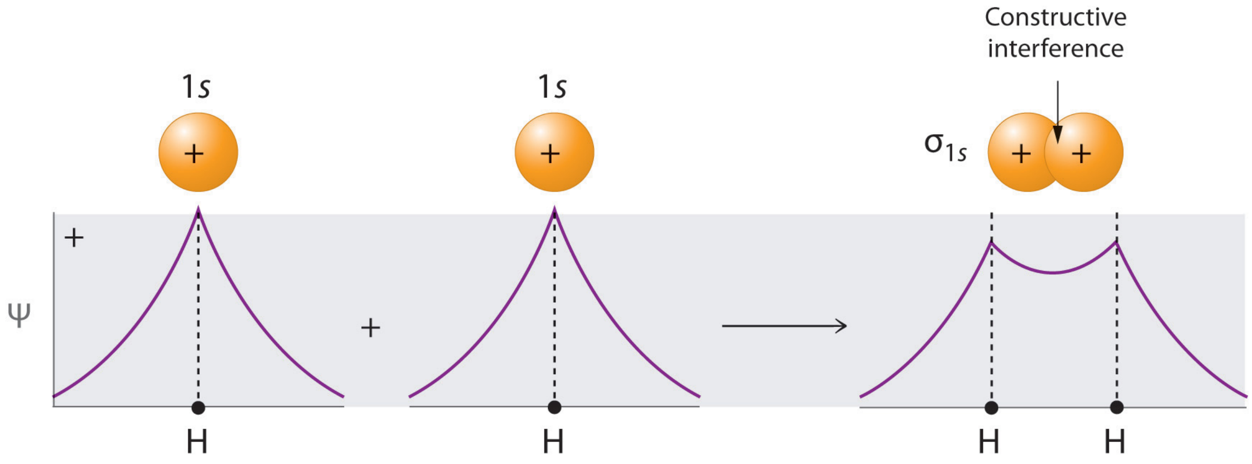
σ bonding
orbital

constructive interference

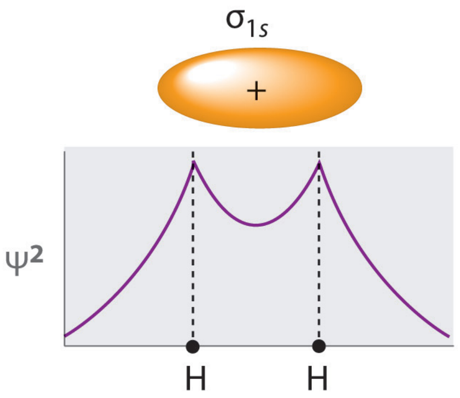


σ* antibonding
orbital

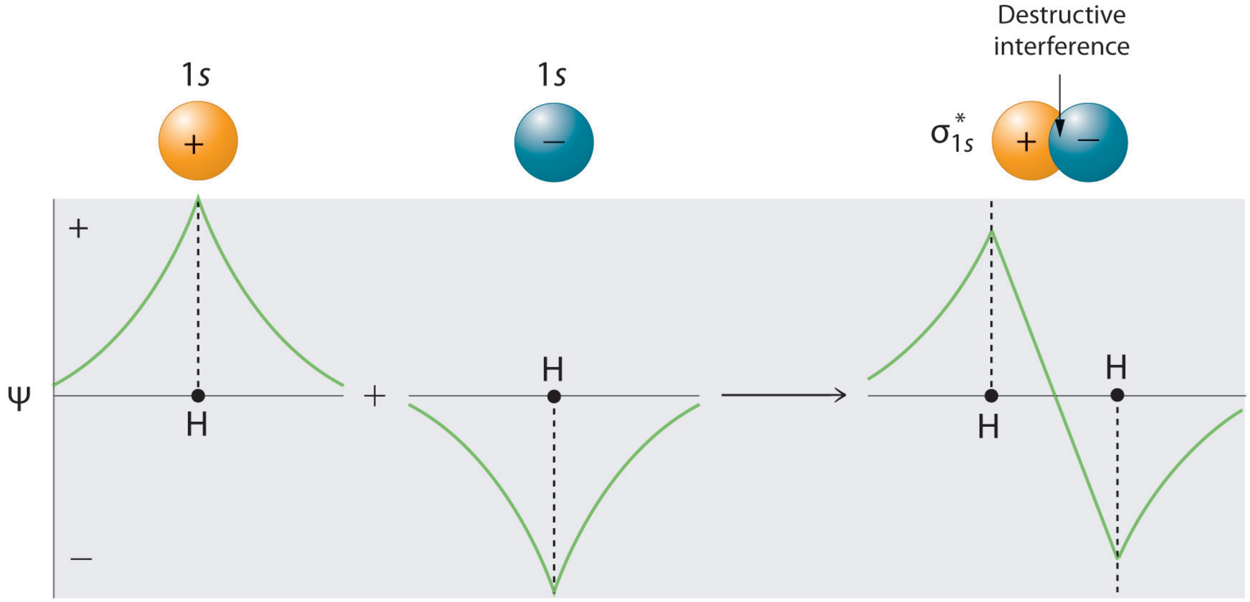
destructive interference



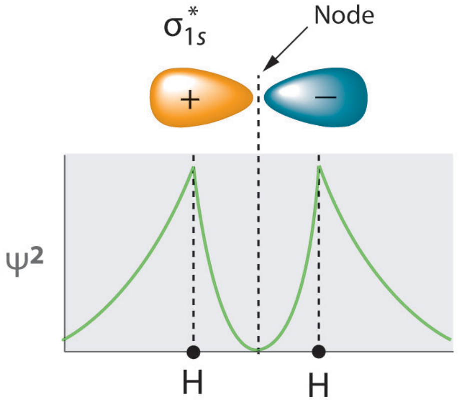
(a) Wave functions combined for σ_{1s}



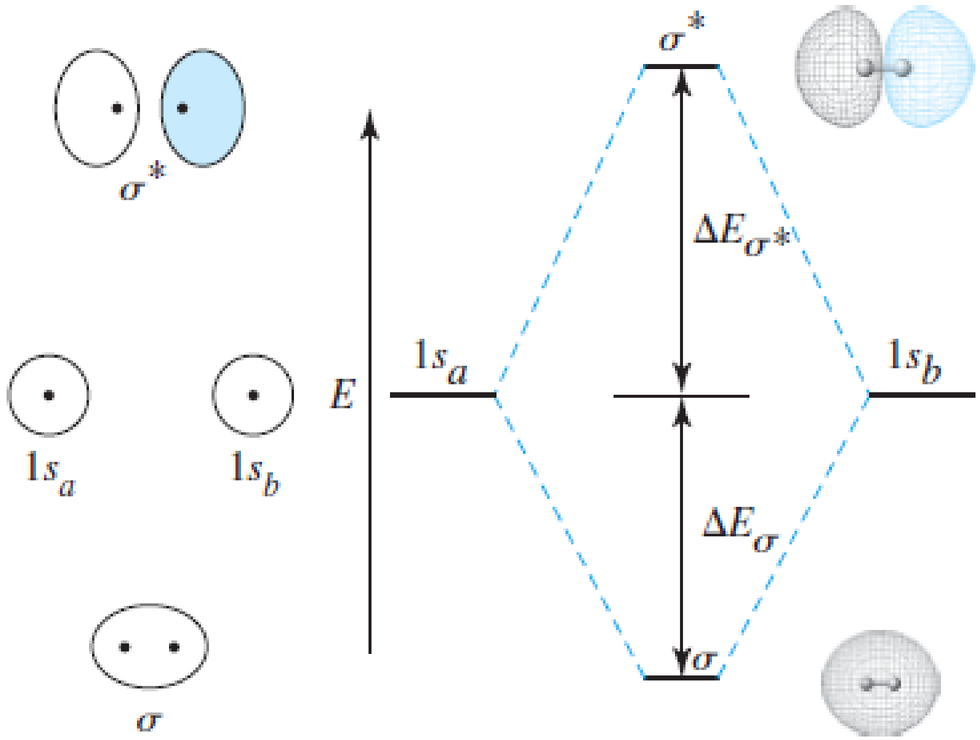
(b) Bonding probability density



(c) Wave functions combined for σ^*_{1s}



(d) Antibonding probability density



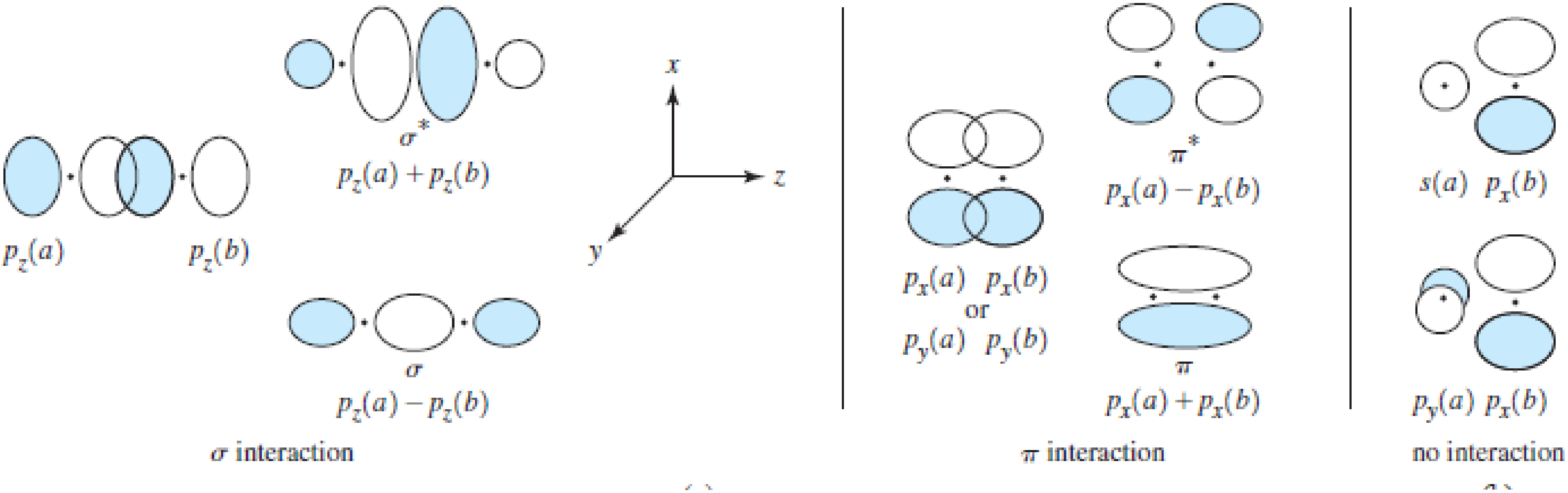
Sigma (σ) bond: Symmetric to rotation about the line connecting the nuclei

Bonding orbital: lower in energy than original atomic orbitals, has increased electron concentration in between two nuclei.

Antibonding orbital: higher in energy than original atomic orbitals, has a node in between two nucei

Forming MOs from p orbitals

p orbitals can form either σ or π (pi) bonds

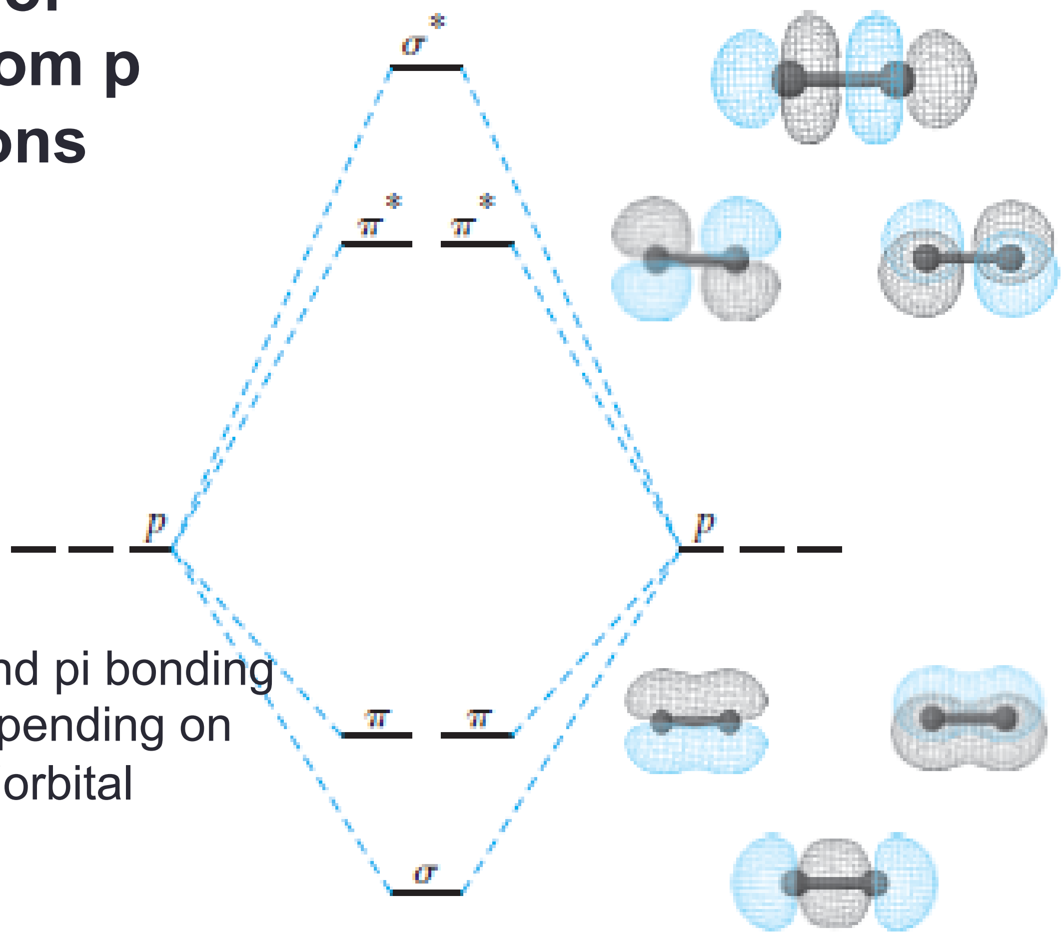


σ and σ* forms between p_z orbitals (z axis is typically chosen as primary axis for bond)

π and π* forms between p_x orbitals, same for p_y orbitals

π bond: contains a node directly along line that joins two nuclei, is antisymmetric with respect to C_2 along bond axis

Relative energy of different MOs from p orbital interactions



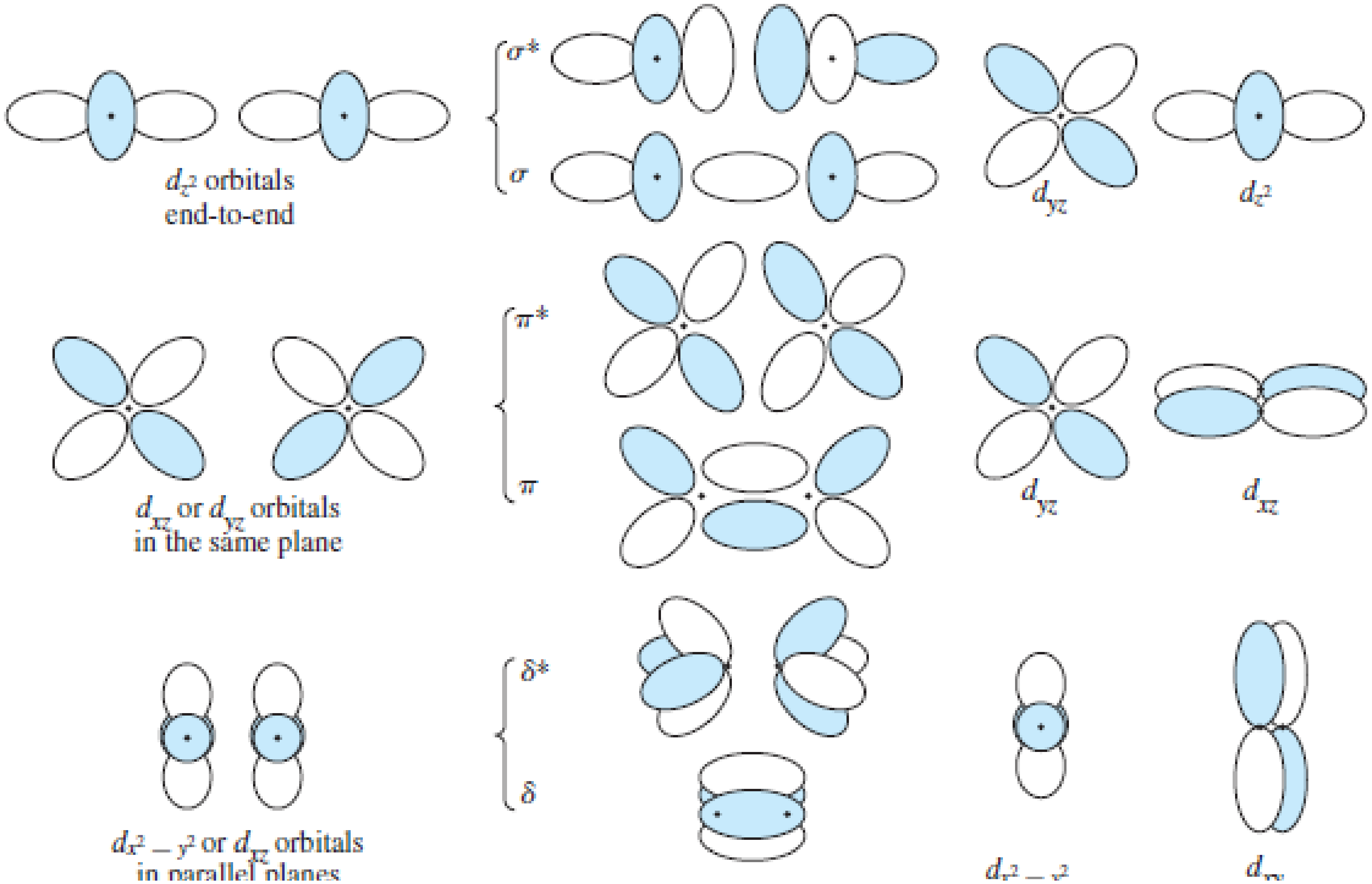
(c)

Note: order of sigma and pi bonding orbitals can change depending on the specific atom (see ‘orbital mixing’)

Note: orbitals with more nodes are higher in energy

Forming MOs from d orbitals

d orbitals can form either σ, π, and δ (delta) bonds



δ bond: contains two nodes directly along line that joins two nuclei, is antisymmetric with respect to C_4 along bond axis

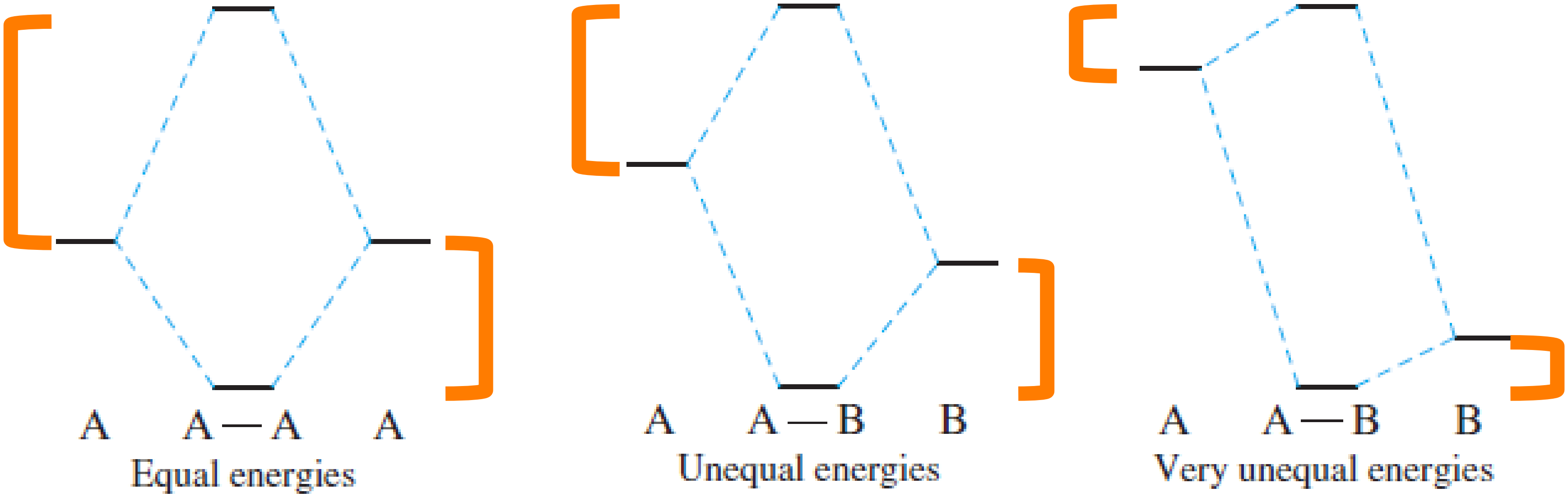
Nonbonding orbitals

- These orbitals are approximately the same energy as their corresponding atomic orbitals

- More info once we get begin building MO diagrams for molecules

Relative energy of atomic orbitals is important!

- Orbitals closest in energy will have the most stabilized bonding orbitals and destabilized antibonding orbitals →interaction is strong
- Orbitals with very different energies will have weak interactions
- Strong interactions and stabilized bonding orbitals provide driving force for bonds to form



Requirements for forming a MO

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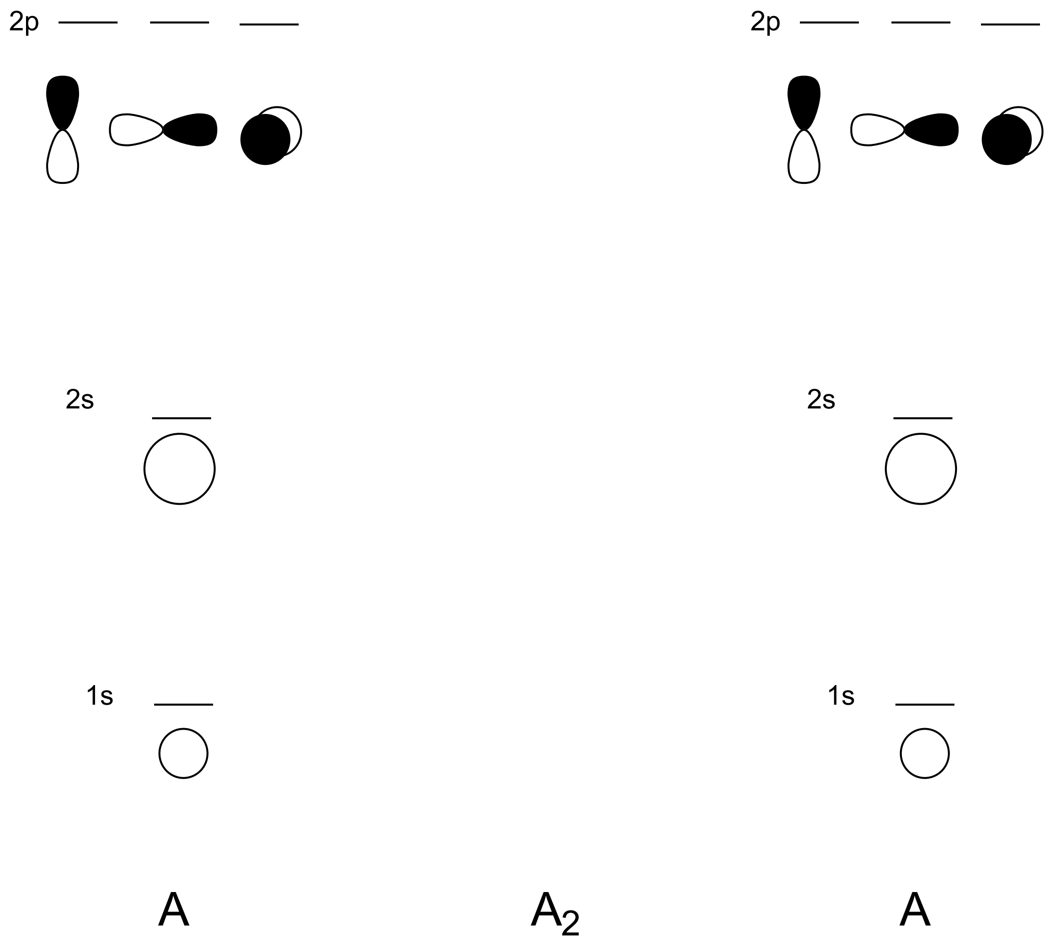
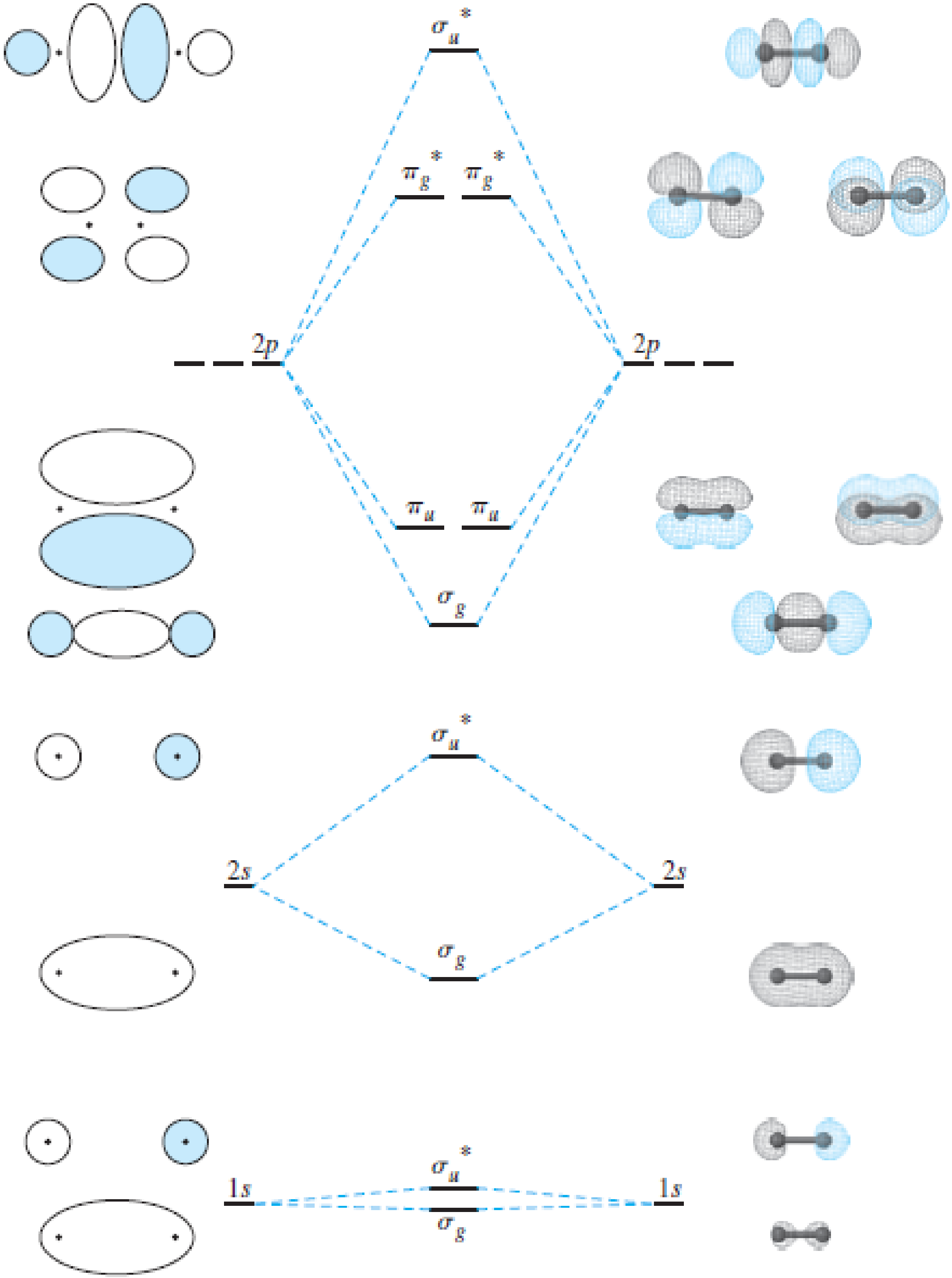
Requirements for overlap

1) The symmetry of the orbitals must be such that regions with the same sign (shaded or not shaded) overlap.
2) The energies of the orbitals must be similar to have significant overlap.
3) The physical distance between the two atoms must be short enough to ensure overlap.

MO diagram for homonuclear diatomic molecules

Consider two identical atoms ‘A’ with n =2,

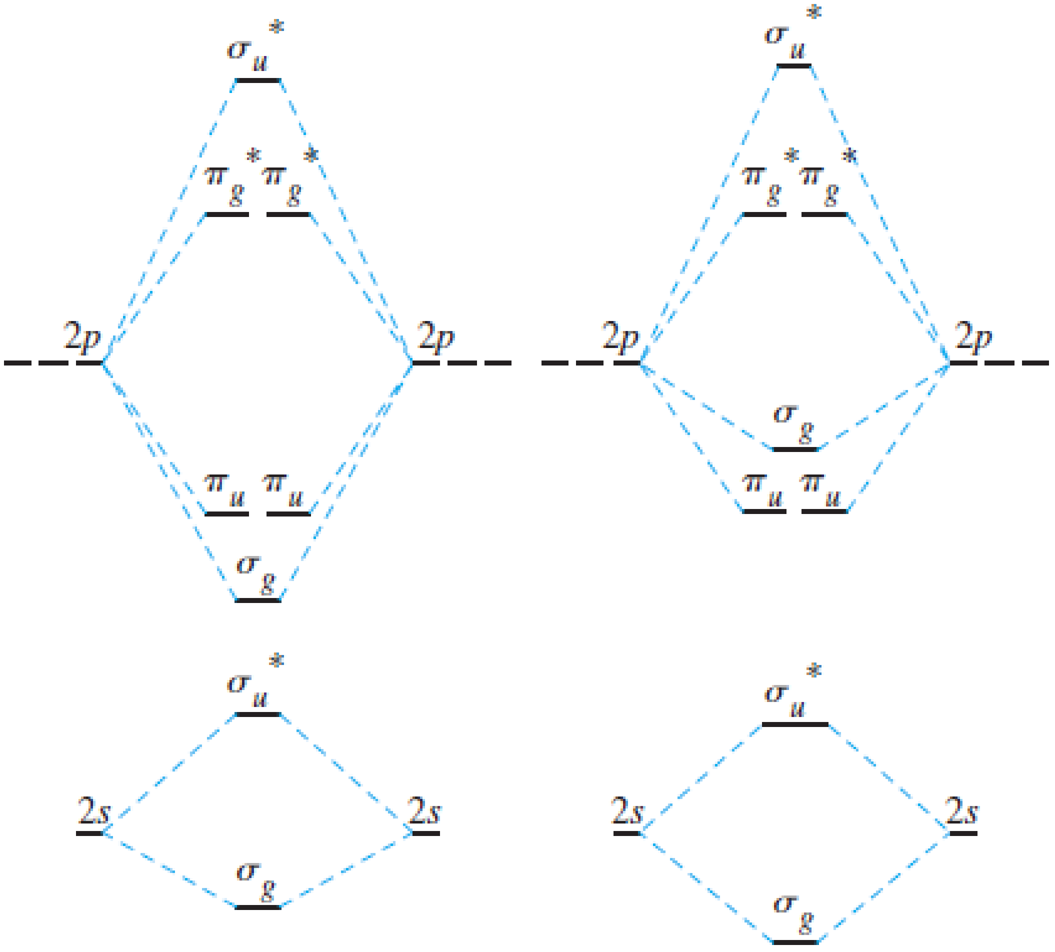




σ_u^*
π_g^*
π_g^*
$2p$
$2p$
π_u
π_u
σ_g
σ_u^*
$2s$
$2s$
σ_g
$1s$
σ_u^*
σ_g
$1s$

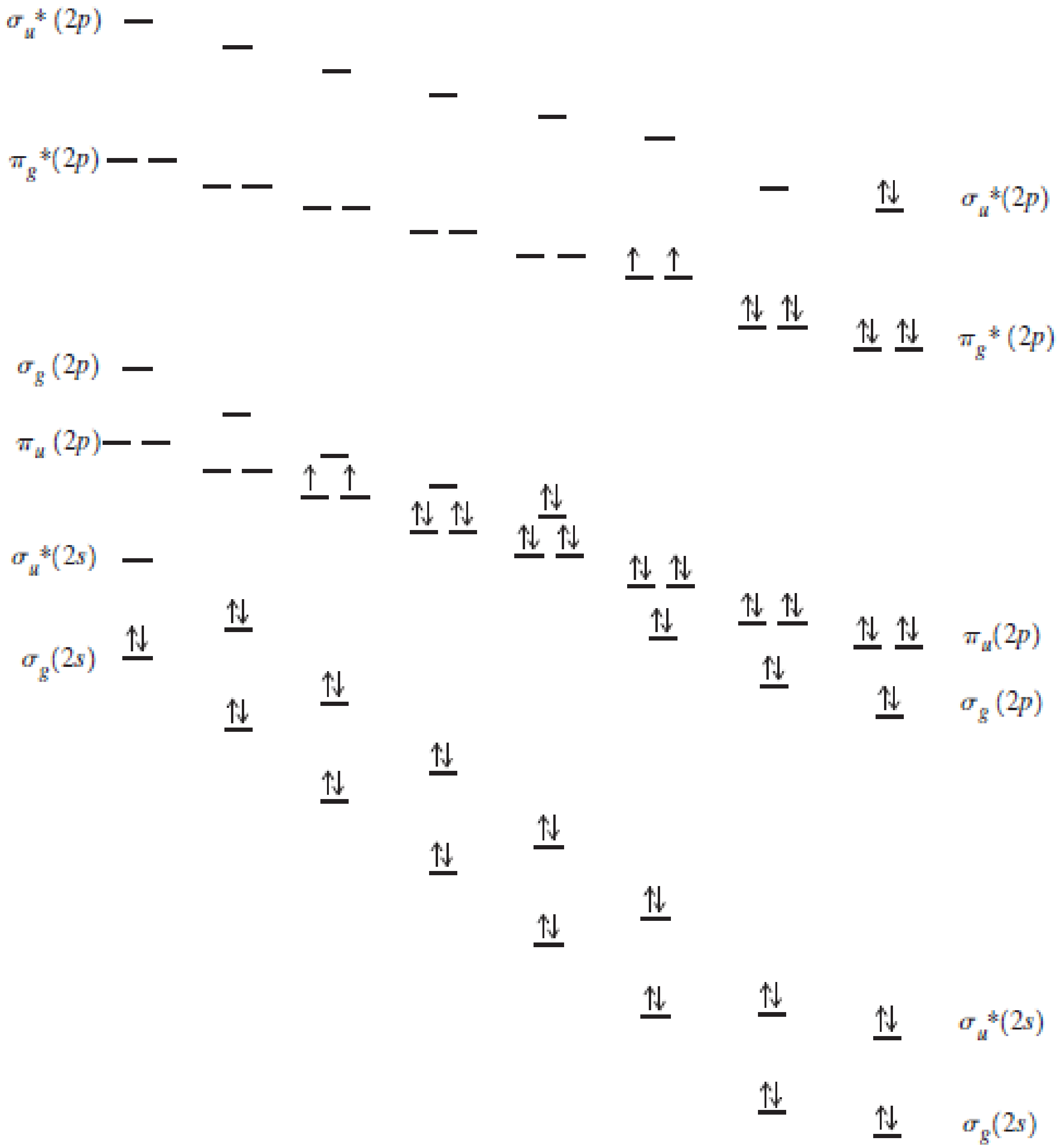
Orbital mixing

- MOs with similar symmetries can ‘mix’, resulting in stabilization of lower energy orbital, destabilization of higher energy orbital
- In some molecules, this results in p_z sigma bond being higher in energy that p_x and p_y pi bonds
- In n=2, mixing occurs for Li_2, Be_2, B_2, C_2, and N_2: importantly, explains magnetic properties of B_2 and C_2!
- There is no mixing for O_2, F_2, Ne_2



No mixing

Mixing of σ_g orbitals



	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	0	1	2	3	2	1	0
Unpaired e⁻	0	0	2	0	0	2	0	0

Bond order

Bond order =

(# of e$^-$s in bonding orbitals - # of e$^-$s in antibonding orbitals)/2