Chemistry 4000
Introduction to Inorganic Chemistry: The Different Perspectives of Bonding
Exam 2
Name:

Show all of your work for full credit.

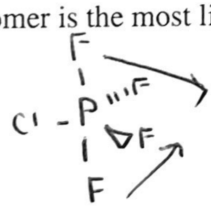
1. (10 points) Given the compound PA_5 where **A** is a halide

8 A. If four of the five halides bound to phosphorus are fluorides and the other is chloride, **DRAW** the two isomers of the compound, **IDENTIFY** their point group, and **DETERMINE** if they are chiral **AND** if they have a dipole moment.

Point Group: C_{3v}
Chiral? No
Dipole moment? Yes

Point Group: C_{2v}
Chiral? No
Dipole moment? Yes

2 B. Which isomer is the most likely structure? Explain.

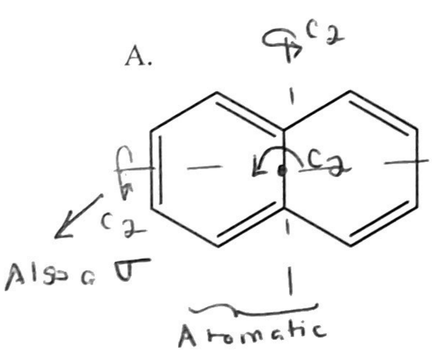


More X substituent in axial position due to the less s orbital contribution for the P. Bent's rule.

2. (20 points) For the following molecules:

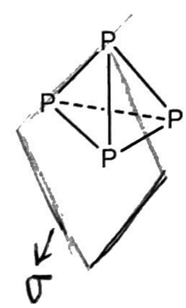
- Point group?
- Centrosymmetric?
- Chiral?
- Dipole Moment?
- Draw where a mirror element exists.

A.



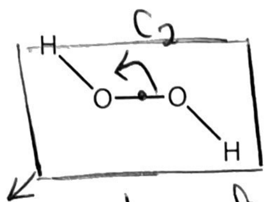
Point Group: D_{2h}
Centrosymmetric: Yes
Chiral? No
Dipole moment: No

B.



Point Group: T_d
C.S.: No
Chiral: No
Dipole moment: No

C.



σ on plane of sheet.

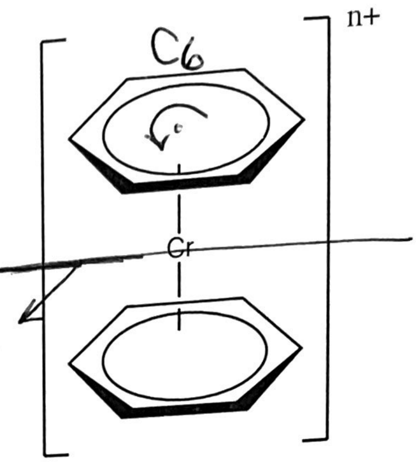
Point Group: C_{2h}

C.S. : Yes

Chiral: No

Dipole moment: No

D.



σ

Point Group: D_{6h}

C.S. : Yes

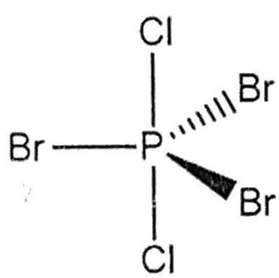
Chiral: No

Dipole moment: No

3. (30 points) Consider the D_{3h} molecule depicted below.

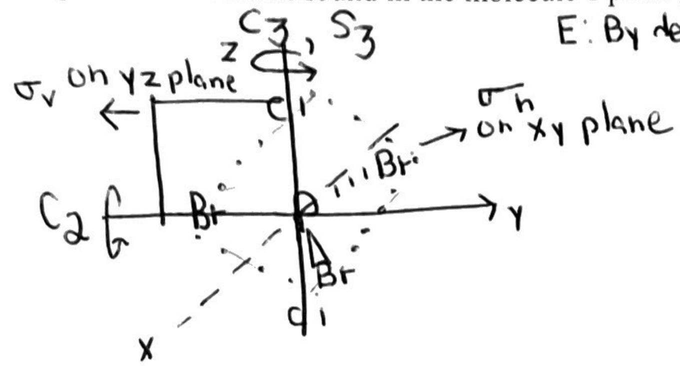
D_{3h} point group

	E	2C3	3C2	σh	2S3	3σv		
A'1	1	1	1	1	1	1		x^2+y^2, z^2
A'2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A''1	1	1	1	-1	-1	-1		
A''2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)



4 A. Draw the molecule on the x,y,z coordinate system and draw one representation each of the operations/elements found in the molecule's point group.

E: By definition, in the same position



2 B. How many states will represent the degrees of freedom? Of these states, how many will represent the translations and how many will represent the rotations?

D.O.F. $= 3N = 3(6) = 18 \Rightarrow$ 18 states

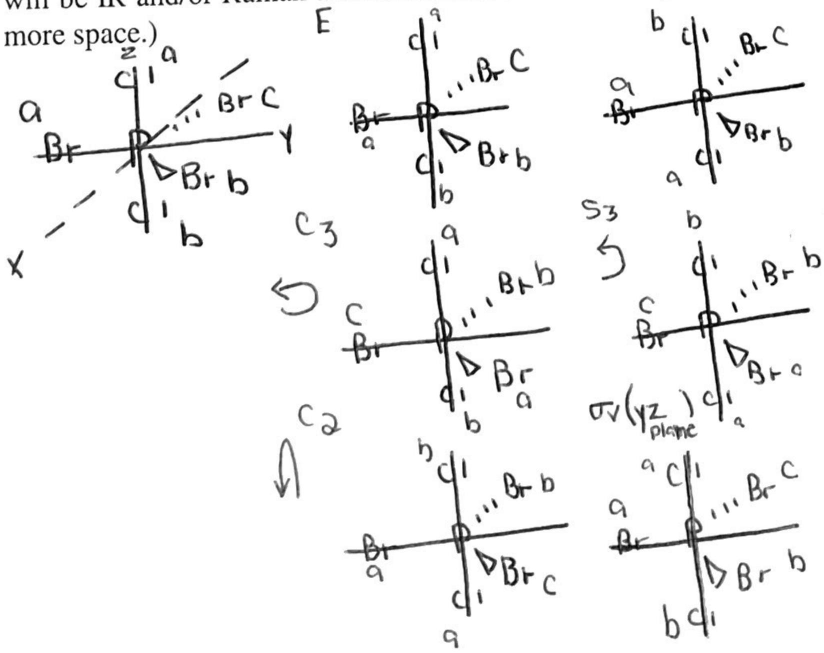
Translations: 3 states

Rotations: 3 states

2 C. How many normal vibrational modes do you expect for this molecule and how many states will represent these vibrational modes?

Normal vibrational modes: $3N-6 = 12$; 12 states

10 D. Determine the reducible representation for the normal vibrational modes and determine which will be IR and/or Raman active. Remember to check your work. (Use the next page if you need more space.)



D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
U.A.	6	3	2	4	1	4
x C.C.	3	0	-1	1	-2	1
Red. Rep.	18	0	-2	4	-2	4

	E	C_3	C_2	σ_h	S_3	σ_v	

$A_1' : \frac{1}{12}[(18\cdot1\cdot1) + (0) + (-2\cdot3\cdot1) + (4\cdot1\cdot1) + (-2\cdot2\cdot1) + (4\cdot3\cdot1)] = \frac{24}{12} = 2$

$18 + 0 + -6 + 4 + -4 + 12$

$A_2' : \frac{1}{12}[18 + 0 + 6 + 4 + -4 + -12] = 1$

$E' = \frac{1}{12}[36 + 0 + 0 + 8 + 4 + 0] = 4$

$A_1'' : \frac{1}{12}[18 + 0 + -6 + -4 + 4 + -12] = 0$

$A_2'' = \frac{1}{12}[18 + 0 + 6 + -4 + 4 + 12] = 3$

$E'' = \frac{1}{12}[36 + 0 + 0 + -8 + -4 + 0] = 2$

Red. Rep. = $2A_1' + 1A_2' + 4E' + 3A_2'' + 2E''$ → 18 States

− Translations $\quad - E' \quad - A_2''$

− Rotations $\quad - A_2' \quad - E''$

$2A_1' + 3E' + 2A_2'' + E''$ → 12 states

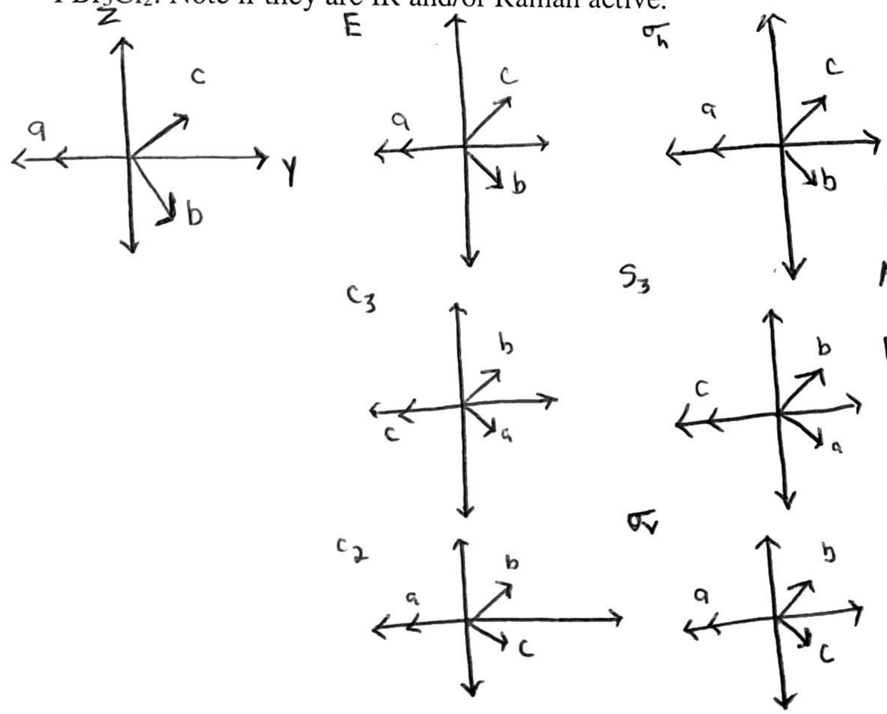
A_1' : Raman

E' : IR + Raman

A_2'' : IR

E'' : Raman

5 E. Define the reducible representation for the vibrational modes of the P-Br stretches within PBr_3Cl_2. Note if they are IR and/or Raman active.



D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
Red Rep.	3	0	1	3	0	1

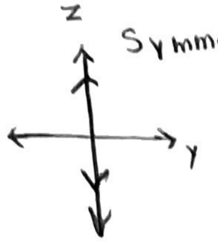
Red. Rep. = $A_1' + E'$

A_1' = Raman

E' = IR + Raman

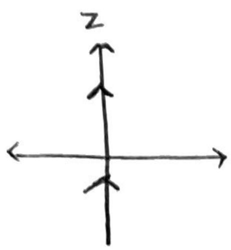
5 F. Define the irreducible representation for the **symmetric stretch** and the **antisymmetric stretch** for Cl-P-Cl within PBr_3Cl_2. Note if they are IR and/or Raman active.

Symmetric stretch



D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
A_1'	1	1	1	1	1	1

Raman



D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
A_2''	1	1	-1	-1	-1	1

IR

2 G. What experiment can you do to determine which Raman active vibrational bands correspond to the P-Br and which to the P-Cl stretches? Explain.

You could isotopically label the Br and see if any of the Raman active vibrations shift in frequency. You could do the same for the Cl to see if any vibration shifts. These shifts would be due to the change in mass of the Br + Cl.

4. (20 points) Let's expand on a problem from quiz #2. We will **construct** the molecular orbital diagram for the sigma interactions in BeF_2.

2 A. What atomic orbitals (AOs) are present in the valence shell of the central atom? Write them all.

Be: $2s^2 2p^0$

$2s, 2p_x, 2p_y, 2p_z$

2 B. What AOs are present in the valence shell of the fluorines? Write them all.

F: $2s^2 2p^5$

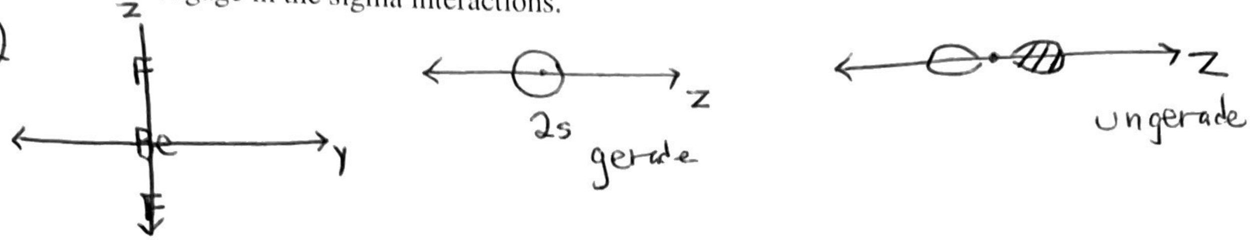
$2s, 2p_x, 2p_y, 2p_z$

2 C. Based on the number of atomic orbitals in the valence shell of the fluorines, **how many** ligand group orbitals (LGOs) can form?

2 F 4 A.O.s + 4 A.O.s → 8 LGOs

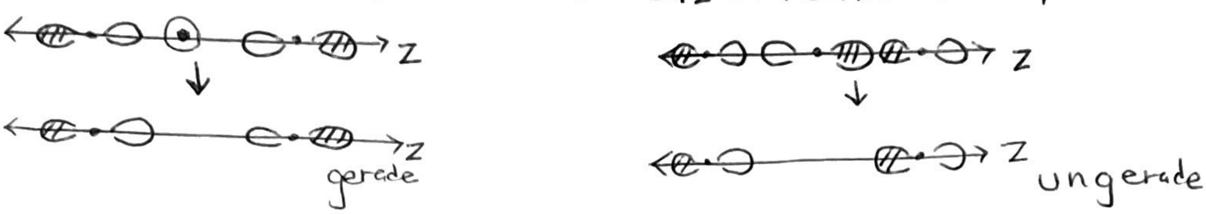
D. **Draw** the compound on the x,y,z coordinate system and then **determine** the central atom AOs that will engage in the sigma interactions.

2



E. **Derive** the LGOs that will engage in the sigma interactions and **identify** which atomic orbitals you used from the fluorines. **Assume** that the 2s orbitals of the fluorines are too low in energy to engage in sigma bonding. I will use the 2pz of the fluorines to yield two LGOs.

2



F. How many LGOs of the number you wrote in part C will remain nonbonding?

2

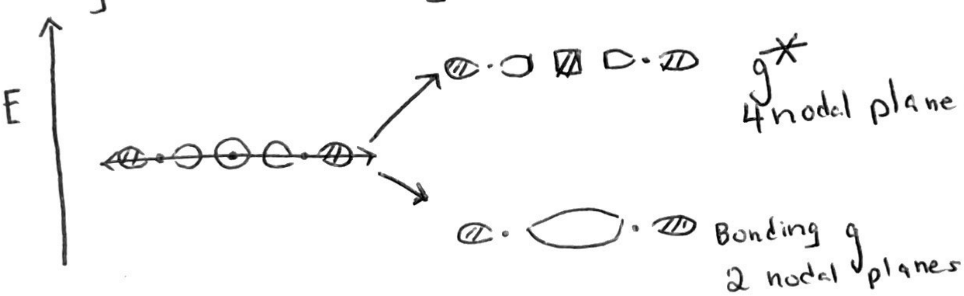
Six LGOs will remain nonbonding.

G. Draw the molecular orbitals for the sigma interactions.

3

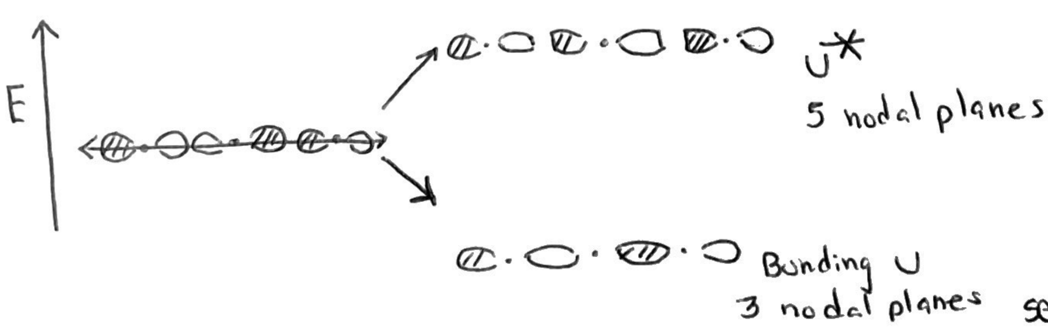
Symmetry matching

gerade A.O. + gerade LGO → 2M.O.s



lowest energy due to partial s character + lowest # of nodes

ungerade A.O. + ungerade LGO → 2M.O.s

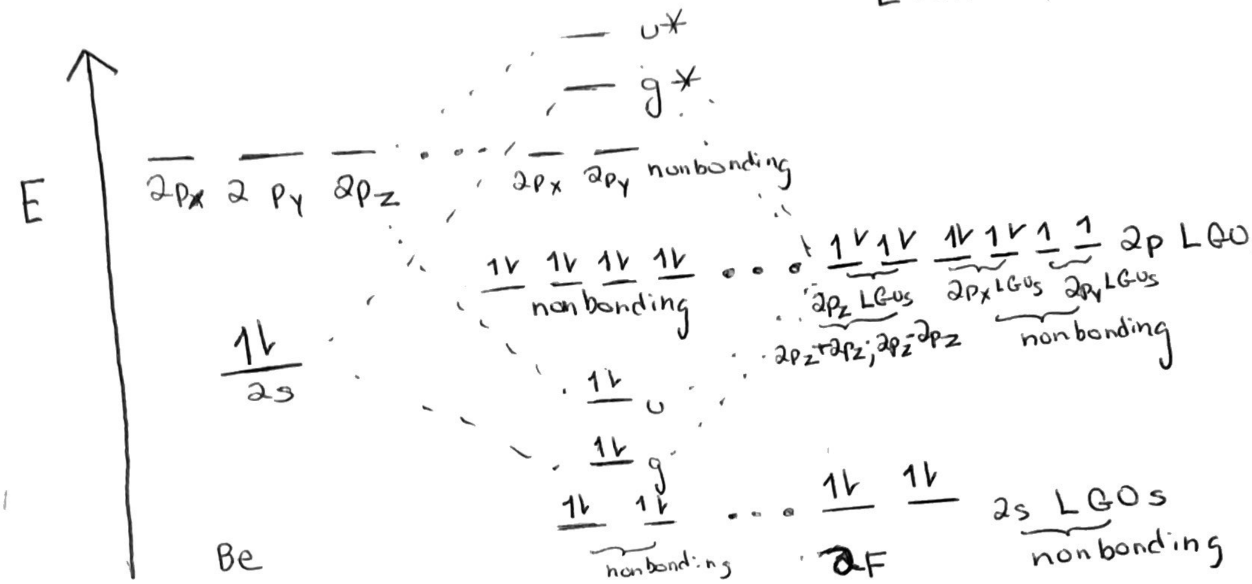


Highest in energy due to highest # of nodes

second lowest energy

5 H. **Construct** the molecular orbital diagram and **explain** your ranking in energy of the MOs. **Determine** the bond order and explain what the bond order means.

Look at part G

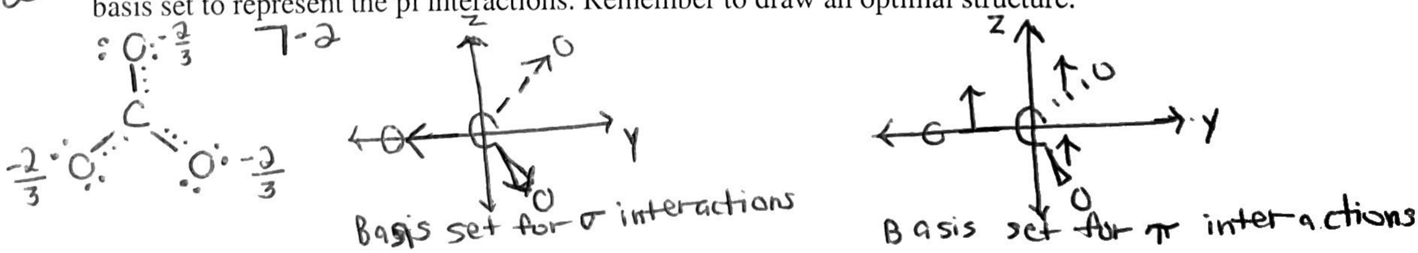


Bond Order = $\frac{1}{2}[4-0] = 2$; 2 Be−F σ bonds

5. (20 points) In class we constructed the partial molecular orbital diagram to study the pi interactions in the NO_3^- anion. **Let's use the same approach for the CO_3^{2-} anion.**

Noncentrosymmetric

2 A. On the x,y,z coordinate system, **draw** a basis set to represent the sigma interaction and **draw** a basis set to represent the pi interactions. Remember to draw an optimal structure.



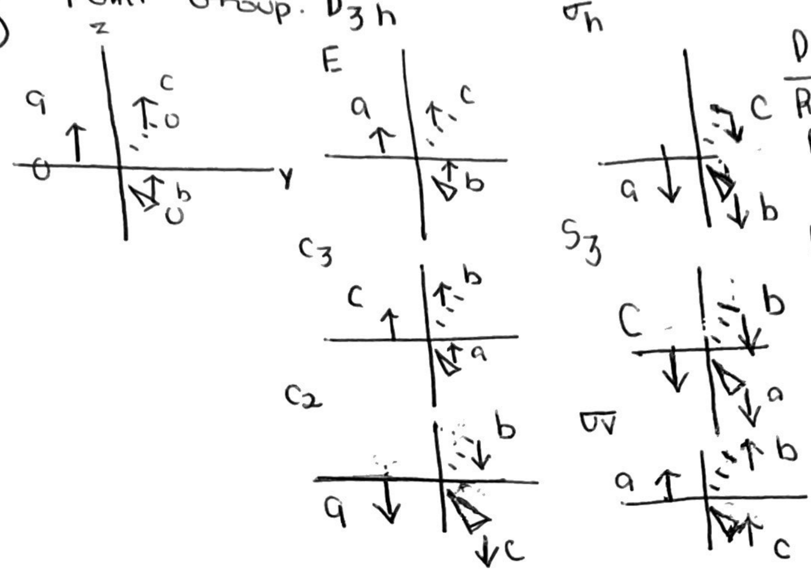
2 B. **How many** states will represent the sigma interactions and **how many** states will represent the pi interactions?

σ interactions: 3 states for 3 σ interactions

π interactions: 3 states for 3 π possible interactions

C. Determine the reducible representation for the pi interactions.

3 Point Group: D_{3h}



D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
Red. Rep.	3	0	-1	-3	0	1

Red. Rep. = $A''_2 + E''$ Three states

a''_2: p_z

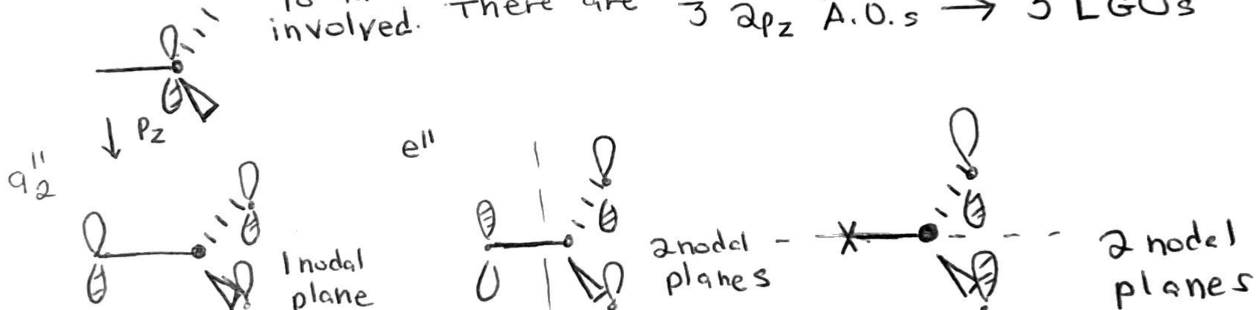
e'': ~~d_{xz}, d_{yz}~~ d-orbitals are not accessible for C

D. Determine which central atom AO(s) will engage in pi interactions.

2 a''_2: (p_z) of the central atom

E. Of the AOs available for the oxygen atoms, **which AOs** can potentially engage in a pi interaction with the central atom AO(s) identified in part D? **Based on your response, how many** LGOs will form and **draw** them?

2 To interact in a pi manner with the $2p_z$ of the Os must be involved. There are 3 $2p_z$ A.O.s → 3 LGOs



F. Draw the MOs that will form.

2 Symmetry matching: a''_2 A.O. + a''_2 LGO → 2 M.O.s

a''^{*}_2 4 nodal planes

a''_2 1 nodal plane

2 G. How many total electrons are available in the CO_3^{2-} **anion**?

Have C + 3 O + 2e⁻ Valence e⁻

$4e^- + 3(6e^-) + 2e^- = 24e^-$

Of these total electrons,
how many will be used for sigma bonding? Refer to your drawing in part A.

6e⁻ for 3 σ

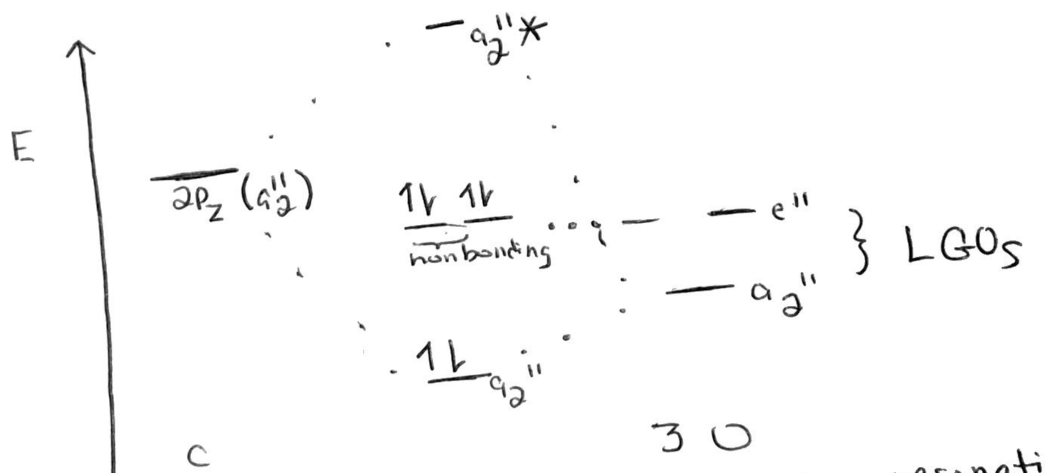
how many will be lone pairs? Refer to your drawing in part A.

12 lone pair e⁻s or 6 lone e⁻ pairs

use deductive reasoning to determine **how many** will be available for pi bonding?

$24e^- - 18e^- = 6e^-$ for pi bonding.

H. **Construct** the partial molecular orbital diagram for the pi interactions. **Determine** the bond
5 order and explain what the bond order means.

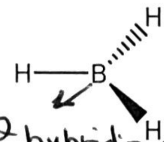


Bond order = $\frac{1}{2}[2-0] = 1$ π interaction resonating through the C–O bonds.

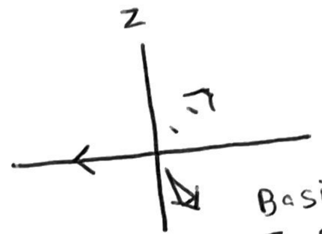
$\frac{1}{3}$ π bond per C–O

+ 3σ C–O bonds from deductive reasoning

Extra Credit. Consider the BH_3 compound.



3 bonded pairs around B; sp^2 hybridization



Basis set; 3 states for 3 σ bonds

Use a combination of valence bond theory and molecular orbital theory to explore the three sigma bonds between B and the H atoms by following the next series of steps or answering the questions.

A. Determine the atomic orbitals of the central atom that hybridize to engage in sigma interactions with the H atoms.

D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
Red. Rep.	3	0	1	3	0	1

Red. Rep. = A' + E' Three states

a': s, ~~d_{z^2}~~

e': (p_x, p_y); ~~$(d_{x^2-y^2}, d_{xy})$~~

d-orbitals not accessible to B.

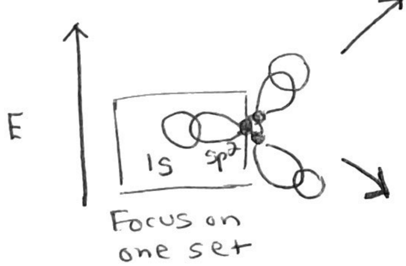
2s, $2p_x$, $2p_y$ ⇒ 3 sp^2 hybrid orbitals

B. Draw the molecular orbitals that will form between the central atom hybrid orbitals and the H atomic orbitals. Note that the H atomic orbitals will be treated individually and not as ligand group orbitals.

3 sp^2 hybrid orbitals + 3 1s AO ⇒ 6 MOs

antibonding M.O.; Three degenerate sets

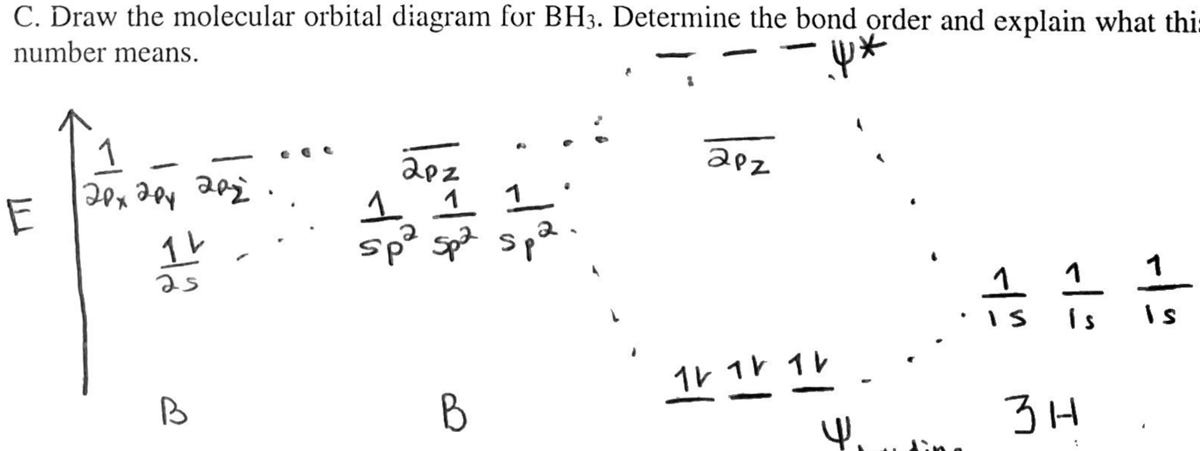
2 nodal planes



Focus on one set

Bonding M.O.; 1 nodal plane; Three sets of degenerate bonding M.Os.

C. Draw the molecular orbital diagram for BH_3. Determine the bond order and explain what this number means.



Bond order = $\frac{1}{2}[6-0]$ = 3 B–H σ interactions