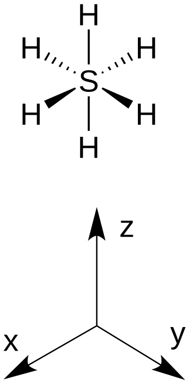
Recommended Reading: 5.1 – 5.7, **15.2-15.11** (3rd/4th edition)
2018 Ch 102 – Problem Set 4
Due: Thursday, May 03 – *Before Class*

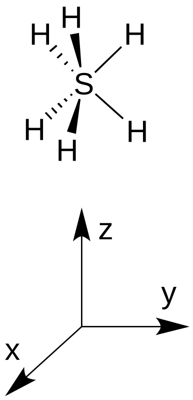
Problem 1 (4 points)

Consider the two possible isomers of hypothetical SH_6, **A** (O_h symmetry) and **B** (D_{3h} symmetry), as shown below. For your MO analysis use the depicted coordinate systems.

A



B



a) Derive the reducible representation of the 6 H 1*s* orbitals (the orbital basis set for the hydrogen atoms), Γ_{6H}, for **A** and **B**. Reduce Γ_{6H} to the corresponding irreducible representations.

b) Draw all the SALCs for these irreducible representations. Label them clearly with Mulliken symbols.

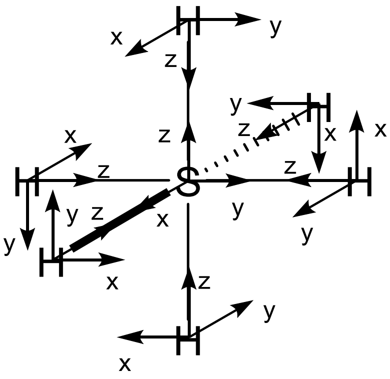
c) Draw the valence orbitals of sulfur (the orbital basis set for the central atom) and assign their irreducible representations.

d) Construct an MO diagram by interacting the hydrogen SALCs with the sulfur valence orbitals. For the purpose of this problem, consider the energy of the ligand atomic orbitals to be lower than that of the central atom atomic orbitals. Label each MO with the appropriate Mulliken symbol, also indicating the relative energy (e.g. 1eg, 2eg, etc.). Draw the MOs. Fill in the electrons. Label the HOMO and LUMO. What is the total bond order in **A** and **B**? Do you predict these molecules to be paramagnetic or diamagnetic?

e) Predict the number of peaks expected in the photoelectron spectrum of **A** and **B**, based on your MO diagrams. Are these isomers of SH_6 distinguishable by this technique?

f) Draw the Lewis dot structure of SH_6, including a resonance form that obeys the octet rule and one that is hypervalent. What is the total bond order predicted in each one? Based on the MO diagrams you derived, which Lewis structure is more consistent with the bonding in SH_6? Explain.

For parts g and h, only geometry A will be analyzed. The molecular motions of SH_6 can be described using symmetry by considering the coordinate system of each atom in the molecule and how they transform with respect to the symmetry operations in the appropriate point group. For each H atom, the z axis was selected along the S-H bond.



The reducible representation for the x, y, and z movements of these axes is shown below:

$\mathbf{O_h}$	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $(=C_4^2)$	*i*	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_{SH6xyz}	21	0	-1	3	-3	-3	-1	0	5	3

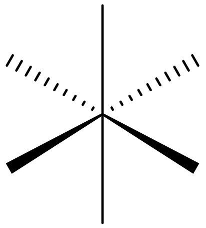
This reduces to the following irreducible representations:

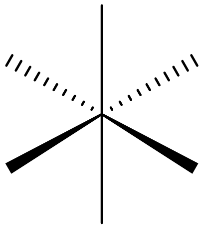
$$\mathbf{\Gamma_{SH6xyz} = A_{1g} + E_g + T_{1g} + T_{2g} + 3\ T_{1u} + T_{2u}}$$

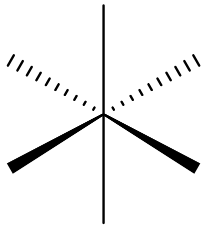
g) Determine which irreducible representations in **A** correspond to translation, rotation, and normal vibration modes.

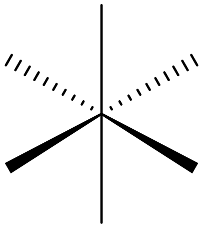
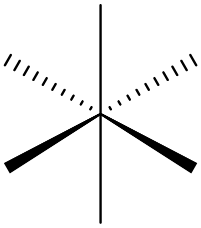
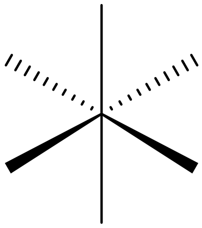
h) How many peaks do you expect to see in the IR spectrum of **A**? Raman spectrum?

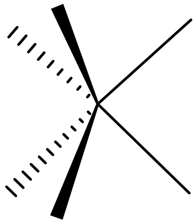
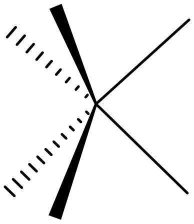
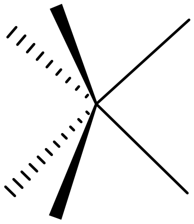
i) Assuming that the S–H stretching modes are well separated from the other vibrations in the IR and Raman spectra of **A** and **B**, the number of peaks observed for the stretches may allow identification of the geometry of the compound. Use the S–H bonds as a basis set to determine the reducible representation for the bond stretches and reduce it. Using the diagrams below, with arrows to indicate lengthening vs. shortening of the bonds, draw the vibrational stretching modes of **A** and **B** and label them with Mulliken symbols. Explain how these stretching modes are IR/Raman active based on changes in the molecule's dipole/polarizability.

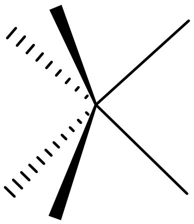
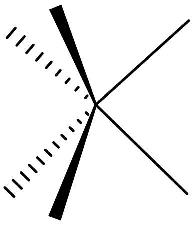
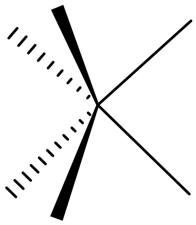






j) How many peaks do you expect in the stretching mode region of the IR and Raman spectra for each of the above geometries (assuming the geometries are "frozen")? Can the two isomers be distinguished using IR and Raman spectroscopy?

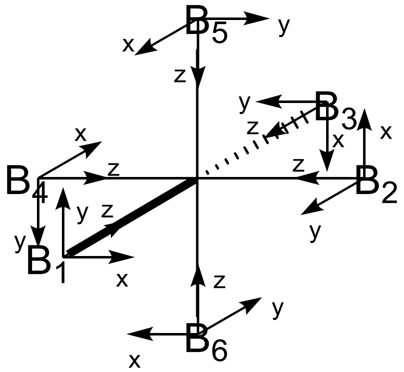
Problem 2 (2 points)

Part I

On page 365 of your textbook you will find a discussion of the octahedral $[B_6H_6]^{2-}$cluster. In this discussion the bonding of the cluster is simplified by only considering the frontier orbitals. Each B-H fragment has only three frontier orbitals, which are shown in the top right figure.

These frontier orbitals can be combined to form the molecular orbital (MO) diagram of the $[B_6H_6]^{2-}$ cluster. Part of this MO is shown and includes molecular orbitals of three symmetries (a_{1g}, t_{1u}, and t_{2g}).

For this problem we will treat the radial frontier orbital separately from the two tangential frontier orbitals. An easy way to do this is to use the axis system shown below, in which each boron has its own x, y, and z axis. The z axis corresponds to the radial orbitals, the x and y axes correspond to the tangential orbitals.



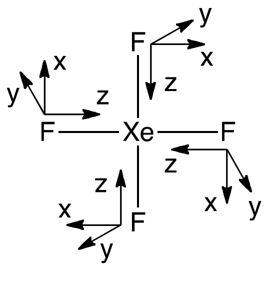
a) Using only the 6 boron p_z orbitals as a basis set, generate a reducible representation Γ_{6Bz} and reduce it to irreducible representations. Note that you can use part of the solution from Problem 1 part i) without additional derivations. No symmetry adapted linear combinations (SALCs) need to be sketched or MO diagram derived.

b) Using the 12 boron p_x and p_y orbitals together as a basis set, generate a reducible representation Γ_{12Bxy}. Reduce the Γ_{12Bxy} representation to the irreducible representations for the bonding framework including only the tangential orbitals. No SALCs need to be sketched or MO diagram derived.

For a check of your work, look at the partial MO diagram on page 365 and confirm that your irreducible representations include those shown. The electronic structure of $[B_6H_6]^{2-}$ was computed and the file is available on the class website, if you are interested in viewing the MOs (not necessary for the solution).

Part II

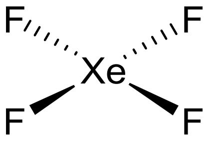
Consider square-planar XeF_4. Construct an MO diagram including the p-orbitals of the fluorine atoms.

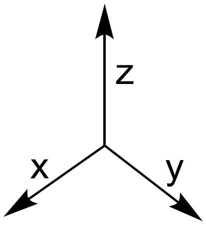


a) For the 4 F atoms, consider a basis set consisting of the 2*s*, $2p_z$, $2p_y$, $2p_x$ atomic orbitals and utilize the coordinate system defined for each F atom as in the drawing above. Derive the reducible representation of the F *s*, p_z, p_y, p_x atomic orbitals, respectively (Γ_{Fs}, Γ_{Fpz}, Γ_{Fpy}, Γ_{Fpx}, respectively). Reduce Γ_{Fs}, Γ_{Fpz}, Γ_{Fpy}, and Γ_{Fpx} to their irreducible representations.

b) Draw all the SALCs that correspond to these irreducible representations. Label them clearly with Mulliken symbols.

c) Draw the valence orbitals of xenon (the orbital basis set for the central atom) and assign their irreducible representations (use the coordinate system below).





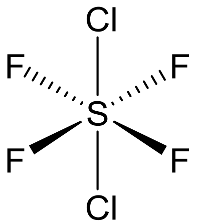
d) Construct an MO diagram by interacting the fluorine SALCs with the xenon valence orbitals. Remember that the energy of the fluorine atomic orbitals is lower than the xenon's. Assume that the molecule is diamagnetic. Label MOs with the appropriate Mulliken symbol (for the non-bonding MOs, which are many, you don't need to label individual orbitals), also indicating the relative energy (e.g. $1e_u$, $2e_u$, etc.). Define the character of these orbitals as bonding, non-bonding or antibonding. Fill in the electrons. Draw only the bonding and antibonding MOs. Comment on their character as σ vs π bonding (or antibonding) interactions.

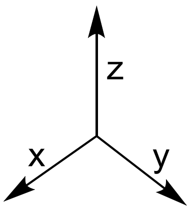
e) What is the total bond order in XeF_4 based on the MO diagram? What is the Lewis dot structure prediction using natural resonance?

f) Using the provided software build XeF_4 (square-planar), and compute its vibrational spectra. What are the computed Xe-F stretching frequencies (in cm^{-1}) in the IR and Raman spectra for each compound? Include a printout of the IR and Raman spectra.

Problem 3 (2 points)

A molecule belonging to the $\mathbf{D_{4h}}$ point group, *trans*-SF_4Cl_2, is shown below.





A number of the molecular orbitals (numbered 20-44) of *trans*-SF_4Cl_2 are depicted on the following pages. *These are sufficient to complete the entirety of the question.* On the class website, a file containing calculations results for the above molecule has been made available. You can open the file in the provided software and use it to visualize MOs for this molecule.

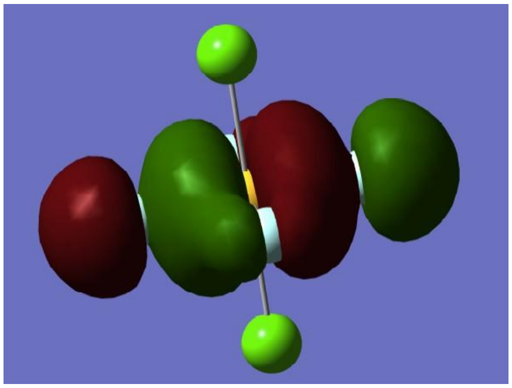
a) Based on the $\boldsymbol{D_{4h}}$ character table, assign a Mulliken symbol to each of the MOs (numbered

20 to 44). See below for an example. Remember that a shorthand method to assign Mulliken symbols is to identify which function (found on the right-hand side of the table) a specific MO is related to. You only need to list the orbital number and the Mulliken symbol (no printouts of the MOs are required).

b) The frontier occupied MOs have primarily contributions from chlorine atomic orbitals rather than fluorine (MOs # 40-43). Explain.

c) $\boldsymbol{C_{4v}}$ is a subgroup of $\boldsymbol{D_{4h}}$ and the above molecule can be analyzed in the lower symmetry point group. Assign Mulliken symbols to MOs # 33 and 40 under $\boldsymbol{C_{4v}}$.

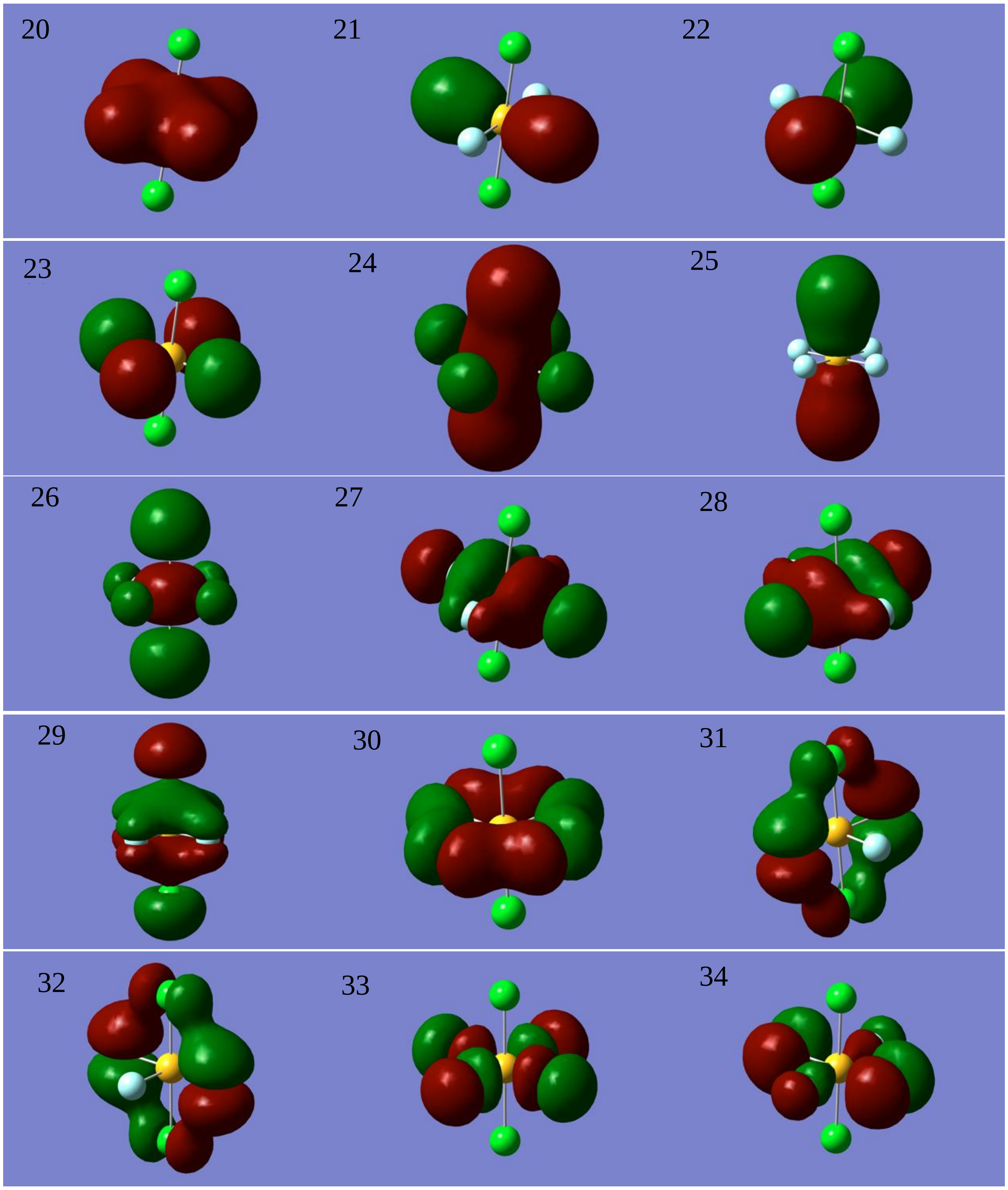
Example:
Shown below is the MO #27.



In order to determine the Mulliken symbol for this MO one needs to check how it transforms under the symmetry operations in $\boldsymbol{D_{4h}}$. Often, one can determine the Mulliken symbol without checking every single operation. For the orbital above, note that rotation around the C_4 axis (intersecting the two Cl atoms – in green in the image) converts this orbital into one that is perpendicular to it (instead of only changing phases). This is a clue that this orbital is part of an E set. Next, one can observe that the MO is antisymmetric with respect to *i*; therefore, the Mulliken symbol for MO #27 is E_u.

An alternative way to find the answer consists in identifying the function that transforms as the orbital. In the case above, ignoring the radial node in the MO (the node passing through the F atoms on the left and on the right), the MO resembles a p_x orbital (it has one planar node and it lies along the x axis). Hence this MO transforms as the p_x orbital which, together with p_y, transforms as E_u. If you visualize the orbitals using the software, remember that orbitals in a degenerate set (such as E) have the same energy – this will allow you to identify the pairs of MOs just by checking the energies listed on the right.

Note that while you can run the calculation yourself, the output file is made available so that all students can work on the same MO list.



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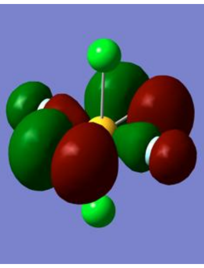

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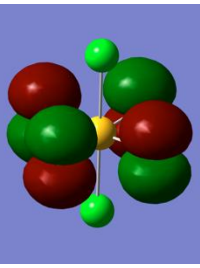

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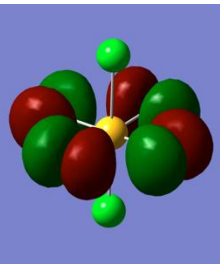

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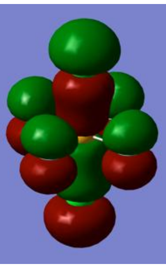

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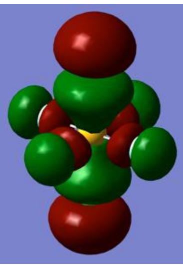

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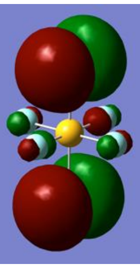

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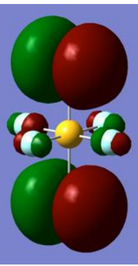

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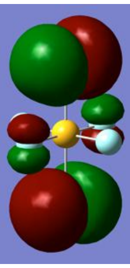

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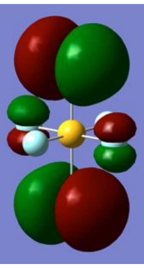

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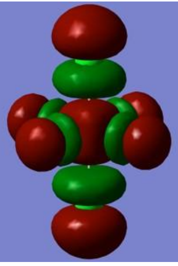

Problem 4 (2 points) ***Read the instruction below and format file names properly***

Pick a topic of interest from the recommended reading (descriptive chemistry) in bold at the beginning of this problem set. Prepare two power point slides including relevant *descriptive chemistry* (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (oxidation states, Lewis dot structures, symmetry, MO theory, etc) and some application of the provided software (since MO theory was covered in class, you are now expected to include some molecular orbital pictures / MO diagram analysis). Email the slides in ***pdf*** format to the TAs by noon on the due date, and turn in a printout of the slides with your problem set. Please format file names as "***FirstName_LastName_PSET#***" and include your name on the first slide.