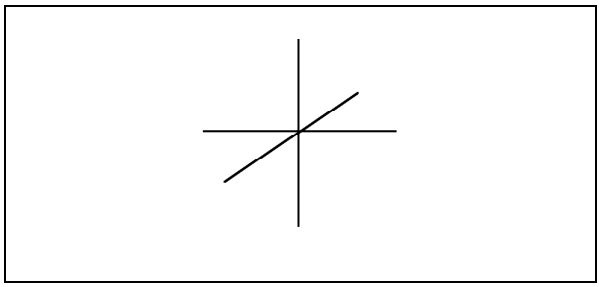
# Chm 451 Fall 2007
# Exam 2 23 October 2007 Name:

**You may use the Study Guides from Days 7 – 13. Five point bonus for not using any of the guides. This exam has a point total of 105 points. You can skip 5 points or answer them all. Your score will be 105 – points missed + bonus. Maximum score = 100%**

**Molecular orbital theory.**

1. Sulfur hexafluoride, $SF_6$, is an octahedral molecule with $O_h$ symmetry. The $O_h$ character table is provided on the back of the periodic table sheet. Use the 10-step approach, as guided below, to create a molecular orbital diagram for $SF_6$.

Step 1. (3 pts) Sketch the B group orbitals needed for σ-bonding for $SF_6$ on a Cartesian coordinate system. This will form the SALC set. In the case of $SF_6$, the s-orbitals on fluorine are very low in energy and can be ignored; σ-bonding will occur with a p-orbital from each fluorine.



Step 2. Determine the point group symmetry of the molecule/ion and look up its character table. Answer: $O_h$

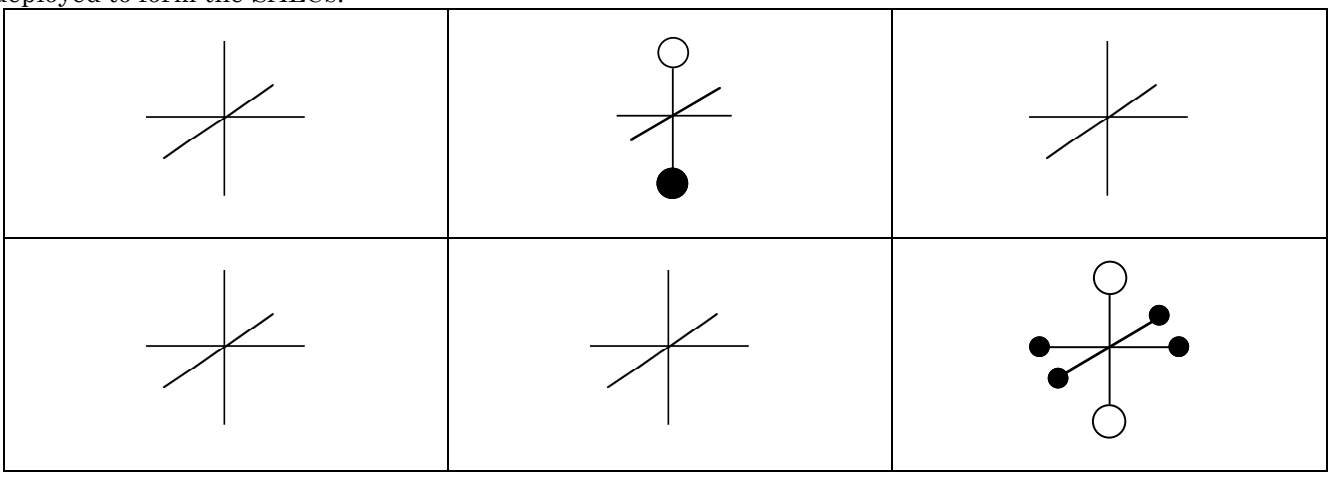
Step 3. (4 pts) Determine the *reducible representation*, Γ. Note: it is not necessary to do each and every symmetry operation in order to go on. If any are ambiguous, skip them for now.

| $O_h$ | E | $8C_3$ | $6\,C_2$ | $6\,C_4$ | $3\,C_2$ | i | $6\,S_4$ | $8\,S_6$ | $3\,\sigma_h$ | $6\,\sigma_d$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Γ | | 0 | 0 | | | | 0 | 0 | | |

Step 4. (5 pts) Determine the irreducible representations.

| $O_h$ | E | $8C_3$ | $6\,C_2$ | $6\,C_4$ | $3\,C_2$ | i | $6\,S_4$ | $8\,S_6$ | $3\,\sigma_h$ | $6\,\sigma_d$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $E_g$ | 2 | –1 | 0 | 0 | 2 | 2 | 0 | –1 | 2 | 0 |

Step 5. (6 pts) Sketch each of the 6 SALCs with appropriate symmetry labels. Shade in the appropriate lobes of the SALC sets. Complete the table on the next page summarizing how the atomic orbitals are deployed to form the SALCs.

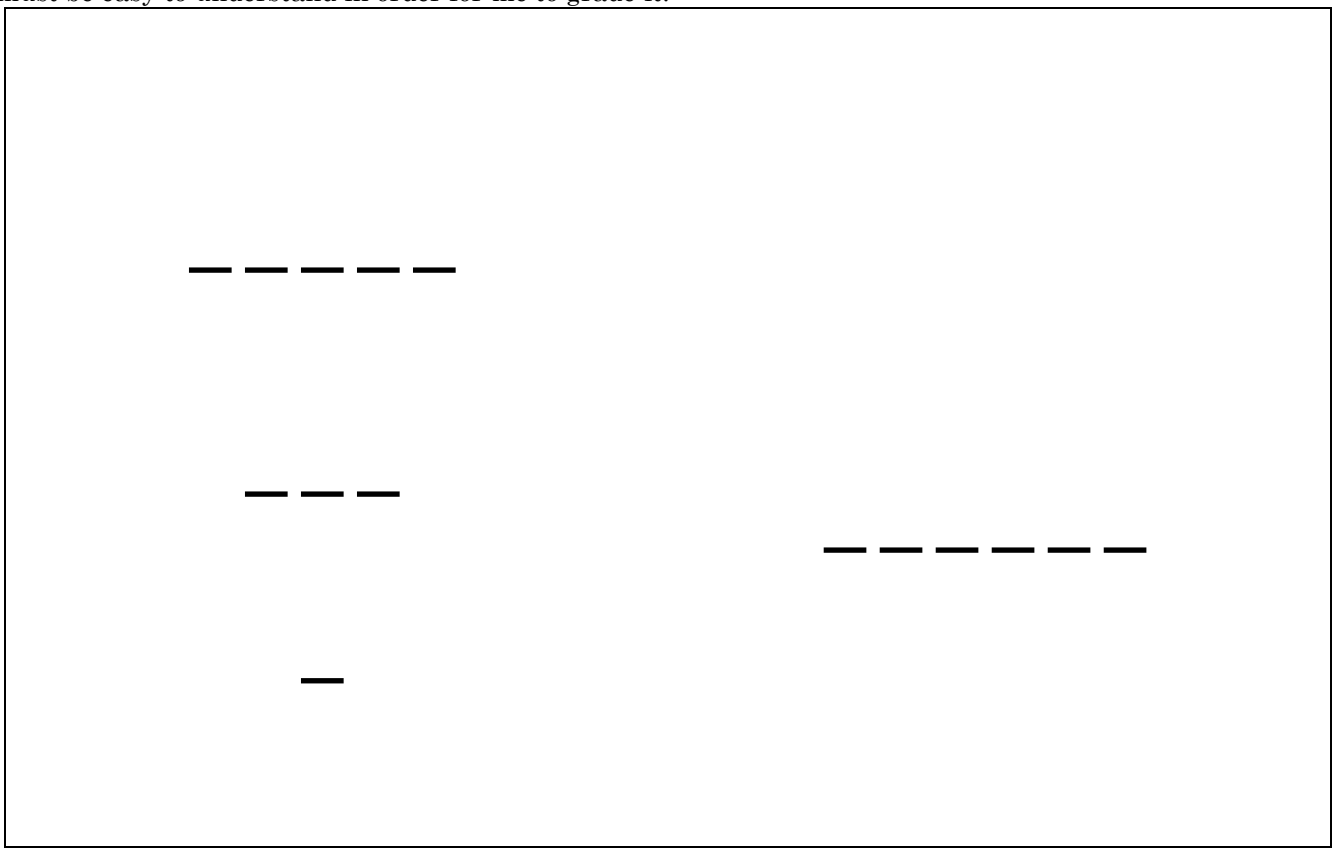


| (symmetry) | AO #1 | AO #2 | AO #3 | AO #4 | AO #5 | AO #6 | Total: |
|---|---|---|---|---|---|---|---|
| SALC (  ) | | | | | | | =1 |
| SALC ( eg#1 ) | 1/3 | 1/3 | 1/12 | 1/12 | 1/12 | 1/12 | =1 |
| SALC ( eg#2 ) | 0 | 0 | 1/4 | 1/4 | 1/4 | 1/4 | =1 |
| SALC (  ) | | | | | | | =1 |
| SALC (  ) | | | | | | | =1 |
| SALC (  ) | | | | | | | =1 |
| Total: | =1 | =1 | =1 | =1 | =1 | =1 | |

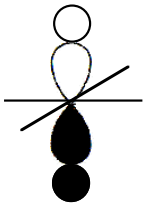
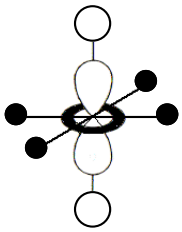
Step 6. (3 pts) List ***all*** of the central atoms <u>valence</u> orbitals (there are 9) and assign each one a symmetry label. In some cases you will need to include empty valence orbitals such as the d-orbitals. This will always be true whenever the octet on the central atom is expanded. In the next step you will compare these orbitals with the SALC set orbitals created in Step 5.

| | | |
|---|---|---|
| s ($a_{1g}$) | $p_z$ ($t_{1u}$) | |
| | | |
| | | |

Step 7. (8 pts) Create a MO energy diagram. I will be checking for labels and for how you connect the atomic and SALC orbitals with lines. I will also be checking for relative energy levels, conservation of orbitals, eetc.. Start with the SALC set having about the same energy as the s-orbital on sulfur. Your diagram must be easy to understand in order for me to grade it.



Step 8. (6 pts) Sketch molecular orbital line drawings from overlapping SALCs from Step 5 with the symmetry appropriate AOs from Step 6. Just sketch the bonding interactions — skip the antibonding. You can do it here or, if you prefer, add them to the MO energy diagram above.

| | | |
|---|---|---|
| |  | |
| | |  |

Step 9. (3 pts) Double check to see if you have conserved orbitals and electrons and then <u>populate the MO diagram</u>. Remember that we only used one electron from each fluorine atom when creating our SALC set. We used all of sulfur's valence electrons.

**Acids and Bases.**

2. (3 pts) In each case, circle the strongest acid in the list:

(a) HBrO $HBrO_2$ $HBrO_3$ $HBrO_4$

(b) $H_2TeO_4$ $H_2TeO_3$ $NaHTeO_4$

(c) HF HCl $H_3PO_4$

3. (5 pts) Circle all Lewis acids. Draw a box around the Lewis bases. Ignore the ones that are neither.

$H_2O$ $N(CH_3)_3$ $AlBr_3$ $Sc^{+3}$ $SiH_4$ $Cl^-$

4 (7 pts) Predict the acid-base nature of each of these salts.

| | | | |
|---|---|---|---|
| $NaNO_3$ | Acidic | Basic | Neutral |
| $NH_4Cl$ | Acidic | Basic | Neutral |
| $KClO_2$ | Acidic | Basic | Neutral |
| $LiC_2H_3O_2$ | Acidic | Basic | Neutral |
| $NaHSO_4$ | Acidic | Basic | Neutral |
| $Na_2SO_4$ | Acidic | Basic | Neutral |
| KI | Acidic | Basic | Neutral |

5(a). (8 pts) Each of these species is a hard or soft acid or base. Write an "x" in the appropriate box under each species.

| | $Li^+$ | $Tl^+$ | $Cl^-$ | $NH_3$ | $Pt^{+2}$ | $Ni^{+2}$ | $OH^-$ | $S^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| hard acid | | | | | | | | |
| soft acid | | | | | | | | |
| hard base | | | | | | | | |
| soft base | | | | | | | | |

(b) (4 pts) What combinations of hard and soft acids and bases make the most stable compounds? What makes certain combinations more stable? Circle one of the three choices in each box.

| | Hard base | Soft base |
|---|---|---|
| Hard acid | More stable due to ionic character<br>More stable due to covalent character<br>Not as stable as other combinations | More stable due to ionic character<br>More stable due to covalent character<br>Not as stable as other combinations |
| Soft acid | More stable due to ionic character<br>More stable due to covalent character<br>Not as stable as other combinations | More stable due to ionic character<br>More stable due to covalent character<br>Not as stable as other combinations |

**On the finer points of ionic compounds.**

6. (5 pts) Uranium crystallizes in a simple cubic unit cell and has a density of 19.05 g/cm$^3$. What is the atomic radius in picometers of uranium?

7. The mineral pyrargyrite, $Ag_3SbS_3$, utilizes the hexagonal lattice system. The sulfides are space-filling and the $Ag^+$ ions occupy one sort of hole (either octahedral or tetrahedral) while the $Sb^{+3}$ ions occupy the other sort of hole.

(a) (2 pts) Which cation do you think occupies each hole and why?

The $Ag^+$ ions occupy the (octahedral or tetrahedral) holes. (Circle either octahedral or tetrahedral.)

The $Sb^{+3}$ ions occupy the (octahedral or tetrahedral) holes.

Why did you pick the one you did? (in 10 words or fewer)

(b) (2 pts) What fraction of octahedral holes would be occupied with your model of what is happening?

(c) (2 pts) What fraction of tetrahedral holes would be occupied with your model of what is happening?

8(a) (3 pts) Which of the compounds listed at right *could* possibly have the fluorite lattice structure? Circle all that could; there may be 0 – 4.

| | |
|---|---|
| $SrF_2$ | $MgCl_2$ |
| RbF | KCl |

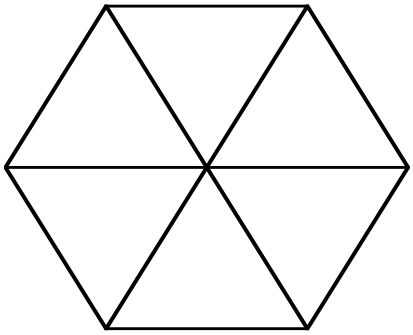
(b) (2 pts) The ***antifluorite*** structure is the same as the fluorite structure except that the cations and anions are switched. Which one of the compounds listed at right *could* exhibit the antifluorite structure?

| | |
|---|---|
| $BeI_2$ | CaO |
| $K_2O$ | CsF |

9. (3 pts) Silicon and tin both exhibit the diamond structure. How many atoms are present per unit cell in the diamond structure?

Answer:

10. At right is the top view of a ***hcp*** lattice. Only the "A" layer is shown.



(a) (2 pts) How many unit cells are represented in the figure?

(b) (2 pts) Draw small circles on the figure where the center of "B" layer atoms would go.

(c) (2 pts) Draw "x" marks on the figure above the centers of the octahedral holes.

11. (3 pts) The diameters of tetrahedral, octahedral and cubic holes are $0.225r_{large}$, $0.414r_{large}$, and $0732r_{large}$, respectively. If an ionic compound had a radius ratio value of 0.500, which type of hole would you predict is occupied by the small ions.

**Circle:** tetrahedral holes octahedral holes cubic holes

12. (3 pts) With each pair of compounds, circle the one with the predicted largest lattice energy.

(a) LiF or LiBr (b) $CaF_2$ or CaO (c) $Na_3N$ or ScN

13. (4 pts) How many formula units (or large atoms/ions) are in each of the following unit cell?

| |
|---|
| (a) base-centered monoclinic |
| (b) body-centered orthorhombic |
| (c) rhombohedron |
| (d) simple triclinic |

14.(5 pts) Print your name here:

| | |
|---|---|
| | Score: |

| $O_h$ | E | $8C_3$ | $6\ C_2$ | $6\ C_4$ | $3\ C_2$ | i | $6\ S_4$ | $8\ S_6$ | $3\ \sigma_h$ | $6\ \sigma_d$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_{1g}$ | 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 | | |
| $E_g$ | 2 | -1 | 0 | 0 | 2 | 2 | 0 | -1 | 2 | 0 | | $z^2$, $x^2 - y^2$ |
| $T_{1u}$ | 3 | 0 | -1 | 1 | -1 | 3 | 1 | 0 | -1 | -1 | ($R_x$, $R_y$, $R_z$) | |
| $T_{2g}$ | 3 | 0 | 1 | -1 | -1 | 3 | -1 | 0 | -1 | 1 | | (xz, yz, xy) |
| $A_{1u}$ | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | | |
| $A_{2u}$ | 1 | 1 | -1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 | | |
| $E_u$ | 2 | -1 | 0 | 0 | 2 | -2 | 0 | 1 | -2 | 0 | | |
| $T_{1u}$ | 3 | 0 | -1 | 1 | -1 | -3 | -1 | 0 | 1 | 1 | (x, y, z) | |
| $T_{2u}$ | 3 | 0 | 1 | -1 | -1 | -3 | 1 | 0 | 1 | -1 | | |

Note:

6 $C_2$: These rotation axes are around axes bisecting the x and y axes (2 axes), the x and z axes (2), and the y and z axes (2).

3 $C_2$: These rotation axes are equal to $C_4^2$.

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**Molecular orbital theory.**

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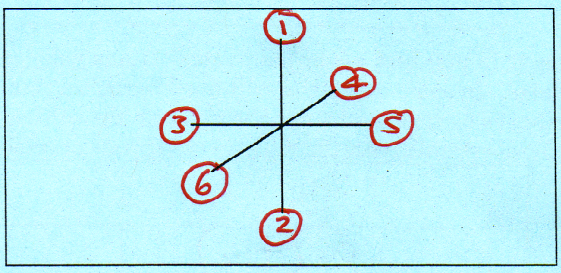
Step 1. (3 pts) Sketch the B group orbitals needed for σ-bonding for $SF_6$ on a Cartesian coordinate system. This will form the SALC set. In the case of $SF_6$, the s-orbitals on fluorine are very low in energy and can be ignored; σ-bonding will occur with a p-orbital from each fluorine.




Step 2. Determine the point group symmetry of the molecule/ion and look up its character table. Answer: $O_h$

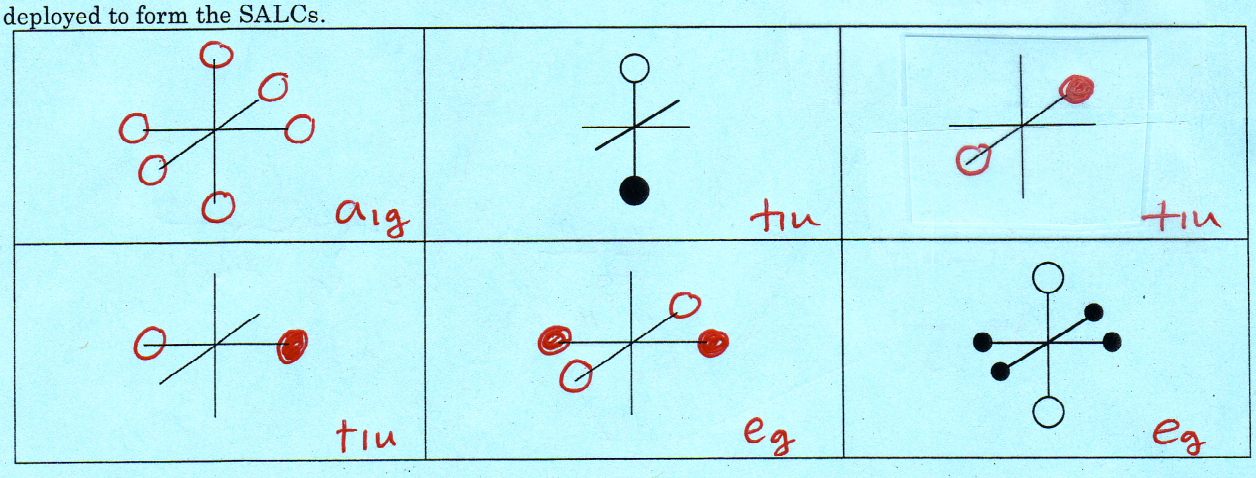
Step 3. (4 pts) Determine the *reducible representation*, Γ. Note: it is not necessary to do each and every symmetry operation in order to go on. If any are ambiguous, skip them for now.

| $O_h$ | E | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2$ | i | $6S_4$ | $8S_6$ | $3\sigma_h$ | $6\sigma_d$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Γ | 6 | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 4 | 2 |

Step 4. (5 pts) Determine the irreducible representations.

| $O_h$ | E | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2$ | i | $6S_4$ | $8S_6$ | $3\sigma_h$ | $6\sigma_d$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $A_{1g}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $E_g$ | 2 | -1 | 0 | 0 | 2 | 2 | 0 | -1 | 2 | 0 |
| $T_{1u}$ | 3 | 0 | -1 | 1 | -1 | -3 | -1 | 0 | 1 | 1 |

Step 5. (6 pts) Sketch each of the 6 SALCs with appropriate symmetry labels. Shade in the appropriate lobes of the SALC sets. Complete the table on the next page summarizing how the atomic orbitals are deployed to form the SALCs.



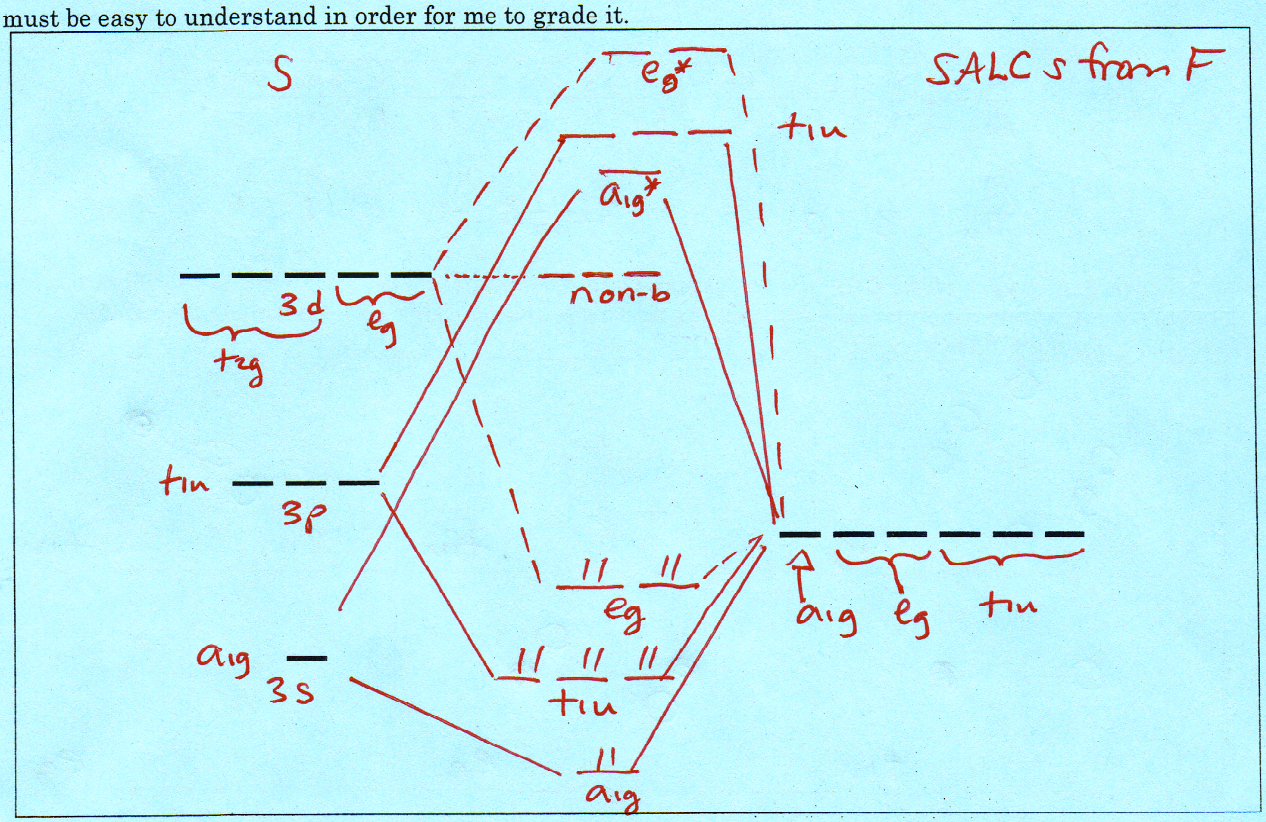
Answers:

| (symmetry) | AO #1 | AO #2 | AO #3 | AO #4 | AO #5 | AO #6 | Total: |
|---|---|---|---|---|---|---|---|
| SALC ( $a_{1g}$ ) | 1/6 | 1/6 | 1/6 | 1/6 | 1/6 | 1/6 | =1 |
| SALC ( eg#1 ) | 1/3 | 1/3 | 1/12 | 1/12 | 1/12 | 1/12 | =1 |
| SALC ( eg#2 ) | 0 | 0 | 1/4 | 1/4 | 1/4 | 1/4 | =1 |
| SALC ( $t_{1u}$ ) | 1/2 | 1/2 | 0 | 0 | 0 | 0 | =1 |
| SALC ( $t_{1u}$ ) | 0 | 0 | 1/2 | 0 | 1/2 | 0 | =1 |
| SALC ( $t_{1u}$ ) | 0 | 0 | 0 | 1/2 | 0 | 1/2 | =1 |
| Total: | =1 | =1 | =1 | =1 | =1 | =1 | |

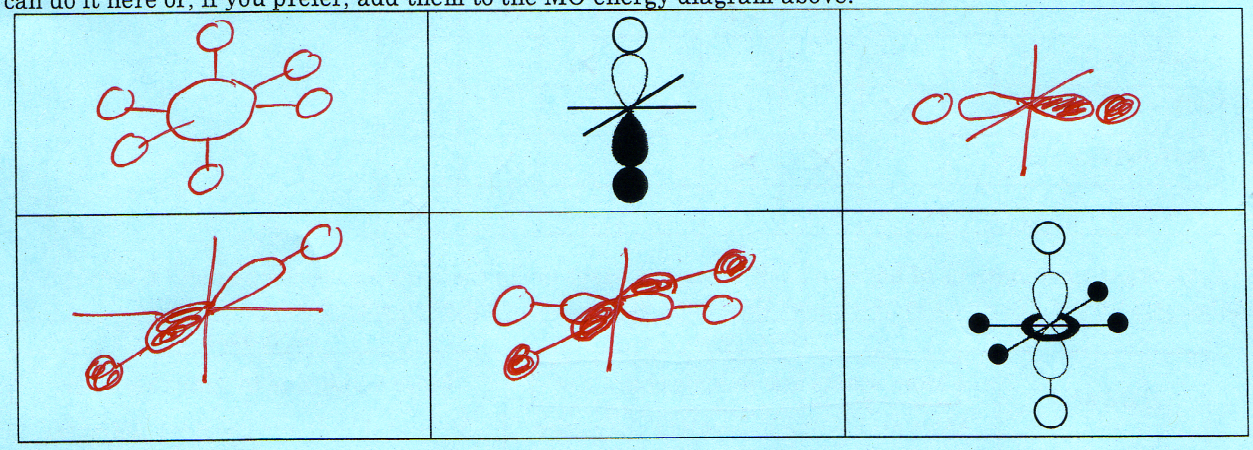
Step 6. (3 pts) List ***all*** of the central atoms <u>valence</u> orbitals (there are 9) and assign each one a symmetry label. In some cases you will need to include empty valence orbitals such as the d-orbitals. This will always be true whenever the octet on the central atom is expanded. In the next step you will compare these orbitals with the SALC set orbitals created in Step 5.

| | | |
|---|---|---|
| s ($a_{1g}$) | $p_z$ ($t_{1u}$) | $p_x$ ($t_{1u}$) |
| $p_y$ ($t_{1u}$) | $d_{z^2}$ ($e_g$) | $d_{x^2-y^2}$ ($e_g$) |
| $d_{xz}$ (nonb) | $d_{yz}$ (nonb) | $d_{xy}$ (nonb) |

Step 7. (8 pts) Create a MO energy diagram. I will be checking for labels and for how you connect the atomic and SALC orbitals with lines. I will also be checking for relative energy levels, conservation of orbitals, eetc.. Start with the SALC set having about the same energy as the s-orbital on sulfur. Your diagram must be easy to understand in order for me to grade it.



Step 8. (6 pts) Sketch molecular orbital line drawings from overlapping SALCs from Step 5 with the symmetry appropriate AOs from Step 6. Just sketch the bonding interactions — skip the antibonding. You can do it here or, if you prefer, add them to the MO energy diagram above.



Step 9. (3 pts) Double check to see if you have conserved orbitals and electrons and then populate the MO diagram. Remember that we only used one electron from each fluorine atom when creating our SALC set. We used all of sulfur's valence electrons.

**Acids and Bases.**

2. (3 pts) In each case, circle the strongest acid in the list:

(a) $HBrO$ $HBrO_2$ $HBrO_3$ $HBrO_4$

(b) $H_2TeO_4$ $H_2TeO_3$ $NaHTeO_4$

(c) $HF$ $HCl$ $H_3PO_4$

3. (5 pts) Circle all Lewis acids. Draw a box around the Lewis bases. Ignore the ones that are neither.

$H_2O$ $N(CH_3)_3$ $AlBr_3$ $Sc^{+3}$ $SiH_4$ $Cl^-$

4 (7 pts) Predict the acid-base nature of each of these salts.

| | | | |
|---|---|---|---|
| $NaNO_3$ | Acidic | Basic | Neutral |
| $NH_4Cl$ | Acidic | Basic | Neutral |
| $KClO_2$ | Acidic | Basic | Neutral |
| $LiC_2H_3O_2$ | Acidic | Basic | Neutral |
| $NaHSO_4$ | Acidic | Basic | Neutral |
| $Na_2SO_4$ | Acidic | Basic | Neutral |
| $KI$ | Acidic | Basic | Neutral |

5(a). (8 pts) Each of these species is a hard or soft acid or base. Write an "x" in the appropriate box under each species.

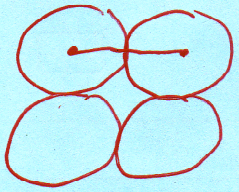
| | $Li^+$ | $Tl^+$ | $Cl^-$ | $NH_3$ | $Pt^{+2}$ | $Ni^{+2}$ | $OH^-$ | $S^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| hard acid | X | | | | | X | | |
| soft acid | | X | | | X | | | |
| hard base | | | X | X | | | X | |
| soft base | | | | | | | | X |

(b) (4 pts) What combinations of hard and soft acids and bases make the most stable compounds? What makes certain combinations more stable? Circle one of the three choices in each box.

| | Hard base | Soft base |
|---|---|---|
| Hard acid | **More stable due to ionic character**<br>More stable due to covalent character<br>Not as stable as other combinations | More stable due to ionic character<br>More stable due to covalent character<br>**Not as stable as other combinations** |
| Soft acid | More stable due to ionic character<br>More stable due to covalent character<br>**Not as stable as other combinations** | More stable due to ionic character<br>**More stable due to covalent character**<br>Not as stable as other combinations |

**On the finer points of ionic compounds.**

6. (5 pts) Uranium crystallizes in a simple cubic unit cell and has a density of 19.05 g/cm$^3$. What is the atomic radius in picometers of uranium?



one face

$e = 2r$

$V = e^3 = 8r^3$

$d = \frac{m}{V} \rightarrow V = \frac{m}{d} = \frac{238\,g}{mol} \left| \frac{mol}{6.02 \times 10^{23}\,atoms} \right| \frac{1\,atom}{19.05\,g} \left| \frac{cm^3}{} \right.$

$= 2.07 \times 10^{-23}\,cm^3$

$e = 2.74 \times 10^{-8}\,cm$

$r = 1.37 \times 10^{-8}\,cm$

$= 137\,pm$

7. The mineral pyrargyrite, $Ag_3SbS_3$, utilizes the hexagonal lattice system. The sulfides are space-filling and the $Ag^+$ ions occupy one sort of hole (either octahedral or tetrahedral) while the $Sb^{+3}$ ions occupy the other sort of hole.

(a) (2 pts) Which cation do you think occupies each hole and why?

The $Ag^+$ ions occupy the (octahedral or tetrahedral) holes. (Circle either octahedral or tetrahedral.)

The $Sb^{+3}$ ions occupy the (octahedral or tetrahedral) holes.

Why did you pick the one you did? (in 10 words or fewer)

$Sb^{+3}$ ions are smaller

(b) (2 pts) What fraction of octahedral holes would be occupied with your model of what is happening?

all

(c) (2 pts) What fraction of tetrahedral holes would be occupied with your model of what is happening?

1/6

8(a) (3 pts) Which of the compounds listed at right *could* possibly have the fluorite lattice structure? Circle all that could; there may be 0 – 4.

| | |
|---|---|
| $SrF_2$ | $MgCl_2$ |
| RbF | KCl |

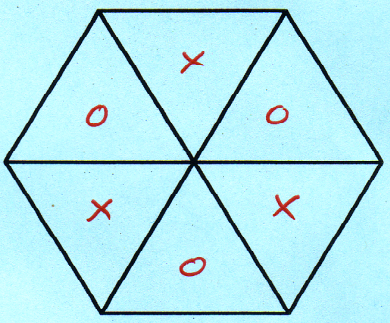
(b) (2 pts) The ***antifluorite*** structure is the same as the fluorite structure except that the cations and anions are switched. Which one of the compounds listed at right *could* exhibit the antifluorite structure?

| | |
|---|---|
| $BeI_2$ | CaO |
| $K_2O$ | CsF |

9. (3 pts) Silicon and tin both exhibit the diamond structure. How many atoms are present per unit cell in the diamond structure?

Answer: eight

10. At right is the top view of a ***hcp*** lattice. Only the "A" layer is shown.




(a) (2 pts) How many unit cells are represented in the figure?

three

(b) (2 pts) Draw small circles on the figure where the center of "B" layer atoms would go.

(c) (2 pts) Draw "x" marks on the figure above the centers of the octahedral holes.

11. (3 pts) The diameters of tetrahedral, octahedral and cubic holes are $0.225r_{large}$, $0.414r_{large}$, and $0732r_{large}$, respectively. If an ionic compound had a radius ratio value of 0.500, which type of hole would you predict is occupied by the small ions.

**Circle:** tetrahedral holes octahedral holes cubic holes

12. (3 pts) With each pair of compounds, circle the one with the predicted largest lattice energy.

(a) LiF or LiBr (b) $CaF_2$ or CaO (c) $Na_3N$ or ScN

13. (4 pts) How many formula units (or large atoms/ions) are in each of the following unit cell?

| | |
|---|---|
| (a) base-centered monoclinic | 2 |
| (b) body-centered orthorhombic | 2 |
| (c) rhombohedron | 1 |
| (d) simple triclinic | 1 |

14.(5 pts) Print your name here:

| | |
|---|---|
| | Score: |