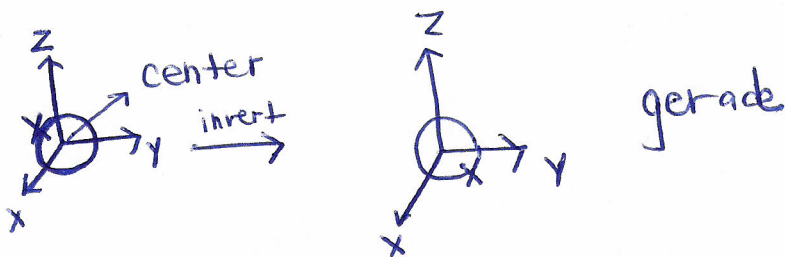
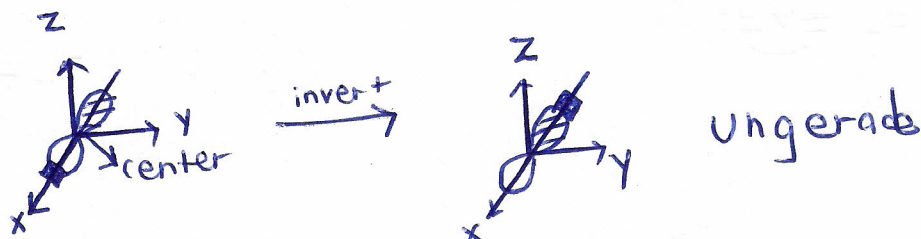


3. (10 points) Draw the following orbitals on the x, y, z coordinate system and show whether they are gerade or ungerade.

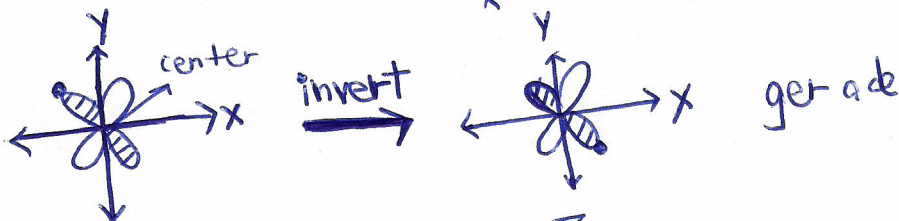
a. s orbital



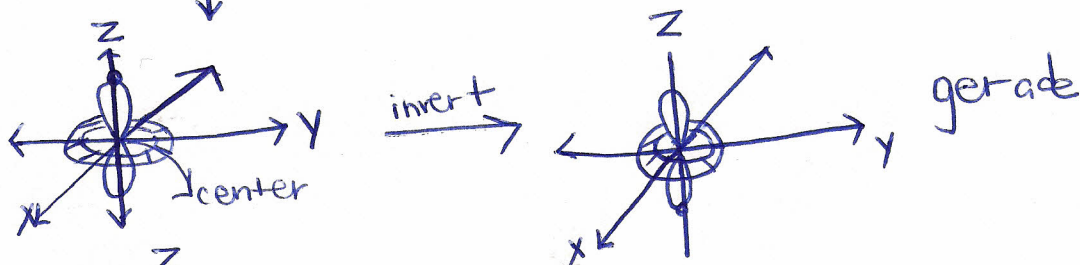
b. p_x orbital



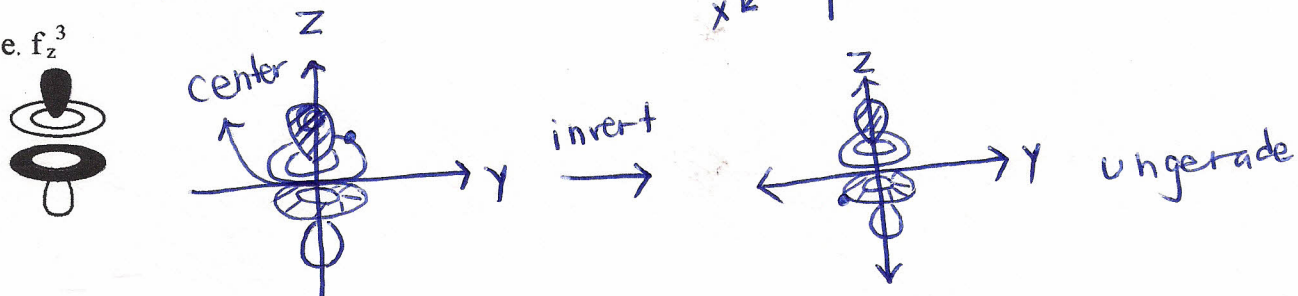
c. d_{xy} orbital



d. d_z^2



e. f_z^3



4. (5 points) Why are Se(VI) compounds less stable than those of S(VI) and Te(VI)?

This is due to the s contraction. The 3d orbitals are poorer shielders and the 4s + 4p e^- are more tightly held than expected.

5. (10 points) Answer the following questions using the character table for the S_4 point group.

S_4	E	S_4	C_2	S_4^3		
A	1	1	1	1	R_z	x^2+y^2, z^2
B	1	-1	1	-1	z	x^2-y^2, xy
E	1	i	-1	-i	(x,y); (R_x, R_y)	(xz, yz)
	1	-i	-1	i		

a. Would a molecule of this point group be chiral? Explain.

No because it has an S_4 symmetry.

b. Would a molecule of this point group have a dipole moment? Explain.

Yes because no S_1 , no C_n ($n > 1$), and no more than one C_n ($n > 1$).

c. What is the symmetry of the translations?

E: x + y

B: z

d. What is the symmetry of the rotations?

A: R_z

E: R_x, R_y

e. Why are there several sets of two basis functions in parenthesis for the E irreducible representation?

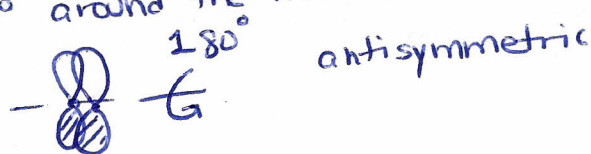
E is a doubly degenerate state and so the basis functions in parenthesis are doubly degenerate.

6. (5 points) How do you distinguish between a sigma and pi bond in terms of symmetry around the internuclear axis?

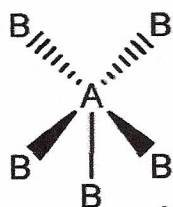
In σ bonds, rotations at any angle around the internuclear axis maintains symmetry.



In π bonds, rotations at 180° around the internuclear axis does not maintain symmetry.



7. (30 points) Consider the molecule depicted below in which A is an element from $n=3$.

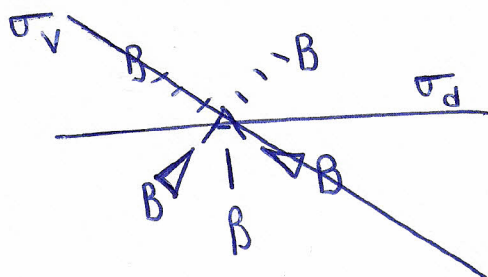
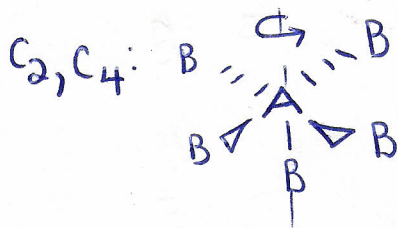


Charac. Contrib.

C_{4v}	3	1	-1	1	1		
	E	$2C_4$	C_2	σ_v	σ_d		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x,y); (R_x, R_y)	(xz, yz)

a. Find one type of ALL of the symmetry elements/operations in the molecule and either describe their locations in words or draw them.

E: Keep the molecule in place



b. How many normal vibrational modes do you expect for this molecule?

$$3N - 6 = 3(6) - 6 = 12$$

Should get 12 normal modes.

c. Give the symmetries of the normal modes and say which will be IR or Raman active.

Basis set: All of the atoms
 $3N = 18$ degrees of freedom

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Unmoved	6	2	2	4	2
x charac cont.	3	1	-1	1	1
$\overline{\text{red}} = 18$	2	-2	4	2	

$$A_1 = \frac{1}{8} [(18 \times 1 \times 1) + (2 \times 1 \times 2) + (-2 \times 1 \times 1) + (4 \times 1 \times 2) + (2 \times 1 \times 2)] = 4$$

$$A_2 = \frac{1}{8} [18 + 4 + (-2) + (-8) + (-4)] = 1$$

$$B_1 = \frac{1}{8} [18 + (-4) + (-2) + 8 + (-4)] = 2$$

$$B_2 = \frac{1}{8} [18 + (-4) + (-2) + (-8) + 4] = 1$$

$$E = \frac{1}{8} [36 + 0 + 4 + 0 + 0] = 5$$

$$\overline{\text{red}} = 4A_1 + 1A_2 + 2B_1 + 1B_2 + 5E$$

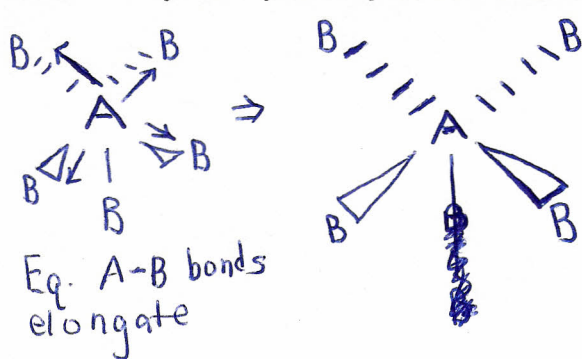
18 degrees of freedom
 + E translations
 + E rotations

$$= 3A_1 + 2B_1 + 1B_2 + 3E \quad 12 \text{ irred. rep.}$$

A_1 : IR + Raman active
 B_1 : Raman active

B_2 : Raman active
 E : IR + Raman active

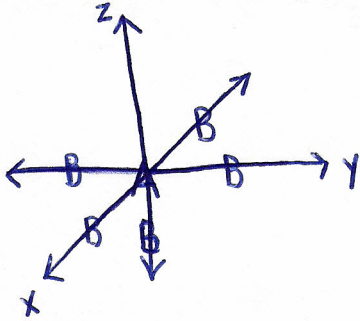
d. What is the symmetry for a symmetric stretch of the A-B bonds in the equatorial plane?



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
	1	1	1	1	1

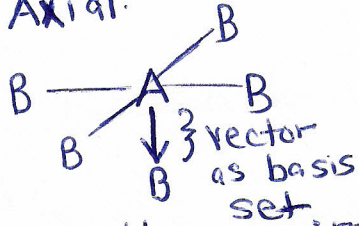
Symmetry: A_1

e. Use group theory to determine the orbital hybridization of the central atom. Determine which orbitals from the axial and equatorial bond positions contribute to the hybridization. Hint: Select a basis set for the axial sigma bonding and equatorial sigma bonding.



Remember to consider the directionality of the orbitals.
 → There are five σ bonds + \therefore 5 hybrid orbitals + 5 irred. rep. total.
 Hybridization should be dsp^3 because created from five atomic orbitals.

Axial:



Should be one irred. rep.

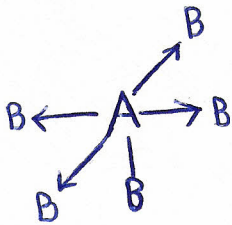
+1: Unmoved
 0: Moved

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Red	1	1	1	1	1

a_1 : ~~p_z~~ , ~~d_{z^2}~~
 p_z is lower in energy
 ↓
 Not optimal directionality

Axial: p_z

Equatorial:



4 vectors: 4 irred. rep.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
	4	0	0	2	0
	4	2	0	-2	0

$$A_1 = \frac{1}{8} [(4 \times 1 \times 1) + (0) + (0) + (2 \times 1 \times 2) + (0)] = 1$$

$$A_2 = \frac{1}{8} [4 + 0 + 0 + (-4 + 0)] = 0$$

$$B_1 = \frac{1}{8} [4 + 0 + 0 + 4 + 0] = 1$$

$$B_2 = \frac{1}{8} [4 + 0 + 0 + (-4 + 0)] = 0$$

$$E = \frac{1}{8} [8 + 0 + 0 + 0 + 0] = 1$$

Red: $1A_1 + 1B_1 + 1E$
 E : ~~d_{xz}, d_{yz}~~ or p_x, p_y
 Not correct directionality.

Equatorial: $p_x, p_y, d_{x^2-y^2}, s$

In total, dsp^3

b_1 : $d_{x^2-y^2}$
 a_1 : s, p_z, d_{z^2} → Too high in energy
 ↓
 Not correct directionality

f. Based on Bent's rule, in which position would a more electronegative ligand prefer to be located. Using your answer for part e to explain.

The more X ligand would prefer the axial position because from the analysis above, the bond has less s character. Also that position is more crowded and it would have to share less e^- density.

8. (10 points) Identify ALL of the atomic states for the s^2d^1 electronic configuration and arrange these states in order of energy starting with the ground state.

$N = \frac{10!}{1!(10-1)!} = 10$ microstates

s^2 $\uparrow \downarrow$ full		d^1 \uparrow									
		m_l									
		$+2 \quad +1 \quad 0 \quad -1 \quad -2$									
		M_L									
		$+2 \quad +1 \quad 0 \quad -1 \quad -2$									
		m_l									
		$+2 \quad +1 \quad 0 \quad -1 \quad -2$									
		M_L									
		$+2 \quad +1 \quad 0 \quad -1 \quad -2$									
		M_S									
		$\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2} \quad -\frac{1}{2} \quad -\frac{1}{2}$									

		M_S	
		$\frac{1}{2} \quad -\frac{1}{2}$	
		M_L	
		$+2 \quad +1 \quad 0 \quad -1 \quad -2$	
		M_L	
		$+2 \quad +1 \quad 0 \quad -1 \quad -2$	
		M_S	
		$\frac{1}{2} \quad -\frac{1}{2}$	

$L = +2$
 $S = \frac{1}{2}$

$2(L) + 1 = 5$ rows } atomic state
 $2(S) + 1 = 2$ columns }

\square : $L = 2$ D
 Mult. = 2
 $J = L + S, \dots, L - S = \frac{5}{2}, \frac{3}{2}$

$E \uparrow$

$2D \rightarrow 2D_{5/2}$
 $\rightarrow 2D_{3/2}$

Valence orbitals are less than half-filled

9. (5 points) Fluorine is the most electronegative element and yet its electron affinity is not as high as you would predict based on periodic trends. Explain.

Due to F's small atomic radius the addition of an e^- would lead to a greater e^-e^- repulsion that would decrease its electron affinity.

Extra Credit:

1. (Explain) Between H^- and F^- which has

a. Higher atomic radius H^- ; experimentally observed

b. Higher ionization energy H^- ; filled 1s orbital

c. Higher electron affinity
Should be comparable because they would not be drawn to an additional e^- .

2. Determine the complete Russell-Saunders term symbols for all of the atomic states of this element and arrange them in order of energy using the microstate table below and properly show the ground state.

$M_L \backslash M_S$	1.5	0.5	-0.5	-1.5
+5		(X)	(X)	
+4		(XX)	(XX)	
+3	(X)	(XXX)	(XXX)	(X)
+2	(X)	(XXXX)	(XXXX)	(X)
+1	(XX)	(XXXXX)	(XXXXX)	(XX)
0	(XX)	(XXXXXX)	(XXXXXX)	(XX)
-1	(XX)	(XXXXXX)	(XXXXXX)	(XX)
-2	(X)	(XXXX)	(XXXX)	(X)
-3	(X)	(XXX)	(XXX)	(X)
-4		(XX)	(XX)	
-5		(X)	(X)	

0: $L=5$
 $S=0.5$
Mult.: $2(S)+1=2$

□: $L=4$
 $S=0.5$

Δ: $L=3$
 $S=1.5$
Mult.: $2(S)+1=4$

○: $L=3$
 $S=0.5$

■: $L=2$
 $S=0.5$

▲: $L=2$
 $S=0.5$

√: $L=+1$
 $S=0.5$

X: $L=+1$
 $S=0.5$



- 2P
- 2D
- 2F
- 2G
- 2H
- - 4P
- - 4F

I omitted the J terms.