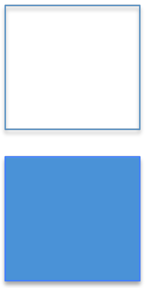
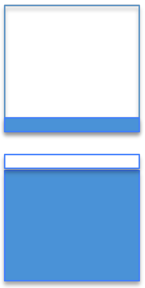
Chm 451 with Dr. Mattson Exam 3 **Name:**

1 December 2011





1. (8 pts) Refer to the first (leftmost) figure at right to answer Question 1.

   1a. What does the overall figure represent?

   1b. What does the blue vs white coloring represent?

   1c. What is the name of the space between the two rectangles?

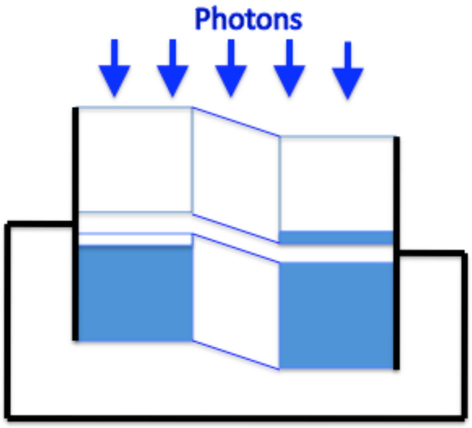
   1d. Might this figure represent a first row transition metal? Why or why not?

2. (6 pts) Refer to the second figure at right (above) to answer Question 2.

   2a. What is the significance of the different appearance of the two figures?

   2b. Does either figure represent a diode?

   2c. Could one switch from the situation represented by <u>right</u> figure to the <u>left</u> figure by changing some condition? If so, what?



3. (2 pts) Very carefully, precisely and meticulously sketch with a single-headed arrow the energy change that is facilitated by the photons in this diagram of a photovoltaic cell (photocell).

4. (4 pts) The atomic radii for similarly charged ions within the same family (group) vary in a surprising way.

	r_+(pm)
V^{+3}	78
Nb^{+3}	86
Ta^{+3}	86

	r_+(pm)
Co^{+3}	69
Rh^{+3}	81
Ir^{+3}	82

	r_+(pm)
Ni^{+2}	83
Pd^{+2}	100
Pt^{+2}	94

4a. What causes the increase when going from the first row to the second row as per these data?

4b. What causes the change noted when going from the second row to the third row as per the data given?

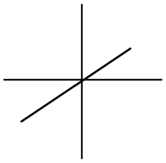
5. (5 points) Complete the following table

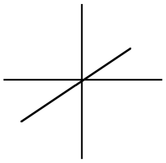
	Coordination number	Charge on metal complex ion	Charge on metal	Predicted geometry
$[Cu(NH_3)_6]SO_4$				
$K_3[Ru(CN)_6]$				
$NH_4[FeCl_4]$				
$[Co(en)_3]_2(SO_4)_3$*				
$[Pd(NH_3)_4]Cl_2$				

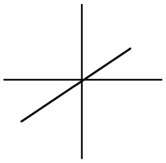
* en is a bidentate chelate ligand

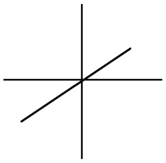
6. (6 pts) How many isomers are possible for each of the following. Sketch them using as many of the octahedral templates as is necessary.

MA_4B_2

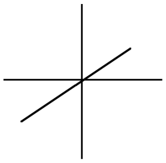


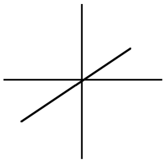


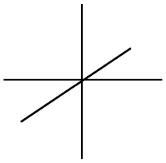


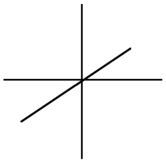


MA_3B_3

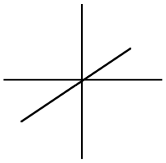


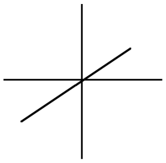


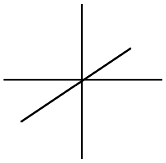


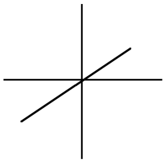


MA_3B_2C

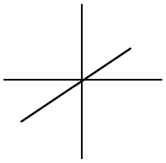


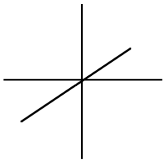






7. (4 pts) None of the sketches above is chiral. Sketch an octahedral molecule that is chiral (along with its enantiomeric pair) using no more than four ligands, A, B, C, and D.





8. (2 pts) Sketch the crystal field splitting pattern for the d-orbitals in an octahedral crystal field. Label each of the five d-orbitals.

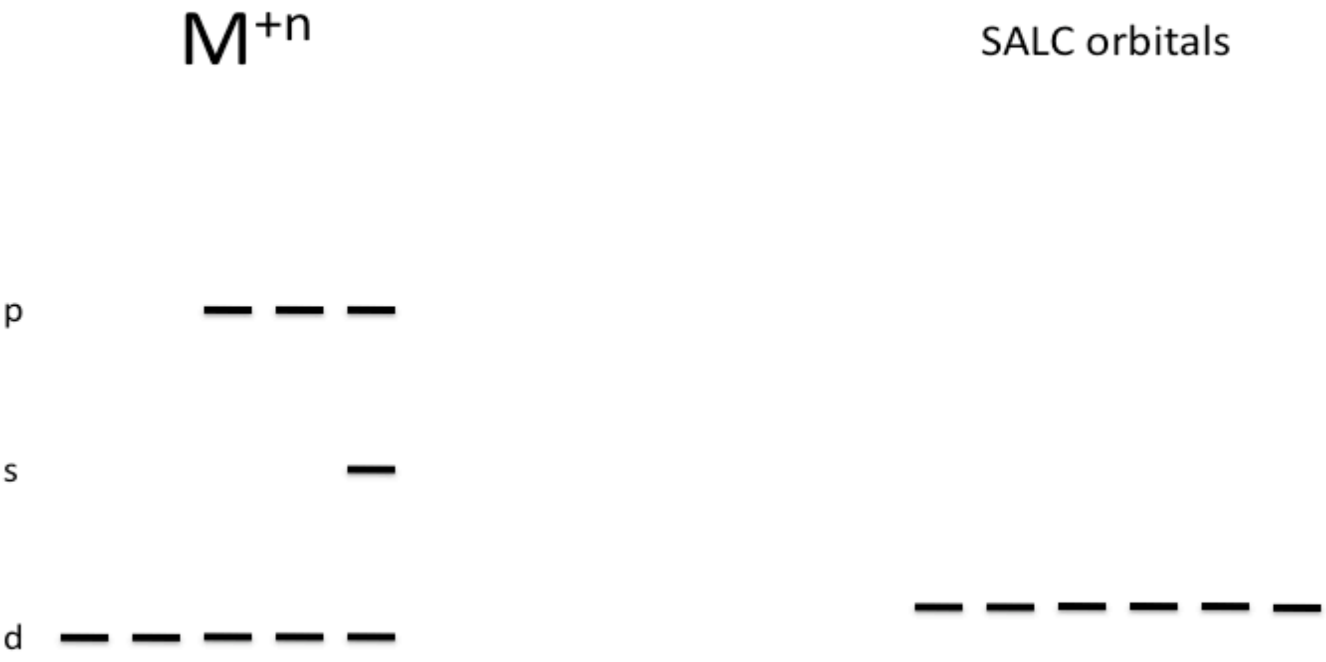
9. (8 pts) Use the diagram above to complete the following table. Note: No two of these have the same number of unpaired electrons (each is unique from the other three.)

	d electron configuration (e.g. d^3)	Predict: high spin, low spin or N/A	Number of unpaired electrons	CFSE (e.g. $0.6\ \Delta_o - 2\ P$)
$[Cu(NH_3)_6](NO_3)_2$				
$K_4[Ru(CN)_6]$				
$(NH_4)_3[VCl_6]$				
$[Mn(H_2O)_6]SO_4$				

10. (3 pts) What are the three conditions necessary for a d^4 octahedral complex to be high spin?

11. (3 pts) The complex ion $Ag(NH_3)_2^+$ is linear. Predict the crystal field splitting pattern predicted for this complex. As always, the principle axis is the z-axis.

12. (6 pts) The octahedral character table appears at the bottom of this page. Given that the six σ-bonding orbitals surrounding a metal ion in an octahedral field transform as A_{1g} + E_g + T_{1u}, complete the MO diagram. All connecting lines must be shown.



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		$x^2 + y^2 + z^2$
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_{1g}	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		(xy, 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		
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		

Questions 13 – 16 refer to the molecular orbital diagram you sketched in the previous problem.

13. (6 pts) Sketch the orbital diagram for the following molecular orbitals. If the MO is part of a degenerate set, sketch only one member of the set.

(a) a_{1g}	(b) t_{1u}	(a) e_g
(d) a_{1g}^*	(e) t_{2g}	(f) t_{1u}^*

14. (2 pts) Populate the MO diagram for $Cr(H_2O)_6^{+3}$.

15. (2 pts) What two molecular orbitals are equivalent to the pattern predicted by crystal field theory.

16a. (2 pt) The t_{2g} orbitals are non-bonding in the MO diagram. When the ligand orbitals are capable of π-bonding to the metal, it is the t_{2g} orbitals that participate in forming MO with the π^* orbitals from the ligands. When this occurs, what happens to the energy level of the formerly non-bonding t_{2g} orbitals?

16b. (1 pt) As a result of what happened in 16a, what happens to the preferred number of valence electrons that the complex should have?

A. the range in electrons is 0 – 22.

B. the range in electrons is 12 – 22.

C. the range in electrons is 12 – 18.

D. the range in electrons is 18 – 22.

E. the number of electrons is 18.

17. Suppose you were to work out the term symbols for d^4 using the method of microstates.

17a. (2 pt) What values of M_S would you use?

17b. (2 pt) What values of M_L would you use?

17c. (2 pt) What is the value of S?

17d. (2 pt) What is the value of L?

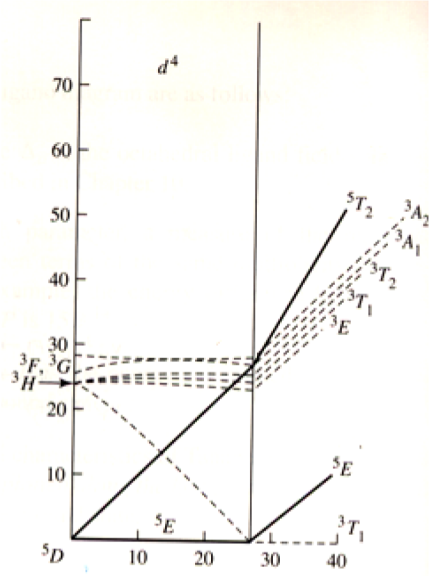
17e. (2 pt) What is the free ion ground state term symbol?

17f. (4 pts) Sketch the energy split that occurs when a high-spin d^4 metal ion is subjected to an octahedral field. Label the new term symbols (using A, T, or E). Add a label for Δ_o. Sketch a representative microstate for each term.

17g. (2 pt) Along with high-spin d^4, what other octahedral d^x configuration would have the same ground and excited state(s)?

17h (4 pt) What tetrahedral electronic configurations, d^x, would have the same ground state as octahedral high-spin d^4?

18a. (1 pt) The Tanabe-Sugano diagram for octahedral d^4 is shown at right. Ignoring Jahn-Teller distortion (which is not shown in the Tanabe-Sugano diagrams), how many d-d transitions are expected (spin allowed) for a high-spin d^4 metal ion in an octahedral field?



18b (1 pt) Will the number of spin-allowed transitions increase, decrease or stay the same when the complex becomes low-spin? Circle one: A. increase B. decrease C. stay the same

19a. (3 pts) Octahedral high-spin d^4 is one of the cases in which a Jahn-Teller distortion is predicted. Sketch the Jahn-Teller energy level splitting that is expected for high-spin d^4 in an octahedral field.

19b. (1 pt) Populate your sketch above with 4 electrons (high-spin).

19c. (2 pt) How many spin-allowed d-d transitions are predicted? Indicate them with arrows on the diagram in 19a.

19d. (1 pt) Is a compression, elongation, either, or neither predicted? **Circle one:**

A. compression B. elongation C. either D. neither

19e. (1 pt) $Cr(H_2O)_6^{+2}$ is an example of a high-spin d^4 ion. It exhibits two bands in the visible spectrum, at 9500 and 14000 cm^{-1}. Is either one a good estimation of Δ_o?

BONUS! (5 pts) The complex ion CoF_6^{-3} exhibits two absorption bands, 11,400 and 14,500 cm^{-1}. Explain these bands and how they account for whether the cobalt ion is high or low spin.

Answers:

1a. A molecular orbital diagram for a network covalent or metallic substance.

1b. The blue part is the molecular orbitals filled with electrons and the white region are the empty molecular orbitals.

1c. band gap

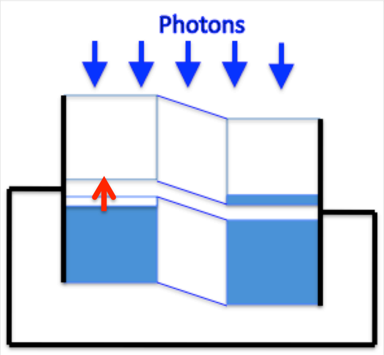
1d. No, metals do not have band gaps

2a. The figure at right shows a Group 4 element (e.g. silicon) at room temperature, where there are a few electrons above the band gap due to thermal excitation (recall Boltzmann distribution).

2b. no

2c. By lowering the temperature, the electrons above the band gap (right figure, top) will relax back to give the ground state figure (the left figure).

3.



4a. A new shell is being filled and size (radius) is expected to increase going down a column.

4b. The increase in size expected (4a) is offset by the lanthanide contraction, basically the increased Z_{eff} caused by the 14 extra protons in the lanthanide series (that occur between the second and third transition row elements.

5. (5 points) Complete the following table

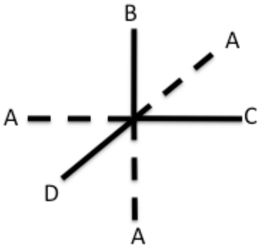
	Coordination number	Charge on metal complex ion	Charge on metal	Predicted geometry
$[Cu(NH_3)_6]SO_4$	6	+2	+2	octahedral
$K_3[Ru(CN)_6]$	6	-3	+3	octahedral
$NH_4[FeCl_4]$	4	-1	+3	tetrahedral
$[Co(en)_3]_2(SO_4)_3$*	6	+3	+3	octahedral
$[Pd(NH_3)_4]Cl_2$	4	+2	+2	square planar

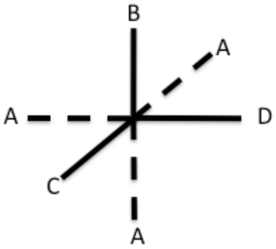
6a. sketches of cis and trans

6b. sketches of fac and mer

6c. there are three: 1. Ligands A fac; 2. Ligands A mer and B trans; 3. Ligands A mer and B cis

7. There are many answers for this one. The pair shown below groups the Ligands A as a fac group and they function as one group in the sense of structure; then B, C, and D can be chiral as per the "tetrahedron." In addition to this one there is one that can be drawn with only three ligands, A, B, and C: make the A groups cis, the B groups cis and the C groups cis.





8. three lower energy orbitals are d_{xz}, d_{yz}, d_{xy}; two higher energy orbitals are d_{z2} and d_{x2-y2}.

9.

	d electron configuration (e.g. d^3)	Predict: high spin, low spin or N/A	Number of unpaired electrons	CFSE (e.g. 0.6 Δ_o - 2 P)
$[Cu(NH_3)_6](NO_3)_2$	d^9	na	1	0.6 Δ_o - 4 P
$K_4[Ru(CN)_6]$	d^6	ls	0	2.4 Δ_o - 3 P
$(NH_4)_3[VCl_6]$	d^2	na	2	0.8 Δ_o
$[Mn(H_2O)_6]SO_4$	d^5	hs	5	0

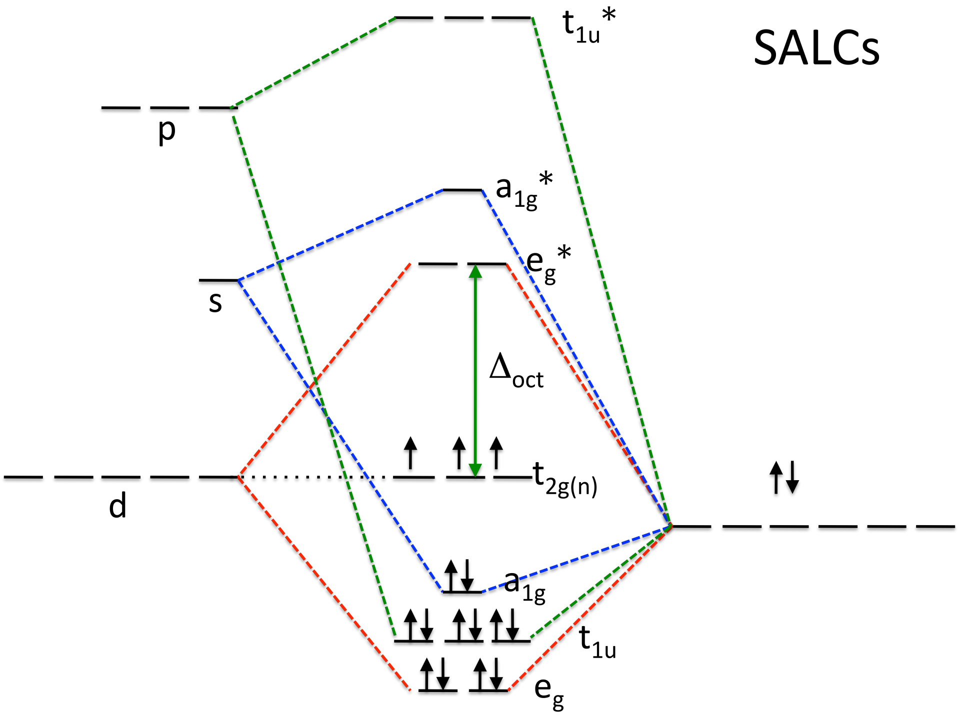
10. 1. Ligand must be weak-field

2. Metal must have small oxidation state

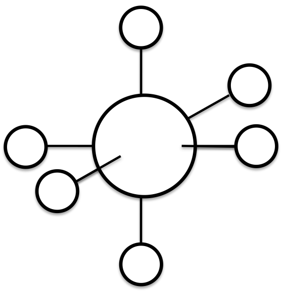
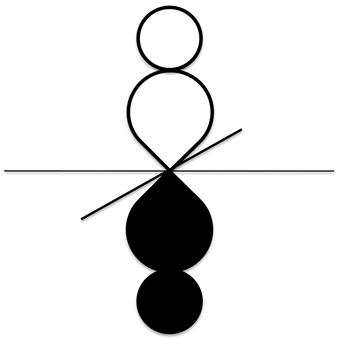
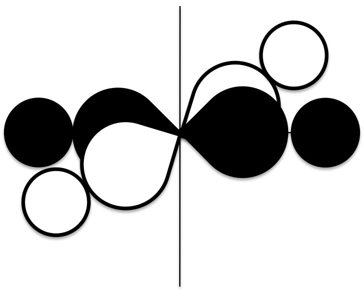
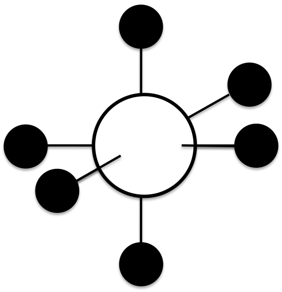
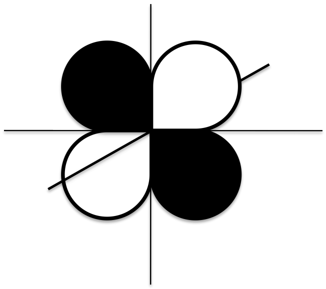
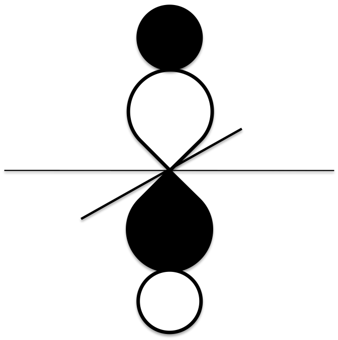
3. Metal must be first row

11. Lowest in energy and degenerate are: d_{xy} and d_{x2-y2}. Next lowest in energy and also degenerate are d_{xz}, d_{yz}. The highest energy orbital is d_{z2}.

12. (6 pts)



13. (6 pts) Sketch the orbital diagram for the following molecular orbitals. If the MO is part of a degenerate set, sketch only one member of the set.

(a) a_{1g} 	(b) t_{1u} 	(a) e_g 
(d) $a_{1g}{}^*$ 	(e) t_{2g} 	(f) $t_{1u}{}^*$ 

14. see MO diagram

15. t_{2g} and $e_g{}^*$

16a. (2 pt) The t_{2g} orbitals, originally non-bonding, become bonding with the π^* orbitals on the cyanide. This greatly increases Δ_{oct}

16b. E

17a. M_S = 2, 1, 0, -1, -2

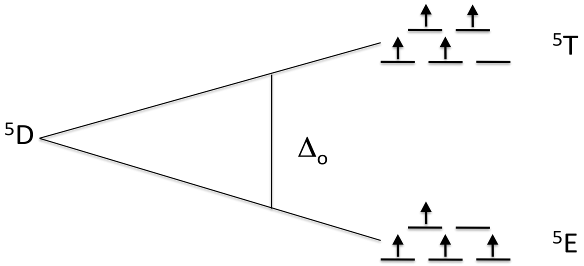
17b. M_L = 6, 5, 4, 3, 2, 1, 0, -1, -2, -3, -4, -5, -6

17c. S = 2

17d. L = 6

17e. ^5D

17f.



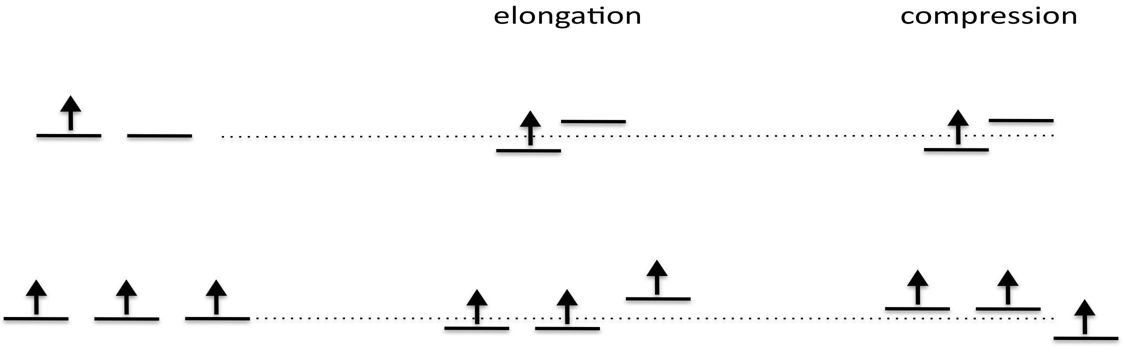
17g. d^9

17h d^1, d^6

18a. one, ^5E → ^5T

18b A

19a and b.



19c. two from either lower orbital to the empty high-energy orbital

19d. C

19e. no

BONUS! Co^{+3} is d^6. In an octahedral field, d^6 low-spin has zero unpaired electrons and no spin-allowed transitions. By contrast, field, d^6 high-spin has 4 unpaired electrons and has one spin-allowed transition, except for JT, which predicts two transitions.