PLTL Worksheet #8:
Bonding in Transition Metals

1. *Review of SALCs*

    a. Consider 6 s orbitals arragned in an octahedral geometry. Deterine and draw for yourself the 6 SALCS that can be formed.
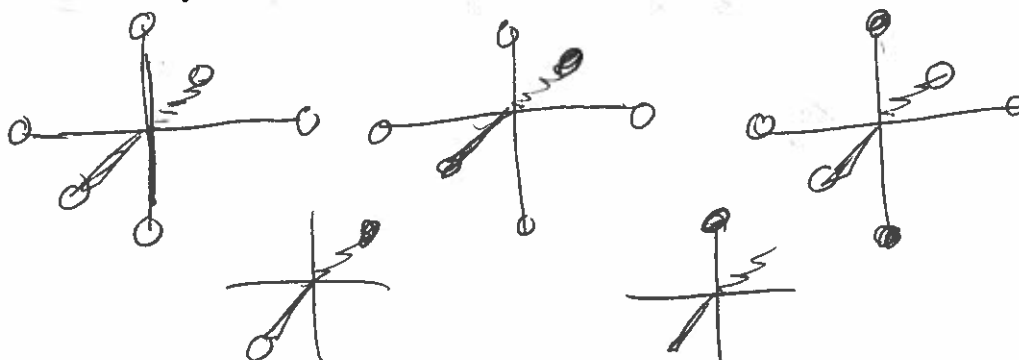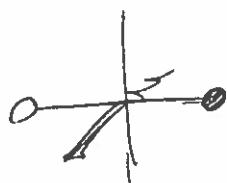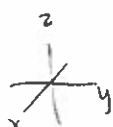
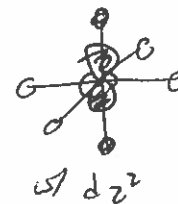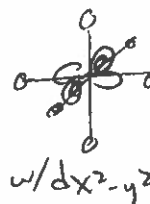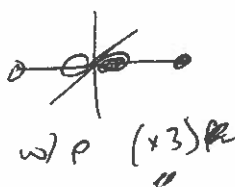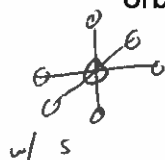   b. Determine the ways in which these SALCs can interact with the d orbitals, s orbitals and p orbitals of the metal center

   w/ s   w/ p (×3)   w/dx²-y²   w/ dz²

    d_{xy}, d_{yz}, d_{xz} or non bonding

    c. Based on your drawings, derive the MO diagram (page 310 of your notes) for an octahedral complex with sigma donor ligands
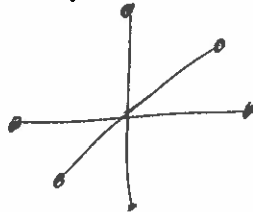
    Cn still have the students dew it out to verify for themselves

2. *CFT: d-orbital splitting for an octahedral complex*

a. To start draw the 5 d orbitals. Be sure to indicate your coordinate system!

d_{z^2} d_{xy} $d_{x^2-y^2}$ d_{yz} d_{xz}
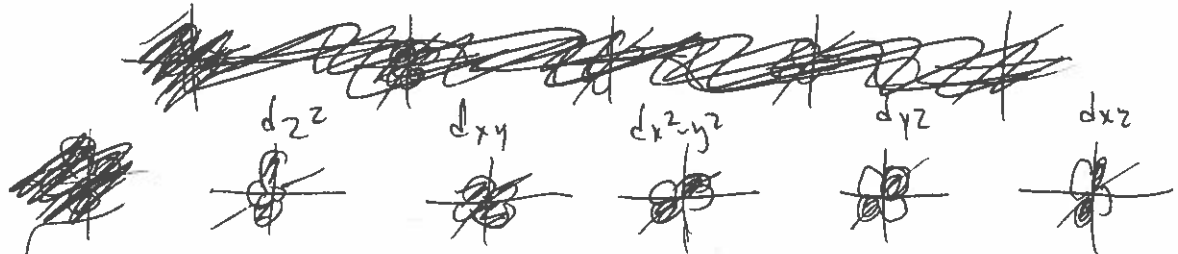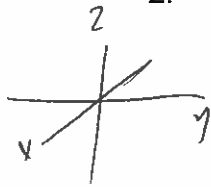
b. Draw an arrangement of (negative) point charges in an octahedral geometry.

c. Draw each d orbital inside of the 6 point charges.

Combine these two drawings.

d. Picture these point charges moving closer and closer to the electron density of the d orbtials. Closer and better interaction of the point charges with the orbtials results in greater e-e repulsion, which is destabilizing. Based on that, which d orbtials would you expect to be destabilized? Stabilized?

$d_{x^2-y^2}$ $\overline{d_{z^2}}$ ← more electron density of orbtal interacting w/ pt charges.   (destabilized)

d_{xz} d_{yz} d_{xy}

← stabilized
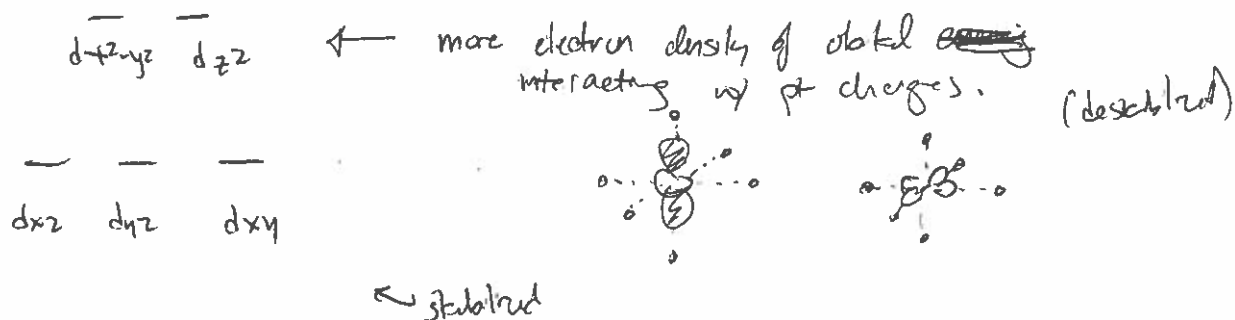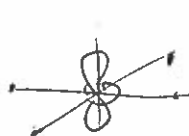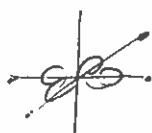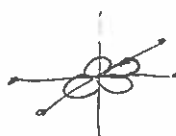
4.   *CFT: d-orbital splitting for a square planar complex*

   a. Draw an arrangement of (negative) point charges in a square planar geometry.

   b. Draw each d orbital inside of the 4 point charges.

dz^2 dx^2-y^2 dxy

not very much interek   must interact   some interek
                                                (more than dz^2)

   c. Picture these point charges moving closer and closer to the electron density of the d orbtials. Closer and better interation of the point charges with the orbtials results in greater e-e repulsion, which is destabilizing. Based on that, which d orbtials would you expect to be destabilized? Stabilized?

   — dx^2-yz

   — dxy
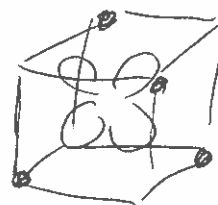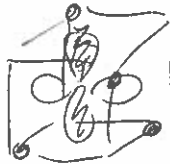
   — dz^2

   — dyz — dxz

Same amount of interek

3. *CFT: d-orbital splitting for tetrahedral complex*

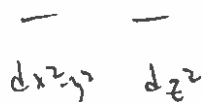   a. Draw an arrangement of (negative) point charges in tetrahedral

   b. Draw each d orbital inside of the 4 point charges.

   (note how tetrahedron would fit into a the x, y, z coordinate

   picture it as a cube w/ points ~ opposite corners.

   note the difference b/w $d_{x^2-y^2}$ and d_{xy}

   ($d_{x^2-y^2}$)

   c. Picture these point charges moving closer and closer to the electron density of the d orbitals. Closer and better interation of the point charges with the orbtials results in greater e-e repulsion, which is destabilizing. Based on that, which d orbtials would you expect to be destabilized? Stabilized?

   ___ ___ ___
   d_{xy} d_{xz} d_{yz}

   ___ ___
   $d_{x^2-y^2}$ d_{z^2}

PLTL Worksheet #9:
Bonding in Transition Metals

1. *More CFT (d-orbital splitting of a trigonal complex)*

    a. To start, draw the 5 d-orbitals. Be sure to assign an consistent coordinate system!
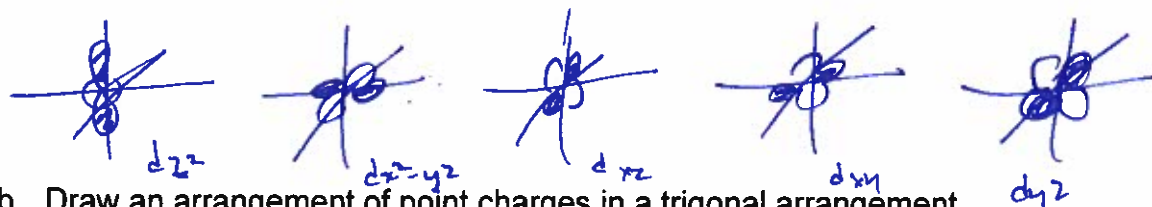
    b. Draw an arrangement of point charges in a trigonal arrangement

    (imagine flat on x y plane)

    c. Draw each d-orbital inside of the 3 point charges

    d. Imagine these point charges moving closer and closer to the electron density of the d orbitals. Which orbitals will be destabilized? Stabilized? Draw the relative energy levels of the orbitals.

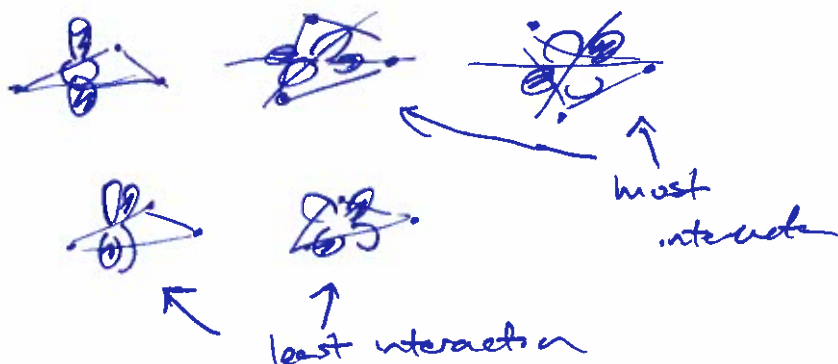2. *More CFT (d-orbital splitting of a square pyramidal complex)*

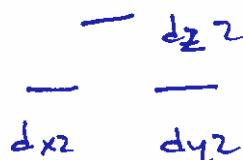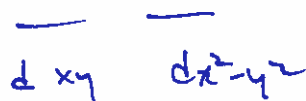   a. To start, draw the 5 d-orbitals. Be sure to assign an consistent coordinate system!

   See prewous

   b. Draw an arrangement of point charges in a ~~trigonal~~ square pyramidal arrangement

   (put the points ryht aley axes)

   c. Draw each d-orbital inside of the ~~3~~ 5 point charges

   d. Imagine these point charges moving closer and closer to the electron density of the d orbitals. Which orbitals will be destabilized? Stabilized? Draw the relative energy levels of the orbitals.
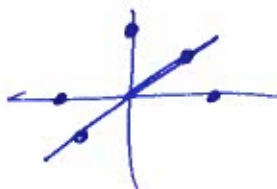
   — $d_{x^2-y^2}$

   — d_{z^2}

   — d_{xy}

   —   —

   d_{yz} d_{xz}

3. *Ligand/Crystal Field Splitting Energy*

   a. Calculate the crystal/ligand field splitting energy for the following:

      i. d^1 $-2/5\,\Delta_o$
      ii. d^3 $-6/5\,\Delta_o$
      iii. LS d^5 $-10/5\,\Delta_o + 2P$
      iv. HS d^5 $0\,\Delta_o$
      v. d^9 $-3/5\,\Delta_o$

   b. Discuss the general trends that exist for the magnitude of Δ_o

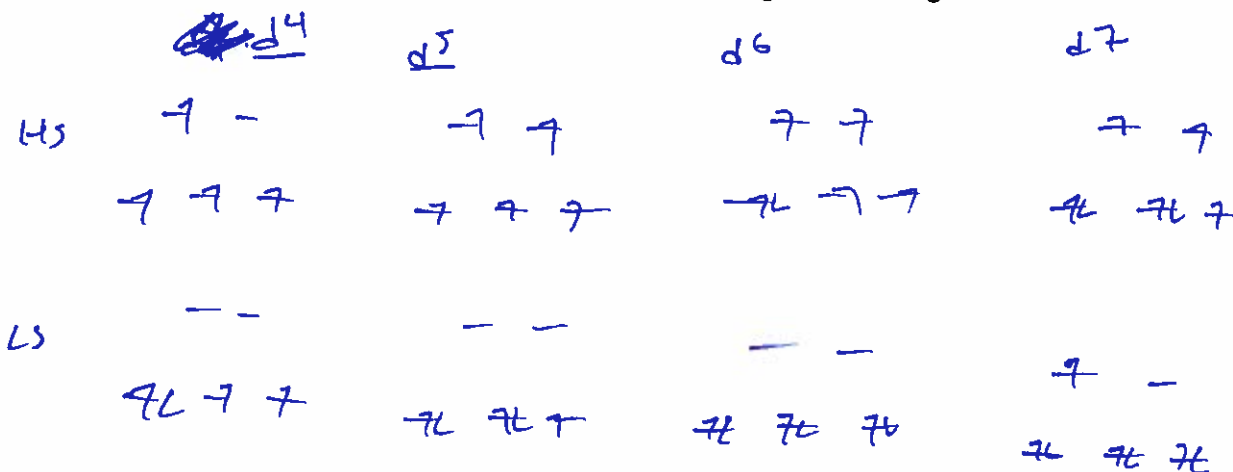   Ligands affect Δ_o
        ∗ note spectrochemical series
      ↑ ox state of metal (divalent → trivalent) increases Δ_o
      2nd and 3rd row transition metals typically have large Δ_o

4. *High Spin / Low Spin*

   a. Is there a trend between the pairing energy relative to the CFSE and the preferred configuration?

      $P_E > \Delta_o$ for high spin

      $\Delta_o > P_E$ for low spin

   b. Which d electron counts are capable of giving rise to both low spin and high spin configurations? Show using orbital diagrams.

      ~~d^4~~ d^5 d^6 d^7

   HS   ↑ –   ↑ ↑   ↑ ↑   ↑ ↑

        ↑ ↑ ↑   ↑ ↑ ↑   ↑↓ ↑ ↑   ↑↓ ↑↓ ↑

   LS   – –   – –   – –   ↑ –

        ↑↓ ↑ ↑   ↑↓ ↑↓ ↑   ↑↓ ↑↓ ↑↓   ↑↓ ↑↓ ↑↓

→ spectrochemical series

c. Predict, based on your knowledge of strong/weak field ligands, whether the following compounds will exist as high spin or low spin. Draw the orbital splitting diagram and show the electrons for each complex.

i. $[Fe(Cl)_6]^{3-}$ HS (Cl is weak field)

d⁵

ii. $[CoF_6]^{3-}$ HS

d⁶   (F is weak field)

iii. $[Ru(NH_3)_6]^{2+}$

LS expected
b/c Ru is 2nd row
d⁶

iv. $[Cr(H2O)_6]^{2+}$

HS, H₂O is weak field

d⁴
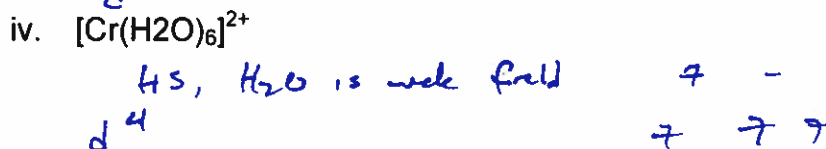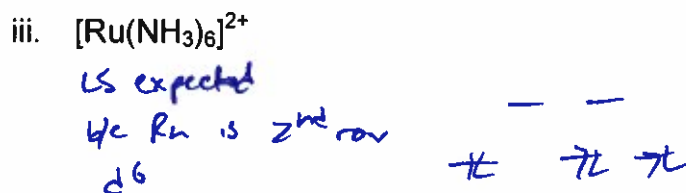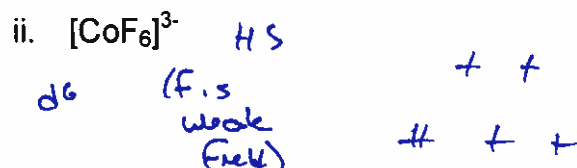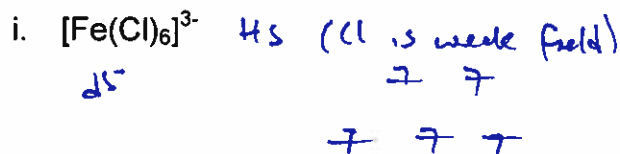
5. The complex $[NiCl_4]^{2-}$ is paramagnetic with two unpaired electrons whereas the compound [Ni(CN)4]2- is diamagnetic. Deduce the geometries of the two compounds and explain the observations in terms of ligand field theory.

- either tetrahedral or square planar
- Ni (II) is d⁸

of T_d & square planar

↑
paramagnetic

therefore,
[NiCl₄]²⁻

diamagnetic ∴ [Ni(CN)₄]²⁻

6. *Term Symbols*
   a. Determine the ground state term symbol for each.

   i. Cr^{3+} free ion   ~~d~~ d^3

   ↑ ↑ ↑ — —
   +2 +1 0 -1 -2

   max $L = 3 \rightarrow F$

   spin multiplicity $2S+1$

   $2(1.5)+1$

   $= 3+1$

   $= 4$

   ∴ ^4F

   ii. d^0 configuration

   — — — — —
   +2 +1 0 -1 -2

   Max $L = 0 \rightarrow S$

   spin multiplicity $2S+1$

   $= 2(0)+1$

   $= 1$

   ∴ ^1S

   iii. Fe^{3+} free ion d^5

   ↑ ↑ ↑ ↑ ↑
   +2 +1 0 -1 -2

   max $L = 0 \rightarrow S$

   spin multiplicity $2S+1$

   $= 2(2.5)+1$

   $= 5+1$

   $= 6$

   ∴ ^6S