3/1:   I) Derive the proper MO diagram for tetrahedral molecules ML_4 using the n d-orbitals, the $(n + l)$ s-orbital, and the $(n + l)$ p-orbitals on the central atom M for

   (a) σ-only ligands;

   Answer. Point group: T_d.

   Basis functions: All four L σ-orbitals, $M(ns)$, $M((n + l)p)$, and $M((n + l)d)$.

   Apply operations, generate reducible representations, and reduce to irreducible representations:
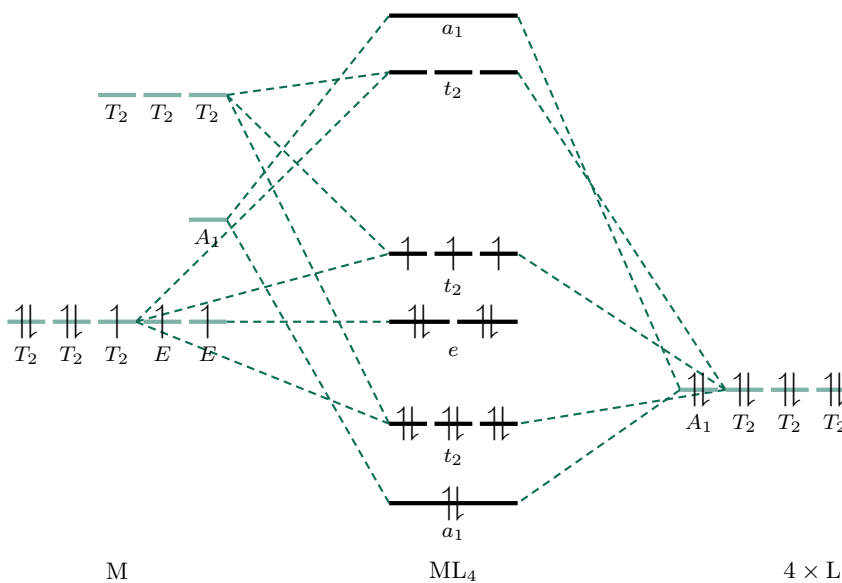
   $$\Gamma_{L\sigma} = (4, 1, 0, 0, 2) = A_1 + T_2$$
   $$\Gamma_{M_{ns}} = A_1$$
   $$\Gamma_{M_{(n+l)p}} = T_2$$
   $$\Gamma_{M_{(n+l)d}} = E + T_2$$

   Combine orbitals by their symmetry, and fill in electrons for a d^7 metal[1].

M ML_4 $4 \times L$

□

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[1]This electron configuration is randomly chosen just to illustrate the point.

(b) π-donor ligands (having low-lying, filled π orbitals);

Answer. Point group: T_d.

Basis functions: All four L σ-orbitals, all eight L $\pi_{x,z}$ orbitals, M(ns), M($(n+l)p$), and M($(n+l)d$).

Apply operations, generate reducible representations, and reduce to irreducible representations:

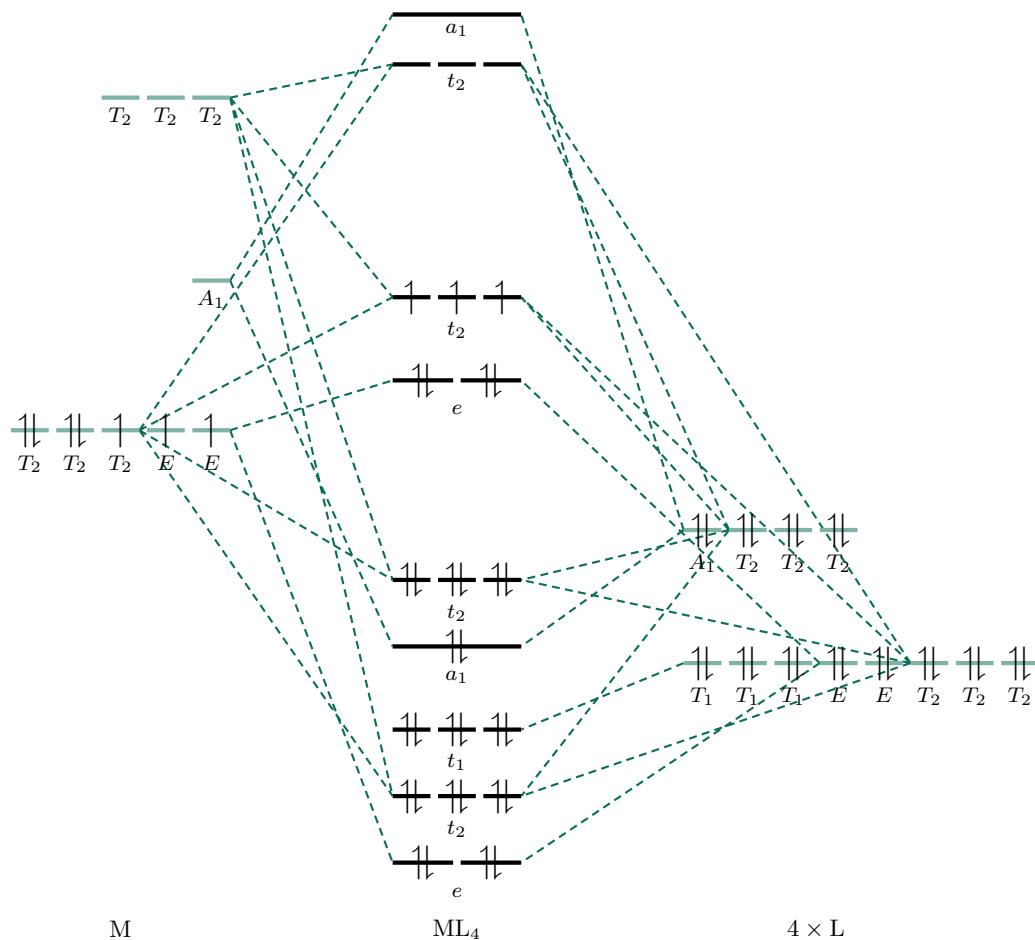$$\Gamma_{L\sigma} = (4, 1, 0, 0, 2) = A_1 + T_2$$
$$\Gamma_{L\pi_{x,z}} = (8, -1, 0, 0, 0) = E + T_1 + T_2$$
$$\Gamma_{M_{ns}} = A_1$$
$$\Gamma_{M_{(n+l)p}} = T_2$$
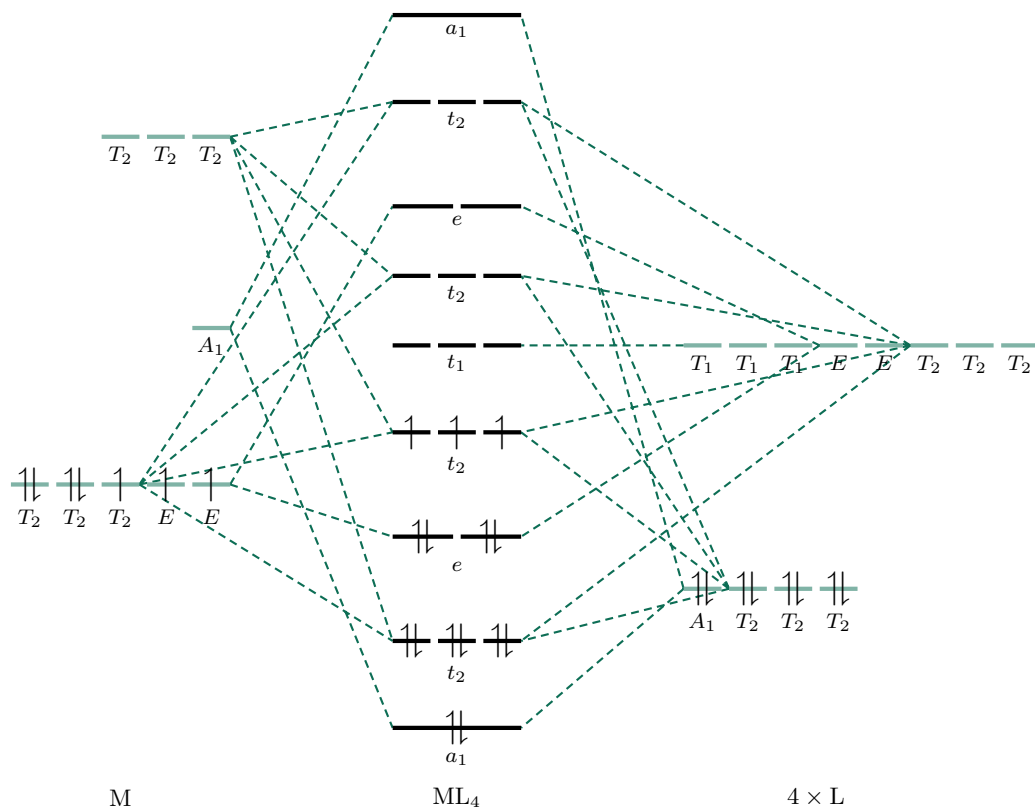$$\Gamma_{M_{(n+l)d}} = E + T_2$$

Combine orbitals by their symmetry, and fill in electrons for a d^7 metal.

(c) π-acceptor ligands (having high-lying, empty π orbitals).
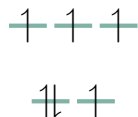
Answer. Same intro analysis as part (b).

II) Do the following problems from Chapter 10: 1, 6, 7, 8, 19, 22.

10.1 Predict the number of unpaired electrons for each of the following:

a. A tetrahedral d^6 ion.

Answer. Tetrahedral means high spin and t_2 orbitals above e. Thus, there will be $\boxed{4}$ unpaired electrons.

$$\uparrow \quad \uparrow \quad \uparrow$$

$$\uparrow\downarrow \quad \uparrow$$

☐

b. $[Co(H_2O)_6]^{2+}$.

Answer. Octahedral cobalt with a 2+ oxidation state means high spin. Thus, there will be $\boxed{3}$ unpaired electrons.

$$\uparrow \quad \uparrow$$

$$\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow$$

☐

c. $[Cr(H_2O)_6]^{3+}$.

Answer. High spin/low spin doesn't matter here; there will be $\boxed{3}$ unpaired electrons, regardless.

$$\text{—} \quad \text{—}$$

$$\uparrow \quad \uparrow \quad \uparrow$$

☐

d. A square-planar d^7 ion.

Answer. Square planar compounds have an orbital arrangement determined by the angular overlap model, and are low spin. Thus, there will be $\boxed{1}$ unpaired electron.

$$\text{—}$$

$$\uparrow$$

$$\uparrow\downarrow \quad \uparrow\downarrow$$

$$\uparrow\downarrow$$

☐
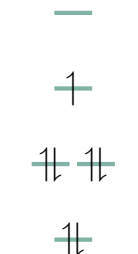
e. A coordination compound with a magnetic moment of 5.1 Bohr magnetons.

Answer. Using the spin-only magnetic moment formula $\mu_S = \sqrt{n(n+2)}$, we can solve for n with the quadratic formula, take the positive answer, and round.

$$5.1 = \sqrt{n(n+2)}$$
$$0 = n^2 + 2n - 5.1^2$$
$$\boxed{n \approx 4}$$

☐

10.6 Predict the magnetic moments (spin-only) of the following species.

    a. $[Cr(H_2O)_6]^{2+}$.

        Answer. We know that $[Cr(H_2O)_6]^{2+}$ has four unpaired electrons. Thus,

$$\mu = \sqrt{4(4+2)} = \sqrt{24}$$
$$\boxed{\mu \approx 4.90\,\text{B.M.}}$$

$\square$

    b. $[Cr(CN)_6]^{4-}$.

        Answer. We know that $[Cr(CN)_6]^{4-}$ has two unpaired electrons. Thus,

$$\mu = \sqrt{2(2+2)} = \sqrt{8}$$
$$\boxed{\mu \approx 2.83\,\text{B.M.}}$$

$\square$

    c. $[FeCl_4]^-$.

        Answer. We know that $[FeCl_4]^-$ has five unpaired electrons. Thus,

$$\mu = \sqrt{5(5+2)} = \sqrt{35}$$
$$\boxed{\mu \approx 5.92\,\text{B.M.}}$$

$\square$

    d. $[Fe(CN)_6]^{3-}$.

        Answer. We know that $[Fe(CN)_6]^{3-}$ has one unpaired electron. Thus,

$$\mu = \sqrt{1(1+2)} = \sqrt{3}$$
$$\boxed{\mu \approx 1.73\,\text{B.M.}}$$

$\square$

    e. $[Ni(H_2O)_6]^{2+}$.

        Answer. We know that $[Ni(H_2O)_6]^{2+}$ has two unpaired electrons. Thus,.

$$\mu = \sqrt{2(2+2)} = \sqrt{8}$$
$$\boxed{\mu \approx 2.83\,\text{B.M.}}$$

$\square$

    f. $[Cu(en)_2(H_2O)_2]^{2+}$.

        Answer. We know that $[Cu(en)_2(H_2O)_2]^{2+}$ has one unpaired electron. Thus,

$$\mu = \sqrt{1(1+2)} = \sqrt{3}$$
$$\boxed{\mu \approx 1.73\,\text{B.M.}}$$

$\square$

10.7 A compound with the empirical formula $Fe(H_2O)_4(CN)_2$ has a magnetic moment corresponding to $2\frac{2}{3}$ unpaired electrons per iron. How is this possible? (Hint: Two octahedral Fe(II) species are involved, each containing a single type of ligand.)

Answer. $[Fe(H_2O)_6]^{2+}$ is a low spin complex with 4 unpaired electrons. $[Fe(CN)_6]^{4-}$ is a high spin complex with 0 unpaired electrons. The compound $[Fe(H_2O)_6]_2[Fe(CN)_6]$ is the simplest combination of the two with empirical formula equal to $Fe(H_2O)_4(CN)_2$. Thus, since this compound has a total of 8 unpaired electrons for 3 Fe atoms, its magnetic moment must correspond to $8/3 = 2\frac{2}{3}$ unpaired electrons. □

10.8 What are the possible magnetic moments of Co(II) in tetrahedral, octahedral, and square-planar complexes?

Answer. For tetrahedral and octahedral complexes, we have $\mu = \sqrt{3(3+2)} = \sqrt{15} \approx 3.87$. For square planar, we have $\mu = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73$. $\qquad\square$

10.19 Explain the order of the magnitudes of the following Δ_o values for Cr(III) complexes in terms of the σ and π donor and acceptor properties of the ligands.

Ligand	F^-	Cl^-	H_2O	NH_3	en	CN^-
Δ_o (cm^{-1})	15 200	13 200	17 400	21 600	21 900	33 500

Answer. Cyanide has by far the greatest magnitude Δ_o because it is the only π-accepting ligand. Ethylenediamine and ammonia form the next group down because they are pure π-donating ligands. Lastly, we have water, chloride, and fluoride because they have π-donating character (within this group, chloride has the lowest value because it has fairly good π-donor abilities, fluoride is in the middle because it has lesser π-donor abilities than chloride, and water has the highest value because it only engages in σ bonding). $\qquad\square$

10.22 Solid CrF_3 contains a Cr(III) ion surrounded by six F^- ions in an octahedral geometry, all at distances of 190 pm. However, MnF_3 is in a distorted geometry, with Mn–F distances of 179, 191, and 209 pm (two of each). Explain.

Answer. The manganese ion has unequally occupied e_g orbitals whereas the chromium one does not, so the former is subject to Jahn-Teller distortion while the latter is not. □

III) Use the Angular Overlap Model to derive the d-orbital splitting diagrams for $M(CO)_5$ complexes having
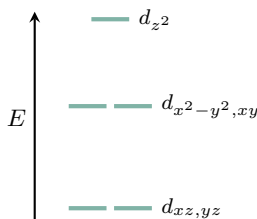
(a) Square pyramidal geometry;

Answer. From the charts in Module 36, we have $e_\sigma = (2, 3, 0, 0, 0)$ and $e_\pi = (0, 0, 4, 3, 3)$. Thus we know that the d-orbital splitting diagram is
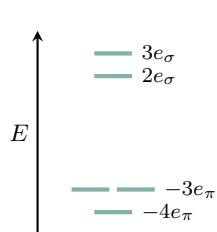

$\square$
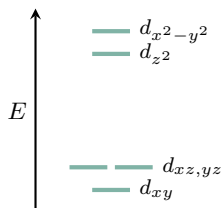
(b) Trigonal bipyramidal geometry.

Answer. From the charts in Module 36, we have $e_\sigma = (\frac{11}{4}, \frac{9}{8}, \frac{9}{8}, 0, 0)$ and $e_\pi = (0, \frac{3}{2}, \frac{3}{2}, \frac{7}{2}, \frac{7}{2})$. Thus we know that the d-orbital splitting diagram is
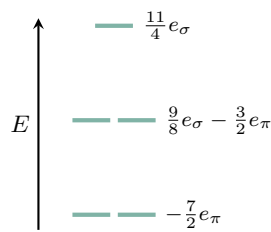

$\square$

(c) Label the orbitals with the appropriate energies in units of e_σ and e_π. Note that degenerate orbitals are those with the same energies — you don't have to use group theory to get this information!

(a) Square pyramidal.   (b) Trigonal bipyramidal.

(d) Determine the relative energies of $Cr(CO)_5$ (based on orbital population) in these two geometries, and use this to predict the structure of $Cr(CO)_5$.

Answer. Assuming a low spin configuration since carbonyl ligands are strong field ligands and noting that chromium has a d^6 configuration, we have

$$E_{\text{square pyramidal}} = 2(-4e_\pi) + 4(-3e\pi) = -20e_\pi$$

$$E_{\text{trigonal bipyramidal}} = 4\left(-\frac{7}{2}e_\pi\right) + 2\left(\frac{9}{8}e_\sigma - \frac{3}{2}e_\pi\right) = \frac{9}{4}e_\sigma - 17e_\pi$$

Since $E_{\text{square pyramidal}} < E_{\text{trigonal bipyramidal}}$, we know that $Cr(CO)_5$ is $\boxed{\text{square pyramidal}}$. $\square$