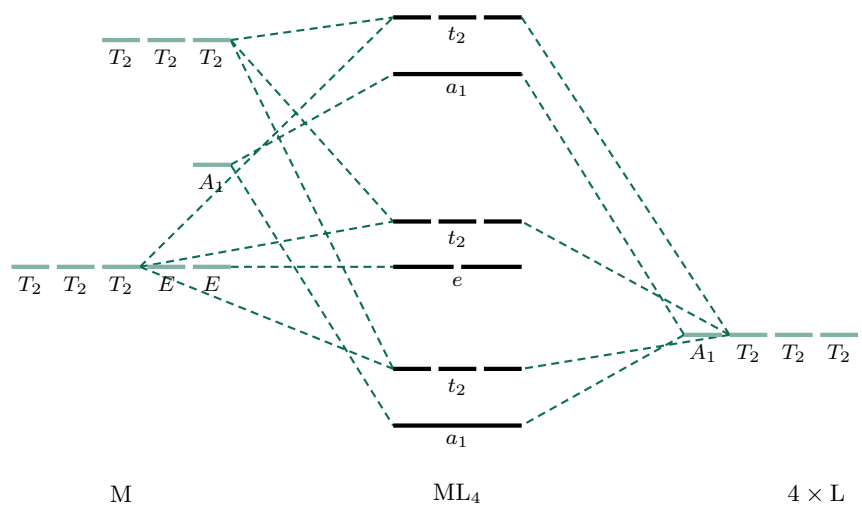
3/1: I) Derive the proper MO diagram for tetrahedral molecules ML_4 using the n d-orbitals, the $(n+l)$ s-orbital, and the $(n+l)$ p-orbitals on the central atom M for

(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:

$$\begin{aligned}
\Gamma_{L\sigma} &= (4,1,0,0,2) = A_1 + T_2 \\
\Gamma_{\mathrm{M}_{ns}} &= A_1 \\
\Gamma_{\mathrm{M}_{(n+l)p}} &= T_2 \\
\Gamma_{\mathrm{M}_{(n+l)d}} &= E + T_2
\end{aligned}$$

Combine orbitals by their symmetry.



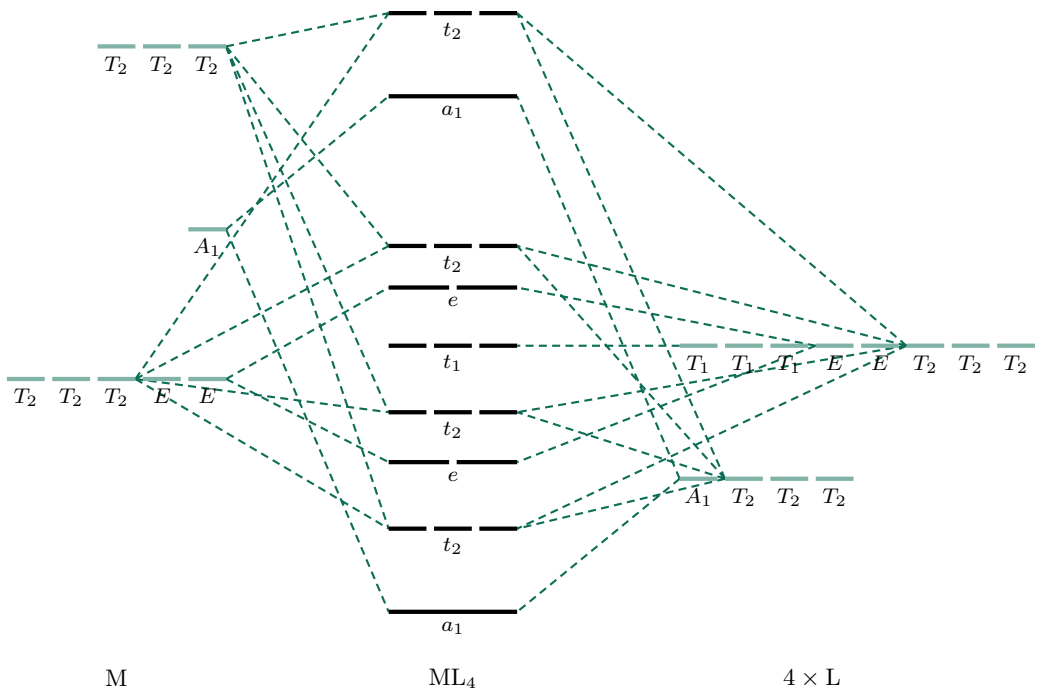
□

(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:

$$\begin{aligned}
\Gamma_{L\sigma} &= (4,1,0,0,2) = A_1 + T_2 \\
\Gamma_{L\pi_{x,z}} &= (8,-1,0,0,0) = E + T_1 + T_2 \\
\Gamma_{\mathrm{M}_{ns}} &= A_1 \\
\Gamma_{\mathrm{M}_{(n+l)p}} &= T_2 \\
\Gamma_{\mathrm{M}_{(n+l)d}} &= E + T_2
\end{aligned}$$

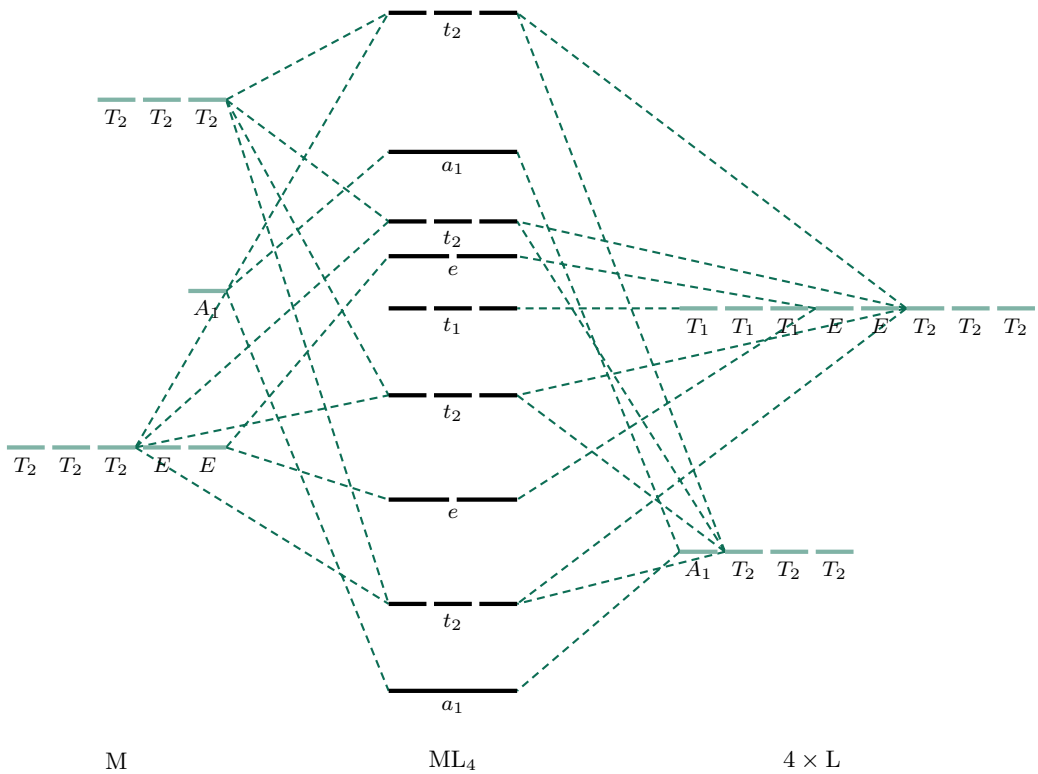
Combine orbitals by their symmetry.



□

(c) π-acceptor ligands (having high-lying, empty π orbitals).

Answer. Same intro analysis as part (b).



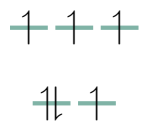
□

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.

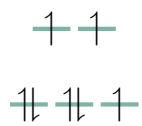
Answer. Tetrahedral means high spin and t_2 orbitals above e. Thus, there will be 4 unpaired electrons.



□

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

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



□

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

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

□

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 1 unpaired electron.

□

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.

$$\begin{aligned} 5.1 &= \sqrt{n(n+2)} \\ 0 &= n^2 + 2n - 5.1^2 \\ n &\approx 4 \end{aligned}$$

□

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, $\mu = \sqrt{4(4+2)} = \sqrt{24} \approx 4.9$. □

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

Answer. We know that $[Cr(CN)_6]^{4-}$ has two unpaired electrons. Thus, $\mu = \sqrt{2(2+2)} = \sqrt{8} \approx 2.82$. □

c. $[FeCl_4]^{-}$.

Answer. We know that $[FeCl_4]^{-}$ has five unpaired electrons. Thus, $\mu = \sqrt{5(5+2)} = \sqrt{15} \approx 5.92$. □

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

Answer. We know that $[Fe(CN)_6]^{3-}$ has one unpaired electron. Thus, $\mu = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73$. □

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

Answer. We know that $[Ni(H_2O)_6]^{2+}$ has two unpaired electrons. Thus, $\mu = \sqrt{2(2+2)} = \sqrt{8} \approx 2.82$. □

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

Answer. We know that $[Cu(en)_2(H_2O)_2]^{2+}$ has one unpaired electron. Thus, $\mu = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73$. □

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. $Fe(H_2O)_6$ is a low spin complex with 4 unpaired electrons. $Fe(CN)_6$ is a high spin complex with 0 unpaired electrons. If we take a weighted average of the spins, we find that the magnetic moment of $Fe(H_2O)_4(CN)_2$ is $\mu = 4 \cdot \frac{4}{6} + 0 \cdot \frac{2}{6} = 2\frac{2}{3}$. □

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 $\mu = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73$. □

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. □

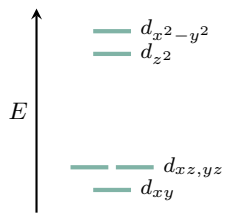
10.22 Solid CrF_3 contains a Cr(III) ion surrounded by six F^- ions in an octahedral geometry, all at distances of 190 pm. However, MnF_3 is in a distorted geometry, with Mn−F distances of 179, 191, and 209 pm (two of each). Explain.

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;

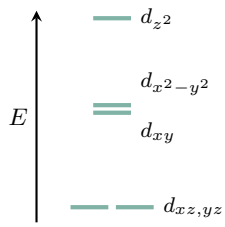
Answer. From the charts in Module 36, we have $e_\sigma = (2, 3, 0, 0, 0)$ and $e_\pi = (0, 0, 4, 3, 3)$. Thus we know that the d-orbital splitting diagram is



□

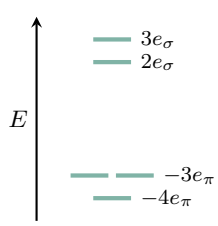
(b) Trigonal bipyramidal geometry.

Answer. From the charts in Module 36, we have $e_\sigma = (\frac{11}{4}, \frac{11}{8}, \frac{9}{8}, 0, 0)$ 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

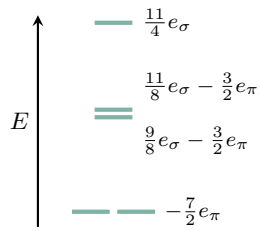


□

(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 high spin configuration since chromium is neutral and noting that chromium has a d^4 configuration, we have

$$E_{\text{square pyramidal}} = 1(-4e_\pi) + 2(-3e\pi) + 2e_\sigma = 2e_\sigma - 10e_\pi$$
$$E_{\text{trigonal bipyramid}} = 2\left(-\frac{7}{2}e_\pi\right) + 1\left(\frac{9}{8}e_\sigma - \frac{3}{2}e_\pi\right) + 1\left(\frac{11}{8}e_\sigma - \frac{3}{2}e_\pi\right) = \frac{5}{2}e_\sigma - 10e_\pi$$

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