(1) In many transition metal complexes (with high coordination numbers) the bonding can be qualitatively illustrated as a combination of (i) n M-L antibonding orbitals, (ii) 9-n non-bonding orbitals, and (iii) n M-L bonding orbitals, where n = the number of ligand SALCS and there are 9 total metal-based orbitals (5-d’s + 3-p’s + 1-s) to consider. (a) Why are there 9-n nonbonding orbitals? (b) What are the nonbonding orbitals for octahedral and tetrahedral complexes?

(2) Construct the molecular orbital diagrams for (a) tetrahedral (MH₄) and (b) octahedral (MH₆) complexes.

(3) Compare and contrast the differences between π-donor and π-acceptor ligands. Give an example of each ligand type.

(4) Compare and contrast the differences between σ-donors and π-donor/acceptor ligands. Give appropriate examples of each ligand and use partial molecular orbital diagrams to support your argument.

(5) For what electronic configurations would you expect strong Jahn-Teller distortion to be favorable?

(6) For the following complex ions determine (a) the number of unpaired electrons, (b) the spin-only effective magnetic moment, and (c) the ligand field stabilization energy.

   (i) [Co(NO₂)₆]⁴⁻  (ii) [Fe(OH₂)₆]³⁺  (iii) [RhF₆]³⁻  (iv) [Zn(en)₃]²⁺  (v) Cr(CO)₆

(7) Inspection of the Spectrochemical Series reveals an interesting but surprising trend for halide ligands. It is found that for halides, the ligand field strengths are:

   \[ F^- > Cl^- > Br^- > I^- \]

   Explain why this is the case. Hint: It may prove useful to draw a simple molecular orbital diagram for each M-X.
The spectrochemical series is a useful tool that can be used to predict or at least correlate magnetic, spectroscopic, and thermodynamic properties of transition metal complexes. For a given transition metal center, the series can be arranged in terms of increasing ligand field strength ($\Delta_0$ or $\Delta_T$). In other words, the HOMO-LUMO gap increases with increasing $\pi$ acidity and $\sigma$ donor strength of the ligands.
Using partial molecular orbital diagrams, describe the effects of $\pi$ bonding ($\pi$ acids vs. $\pi$ bases) on the ligand field splitting (HOMO-LUMO gap, $\Delta_o$) in an octahedral complex. (20 points)

5. See Table at bottom of page 371 (3rd Ed.) in textbook.

<table>
<thead>
<tr>
<th># e$^\prime$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>h.s. J-T?</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>l.s. J-T?</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6. (i) **Co**

(ii) **Fe**

(a) 3 unpaired electrons \( (S = 3/2) \)
(b) \( \mu_{\text{eff}} (\mu_B \text{ or B.M.}) = g[s(s + 1)]^{0.5} \)
(c) \( \text{LFSE} = 5(-2/5) + 2(+3/5) = -4/5 \Delta_o \)

(a) 5 unpaired electrons \( (S = 5/2) \)
(b) \( \mu_{\text{eff}} (\mu_B \text{ or B.M.}) = 5.92 \mu_B \)
(c) \( \text{LFSE} = 5(-2/5) + 2(+3/5) = 0 \)

(iii) **Rh**

(iv) **Zn**

(a) 0 unpaired electrons \( (S = 0) \)
(b) \( \mu_{\text{eff}} = 0 \mu_B \)
(c) \( \text{LFSE} = 6(-2/5) = -12/5 \Delta_o \)

(a) zero unpaired electrons \( (S = 0) \)
(b) \( \mu_{\text{eff}} = 0 \mu_B \)
(c) \( \text{LFSE} = 6(-2/5) + 4(+3/5) = 0 \)

(v) **Cr**

(a) zero unpaired electrons \( (S = 0) \)
(b) \( \mu_{\text{eff}} = 0 \mu_B \)
(c) \( \text{LFSE} = 6(-2/5) = -12/5 \Delta_o \)

7. **Modified version of problem 10-13 in textbook using Table 10-13 (3rd Ed.)**

**Ligand field strengths:** \( F^- \succ Cl^- \succ Br^- \succ I^- \)

For a given \([\text{Cr}^{III}X_6]^{3-}\) complex, where \( X^- = F, \text{Cl, Br, I} \):

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( F^- )</th>
<th>( Cl^- )</th>
<th>( Br^- )</th>
<th>( I^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta_o ) (cm(^{-1}))</td>
<td>16,600</td>
<td>13,180</td>
<td>12,340</td>
<td>620</td>
</tr>
</tbody>
</table>

Decreasing \( \sigma \) and \( \pi \) donation is found when E.N. of \( X^- \) decreases (see \( e_\sigma \) and \( e_\pi \)).

The partial M.O. (octahedral \( M^{III}X_6^{3-} \) complex) diagram qualitatively scales as a function of \( X^- \):

\( F^- \) is generally thought of as a good \( \sigma \) donor while \( I^- \) is weaker in comparison.

\( F^- \) is generally thought of as a poor \( \pi \) donor while \( I^- \) is a better one.

\( F^- \) gives good M-X orbital overlap while \( I^- \) is poor in comparison.

So, \( \Delta_o \) is largest for \( F^- \) and smallest for \( I^- \)