Need for More Sophisticated Theories

- Quantitative predictions of CFT are based on a purely electrostatic model.
  - They require empirical corrections in order to give satisfactory agreement with experimental results (e.g., electronic spectra).
  - Empirically corrected CFT is known as modified crystal field theory, or more commonly ligand field theory (LFT).

- The need for corrections to CFT arises from metal-ligand orbital overlap.
  - This implies a certain amount of covalence in the M-L interactions.
    - There is less repulsion between \( d \) electrons in a complex ion than in the free gaseous ion.
    - Covalent interaction with ligands allows metal electrons to be delocalized onto the ligands, lessening repulsions.
    - In effect, taking a CFT view, the \( d \) orbitals have been “expanded” by the presence of the ligands.
The Nephelauxetic Effect

- The disparity between free-ion and complex-ion electronic state energies is the so-called *nephelauxetic effect* (Gk., *nephelē* = cloud + *auxēsis* = growth; hence, “cloud-expanding”), which depends upon both the metal ion and ligand.

  - For a given metal ion, the ability of ligands to induce this cloud expanding increases according to a *nephelauxetic series*:

    \[
    F^- < H_2O < NH_3 < en < ox < SCN^- < Cl^- < CN^- < Br^- < I^- \]

  - Note that the ordering of ligands in the nephelauxetic series is not the same as the spectrochemical series.

- By using empirically determined constants for both ligands and the central metal ion it is possible to reconcile the ligand field model of a complex with quantitative spectroscopic results.

  - The need to modify CFT to account for the nephelauxetic effect suggests that a molecular orbital approach might be useful.

    - An MO model could be adjusted for various degrees of M-L orbital overlap, representing a range from polar covalent bonding to nearly ionic interactions.

    - An MO approach might allow us to understand the relationship between orbital overlap and the energy separations among *d* orbitals in fields of various geometries.
Sigma-only MOs for ML₆ (O₉)

Pendant Atom SALCs:

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>8C³</th>
<th>6C²</th>
<th>6C⁴</th>
<th>3C₂</th>
<th>i</th>
<th>6S⁴</th>
<th>8S₃</th>
<th>3σₙ</th>
<th>6σ₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γₜ</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

Γₜ = A₁g + E₉ + T₁u

Thus, we can define six SALCs with three different symmetries, which can form bonding and antibonding combinations with like symmetry AOs on the central metal ion.

AOs on M:

\[ s = a_{1g}, \quad (pₓ, pᵧ, pᶻ) = t_{1u}, \quad (dₓ²₋ᵧ², dᶻ²) = e₉, \quad (dₓᵧ, dₓz, dᵧz) = t₂g \]

😊 The symmetries of the d orbitals are, of course, the same as noted in our considerations of CFT.

- \[ s, pₓ, pᵧ, pᶻ, dₓ²₋ᵧ², dᶻ² \] orbitals have the proper symmetries to form bonding and antibonding combinations with matching symmetry SALCs.

- The three \( t₂g \) orbitals \( (dₓᵧ, dₓz, dᵧz) \) have no matching SALCs and must remain nonbonding. This is a consequence of the orientation of these orbitals relative to the ligands.
SALC Equations

\[ a_{1g} \]
\[ \Sigma_a = \frac{1}{\sqrt{6}} (\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z}) \]

\[ e_g \]
\[ \Sigma_{z^2} = \frac{1}{2\sqrt{3}} (2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y}) \]
\[ \Sigma_{x^2-y^2} = \frac{1}{2} (\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y}) \]

\[ t_{2g} \]
\[ \Sigma_z = \frac{1}{\sqrt{2}} (\sigma_z - \sigma_{-z}) \]
\[ \Sigma_x = \frac{1}{\sqrt{2}} (\sigma_x - \sigma_{-x}) \]
\[ \Sigma_y = \frac{1}{\sqrt{2}} (\sigma_y - \sigma_{-y}) \]
ML$_6$ Sigma-Only MO Scheme

\[ p \, (t_{1u}) \]
\[ s \, (a_{1g}) \]
\[ d \, (e_g + t_{2g}) \]
\[ t_{1u}^* \]
\[ a_{1g}^* \]
\[ e_g^* \]
\[ e_g \]
\[ t_{2g} \]
\[ \Delta_0 \]
\[ (a_{1g} + e_g + t_{1u}) \]

SALCs
The twelve electrons provided by the ligands alone fill the lowest three levels of MOs ($a_{1g}$, $t_{1u}$, and $e_g$).

Any electrons provided by the metal ion will result in an equivalent filling of the $t_{2g}$ level and if necessary the $e_g$ level.

Electron filling above the six MOs in the lowest three levels is identical to the presumed filling of $d$ orbitals in the CFT model.

As with the CFT model, both high and low spin ground states are possible for $d^4$ through $d^7$ metal ion configurations.

In the MO scheme $\Delta_0$ or $10Dq$ is defined as the energy separation between the $t_{2g}$ and $e_g^*$ levels.

The lower $t_{2g}$ orbitals are nonbonding and can be taken as essentially the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals of the metal ion, which is not materially different from the CFT view.

The upper $e_g^*$ orbitals are now seen as antibonding molecular orbitals.

Although antibonding, the $e_g^*$ MOs when occupied involve sharing of electron density between the metal ion and the ligands.
Adjustments for Covalence

- We can make allowances for varying degrees of covalent interaction between the metal ion and ligands by adjusting the MO scheme.
  - No adjustment of the scheme can change the localized character of the $t_{2g}$ orbitals.
- Electrons occupying the $e_g^*$ MO will have more or less delocalization onto the ligands depending upon the relative energies of the metal ion $d$ orbitals and the ligand $sigma$ orbitals.
  - If metal $d$ orbitals lie higher in energy than ligand $sigma$ orbitals, the $e_g^*$ MOs will lie closer to the metal $d$ orbitals and will have more metal ion character than ligand character.

In this case, $e_g^*$ electron density will be more localized on the metal.

If the disparity in levels is extreme, this becomes an ionic model in which the $e_g^*$ MOs are essentially metal $d$ orbitals, like the CFT approach.

Thus, the CFT model is a special case in the MO approach.
Adjustments for Covalence

- As the energies of the metal ion $d$ orbitals and the ligand $\sigma$ orbitals become more comparable, the degree of electron sharing (covalence) will become greater.
  - More of the $e_g$* electron density will be delocalized toward the ligands.
Adjustments for Covalence

- If the ligand \( \sigma \) orbitals were to lie significantly higher than the metal ion \( d \) orbitals, \( e_g^* \) electron density would be predominantly localized on the ligands.
MO Interpretation of Nephelauxetic Effect
Sigma-Only Case

\[ F^- < H_2O < NH_3 < en < ox < SCN^- < Cl^- < CN^- < Br^- < I^- \]

- The weakest ligands in the nephelauxetic series (F\(^-\), H\(_2\)O, and NH\(_3\)) have low energy atomic or molecular orbitals relative to transition metal ion \(d\) orbitals.
  - This is more in keeping with the "quasi-ionic" model:

```
M       L
```

```
\( e_g^* \)
```

\( d \)

\( \sigma \)

\( e_g \)

- For complexes with these ligands, both \(t_{2g}\) and \(e_g^*\) electron density is essentially localized in metal \(d\) orbitals, not unlike the assumptions of the CFT model.
CFT vs. MO - Sigma Only Case

- MO is capable of better quantitative agreement without fundamentally changing the model.

- Electron filling in the MO model in the highest occupied MOs is the same as in the CFT model:
  - Orbital symmetries are the same.
  - Orbital ordering is the same.
  - Electron filling is the same.
  - $\Delta_o$ is defined as the gap between the same symmetry orbital levels.

💡 For qualitative purposes (electronic configurations, magnetic properties, qualitative visible spectra interpretation) CFT is equivalent to MO and is easier to apply.

😊 The qualitative agreement between CFT and MO is general.
ML₆ Complexes with Pi Bonding

To include \(pi\) bonding in our MO scheme for octahedral ML₆ complexes we use the following twelve vectors as a basis for a representation of SALCs.

- These vectors might indicate
  - Occupied \(p\) orbitals (other than those engaged in \(sigma\) bonding), such as the \(np_x\) and \(np_y\) orbitals on halide ligands in complexes like \(\text{CrX}_6^{3-}\) (\(X = \text{F}^-, \text{Cl}^-\)).
    - These are classified as \textit{donor ligands}, because they have electrons to contribute to the \(pi\) system of the complex.
  - Other unoccupied \(pi\) symmetry AOs or MOs on the ligands, such the empty \(\pi^*\) antibonding MOs of CO and \(\text{CN}^-\) in complexes like \(\text{Cr(CO)}_6\) and \([\text{Fe(CN)}_6]^{4-}\).
    - These are classified as \textit{acceptor ligands}, since they receive electron density from the \(pi\) system.
Representation for Pi-SALCs

\[
\Gamma_{\pi} = T_{1g} + T_{2g} + T_{1u} + T_{2u}
\]

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
<th>$3C_2$</th>
<th>$i$</th>
<th>$6S_4$</th>
<th>$8S_6$</th>
<th>$3\sigma_h$</th>
<th>$6\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{\pi}$</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Matching $\Gamma_\pi$ with Metal AOs

$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

$T_{2g}$: Can form $pi$-bonding and antibonding combinations between the $t_{2g}$ orbitals ($d_{xy}$, $d_{xz}$, $d_{yz}$) and $T_{2g}$ $\pi$-SALCs.
○ This will change the character of the $t_{2g}$ level, which we previously had identified as nonbonding in the $sigma$-only MO scheme.

$T_{1u}$: Can form $pi$-bonding and antibonding combinations between the three $np$ orbitals ($t_{1u}$) and the three $T_{1u}$ SALCs.
○ However, we have already used these metal ion $np$ AOs to form bonding and antibonding $\sigma$-MOs with the $T_{1u}$ $\sigma$-SALCs.
○ The $sigma$ interactions are likely to result in more effective overlaps

Assume that the $np$ orbitals have only minimally effective interactions with the $T_{1u}$ $\pi$-SALCs; i.e. virtually nonbonding or only weakly bonding in certain complexes.

$T_{1g}$ and $T_{2u}$: No AO matches, so strictly nonbonding.
$T_{2g}$ SALCs and Their Pi-Bonding LCAOs

\[ \Pi_{xz} = \frac{1}{2}(\pi_1 + \pi_2 + \pi_3 + \pi_4) \]
\[ \Pi_{yz} = \frac{1}{2}(\pi_5 + \pi_6 + \pi_7 + \pi_8) \]
\[ \Pi_{xy} = \frac{1}{2}(\pi_9 + \pi_{10} + \pi_{11} + \pi_{12}) \]

\[ d_{xz} + \Pi_{xz} \]

Similar matches with the other two SALCs.
Virtually Nonbonding $T_{1u}$ SALCs

\[ \Pi_z = \frac{1}{2}(\pi_1 - \pi_3 + \pi_5 - \pi_7) \]
\[ \Pi_x = \frac{1}{2}(\pi_2 - \pi_4 + \pi_{10} - \pi_{12}) \]
\[ \Pi_y = \frac{1}{2}(\pi_6 - \pi_8 + \pi_9 - \pi_{11}) \]

\[ p_z + \Pi_z \]

Similar matches with the other two SALCs.
Strictly Nonbonding $T_{1g}$ and $T_{2u}$ SALCs

$T_{1g} (xz)$

Similar form for the other two SALCs.

$T_{2u} (z)$

Similar form for the other two SALCs.
Impediments to Forming a General MO Scheme

- The energy ordering and the nature of the MOs will be affected by the following factors:
  - Identity of the central metal ion
  - Identity of the ligands
  - Relative energies of the orbitals on metal and ligands
  - The nature and effectiveness of the $\sigma$ and $\pi$ orbital interactions
  - Electron filling in ligand orbitals

.Reverse Smiley It is not possible to construct a detailed MO scheme that will have general applicability to a range of octahedral complexes.

луш The best we can hope for is a simplified scheme that identifies interacting orbitals by symmetry type, approximates their bonding type, and arranges MOs of the same type in a plausible relative energy order.

- The simplified scheme makes no attempt to distinguish between the energies of same-type orbitals with different symmetries.
Simplified General MO Scheme for ML₆

- σ* antibonding
- t₁ᵤ
- np
- t₁ᵤ
- ns
- a₁g
- e₉
- Δ₀
- π* antibonding
- t₂g
- (n - 1)d
- e₉ + t₂g
- π₀ nonbonding
- t₁g + t₂u
- π nonbonding or weakly bonding
- t₁u
- π bonding
- t₂g
- σ bonding
- a₁g + e₉ + t₁u
- σ-SALCs
- a₁g + e₉ + t₁u
- π-SALCs
- t₁g + t₂g + t₁u + t₂u
- ML₆ - SALCs
Example: CrF$_6^{3-}$

- Cr$^{3+}$ ion has a $d^3$ configuration, and therefore supplies three electrons.

- Assuming that the 2s electrons are nonbonding, each F$^-$ ion supplies six electrons, making a total of 36 electrons from ligands.

  Thus, we should fill our scheme with 39 electrons.

- Thirty-six electrons are sufficient to fill all levels through the nonbonding $t_{1g}$ and $t_{2u}$ MOs.

- The remaining three electrons occupy individual $t_{2g}$ $\pi^*$ MOs, resulting in a configuration $(t_{2g}^*)^3$, equivalent to the CFT model’s configuration $t_{2g}^3$.

- $\Delta_o$ is defined as the energy gap between the $pi$ antibonding $t_{2g}^*$ level and the $sigma$ antibonding $e_g^*$ level.

- The energies of the $t_{2g}^*$ and $e_g^*$ levels will be sensitive to differences in the effectiveness of metal-ligand $pi$ and $sigma$ interactions, respectively.
  - The interplay between $sigma$ and $pi$ bonding strength affects the magnitude of $\Delta_o$.
  - The relative abilities of a ligand to engage in $sigma$ and $pi$ bonding help determine its position in the spectrochemical series.
Sigma and Pi Bonding in $T_d$ ML$_4$ Complexes

Assumptions:

- Each of the ligands possesses one or more sigma orbitals directed at the central metal ion and pairs of pi orbitals perpendicular to the M-L bond axis.

- Ligands are monatomic ions, such as halide ions, which could use ns and np$_z$ orbitals for sigma interactions and np$_x$ and np$_y$ orbitals for pi interactions with the metal ion (n - 1)d, ns, and np orbitals.
  - For simplicity, assume that ligand ns orbitals are essentially nonbonding.
  - Assume only np orbitals have significant overlap with the metal ion orbitals.

Symmetry of M AOs:

- $s = a_1$
- $p_x, p_y, p_z = t_2$
- $d_{x^2-y^2}, d_{z^2} = e$
- $d_{xy}, d_{xz}, d_{yz} = t_2$

⚠️ Once again, the symmetries of the d orbitals are the same as we noted in the CFT approach.
Sigma SALC Representation and MOs

- Same as sigma SALCs of hydrogens in methane.
  \[ \Gamma_\sigma = A_1 + T_2 \]

- The \( A_1 \) \( \sigma \)-SALC has appropriate symmetry to form \textit{sigma} combinations with metal \( ns \) orbitals, although the effectiveness of the overlap may be limited.

- The \( T_2 \) \( \sigma \)-SALCs have appropriate symmetry to form \textit{sigma} combinations with \( np_z \), \( np_y \), and \( np_x \) orbitals on the metal ion.
  - However, the \( d_{xz} \), \( d_{yz} \), and \( d_{xy} \) orbitals also have \( T_2 \) symmetry and can likewise form combinations with these SALCs.
  - There may be some degree of \( d-p \) mixing in the \( t_2 \) \( \sigma \)-MOs.

- In constructing our MO scheme we will assume, for simplicity, that the \( t_2 \) \( \sigma \)-MOs are formed principally with the metal \( np \) orbitals, although \( d-p \) mixing may be appreciable in specific complexes.
Only the operations $E, 8C_3 (= 4C_3 + 4C_3^2)$ do not move the eight vectors off their positions. All other characters are 0 in $\Gamma_\pi$.

The character for each pair of vectors perpendicular to a three-fold axis is given by the operator matrix in the expression

$$\begin{bmatrix}
-1/2 & -\sqrt{3}/2 \\
\sqrt{3}/2 & -1/2
\end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x' \\ y' \end{bmatrix}$$

$$\chi(C_3) = -1$$
Pi SALCs and MOs

\[
\begin{array}{c|cccc}
T_d & E & 8C_3 & 3C_2 & 6S_4 & 6\sigma_d \\
\hline
\Gamma_\pi & 8 & -1 & 0 & 0 & 0
\end{array}
\]

\[\Gamma_\pi = E + T_1 + T_2\]

- The \( T_1 \) SALCs have no match in metal atom AOs and will be nonbonding.
- The \( E \) SALCs will form \( \pi \) combinations with the \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals on the metal atom.
- The \( T_2 \pi \)-SALCs, like the \( T_2 \sigma \)-SALCs, can potentially form combinations with both \( t_2 (n - 1)d \) and \( np \) orbitals on the metal atom, so the MOs that are formed may involve some degree of \( d-p \) mixing.
- We have assumed that the \( t_2 \sigma \)-MOs mainly use the \( np \) orbitals.
  - We will assume that the \( t_2 \pi \)-MOs are formed principally with the metal \((n - 1)d\) orbitals; i.e., \( d_{xy}, d_{xz}, d_{yz} \).
- The distinction between \( t_2 \sigma \)-MOs and \( t_2 \pi \)-MOs is not as clean as we might like.
  - None of the metal \( t_{2g} \) orbitals is directed at ligands (the ideal orientation in \( \sigma \) bonding).
  - None of the metal \( t_{2g} \) orbitals is oriented at right angles to the bond axis (the ideal orientation in \( \pi \) bonding).
  - Therefore, each type of MO has some of the character of the other type in this case.
  - For simplicity, we will assume that the bonding \( t_{2g} \) MOs are either essentially \( \sigma \) or \( \pi \), and that the mixing is more pronounced in the antibonding MOs.
Simplified Qualitative MO Scheme for ML₄ (T₅)

- σ*, π* antibonding
- np
- t₂
- ns
- a₁
- (n - 1)d
- e + t₂
- π₀ nonbonding
- t₁
- π bonding
- e
- π bonding
- t₂
- σ bonding
- a₁ + t₂
- Δ₁
- e + t₁ + t₂
- π-SALCs
- e + t₁ + t₂
- σ-SALCs
- a₁ + t₂
- σ bonding
- a₁ + t₂
- e + t₂
- σ* antibonding
- n₁
- t₂
- π* antibonding
- e
Equivalence of CFT and MO Models of ML$_4$ ($T_d$)

Example: NiCl$_4^{2-}$

- The four Cl$^-$ ligands supply six electrons each, for a total of 24.
- Ni$^{2+}$ is a $d^8$ ion, so the total number of electrons is 32.
- Twenty-four electrons will fill all lower levels through the $t_1$ nonbonding level in our scheme.
- The remaining eight electrons will fill the antibonding $e$ and $t_2$ levels, giving a configuration $(e^*)^4(t_2^*)^4$.
  - The two unpaired electrons in the upper $t_2^*$ orbitals make the complex paramagnetic.
  - This is equivalent to the CFT configuration $e^4t_2^4$.
- Like the CFT model, $\Delta_t$ is defined in the MO model as the energy separation between the antibonding $e^*$ and $t_2^*$ MOs.

Like the octahedral case, the essential parameters of the CFT model are similarly defined in the MO model.