## 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., *nephel*$\bar{e}$ = cloud + *aux*$\bar{e}$*sis* = 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.

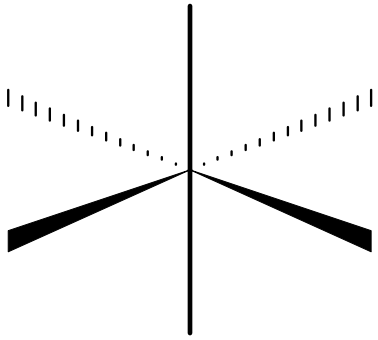
    - By using empirically determined constants for both ligands and the central metal ion it is possible to reconcile the ligand field model of a complex with quantitative spectroscopic results.

        ☞ 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 $ML_6$ ($O_h$)



Pendant Atom SALCs:

| $O_h$ | $E$ | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2$ | $i$ | $6S_4$ | $8S_3$ | $3\sigma_h$ | $6\sigma_d$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_\sigma$ | 6 | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 4 | 2 |

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$

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:

$s = a_{1g}$ $(p_x, p_y, p_z) = t_{1u}$ $(d_{x^2-y^2}, d_{z^2}) = e_g$ $(d_{xy}, d_{xz}, d_{yz}) = t_{2g}$

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

- $s$, $p_x$, $p_y$, $p_z$, $d_{x^2-y^2}$, $d_{z^2}$ orbitals have the proper symmetries to form bonding and antibonding combinations with matching symmetry SALCs.

- The three $t_{2g}$ orbitals ($d_{xy}$, $d_{xz}$, $d_{yz}$) have no matching SALCs and must remain nonbonding. This is a consequence of the orientation of these orbitals relative to the ligands.

# SALC Equations

$a_{1g}$

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

$e_g$

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

$$\Sigma_{x^2-y^2} = \frac{1}{2}(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$$

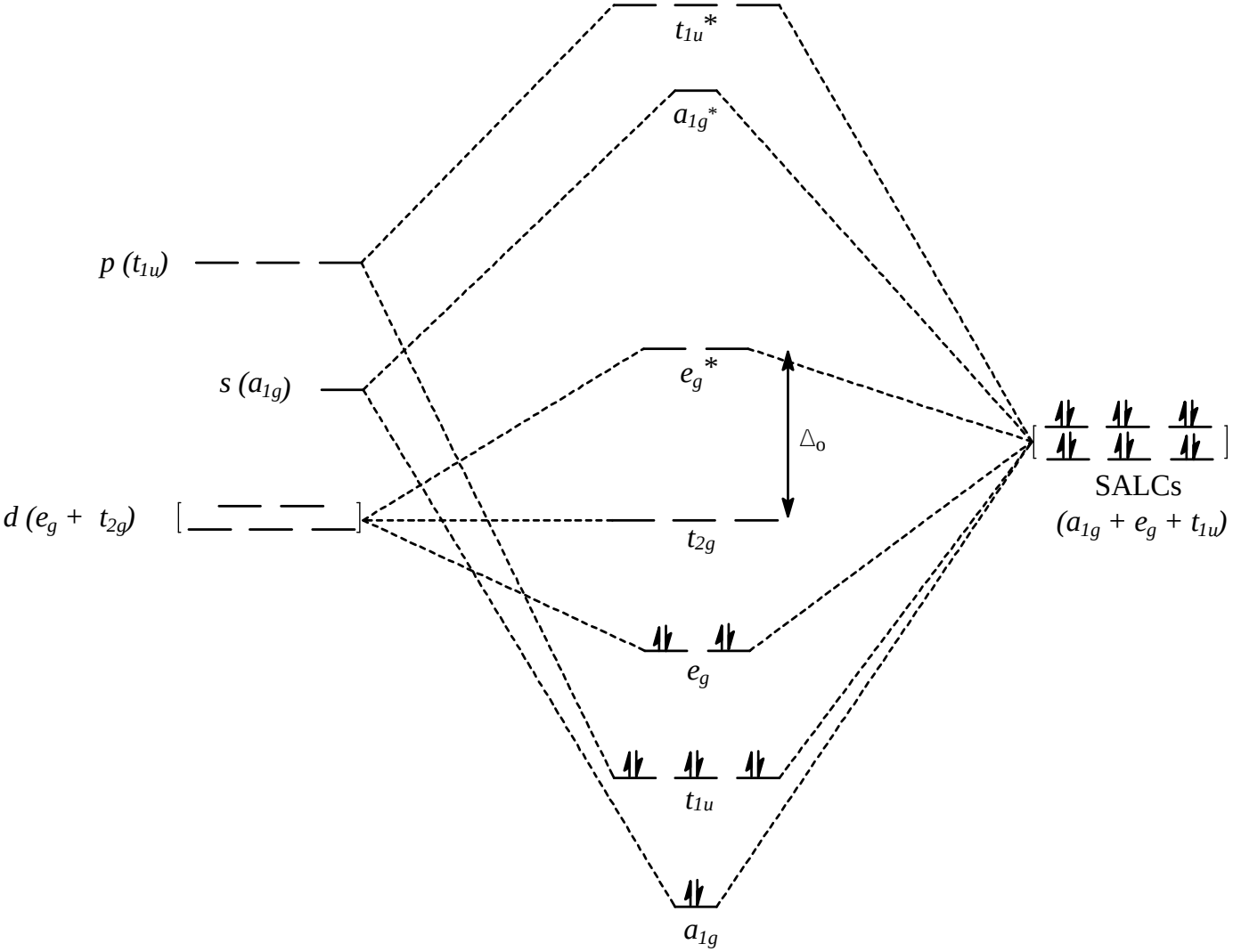
$t_{2g}$

$$\Sigma_z = \frac{1}{\sqrt{2}}(\sigma_z - \sigma_{-z})$$

$$\Sigma_x = \frac{1}{\sqrt{2}}(\sigma_x - \sigma_{-x})$$

$$\Sigma_y = \frac{1}{\sqrt{2}}(\sigma_y - \sigma_{-y})$$

# $ML_6$ Sigma-Only MO Scheme



## Sigma-Only Model of $ML_6$

- 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.

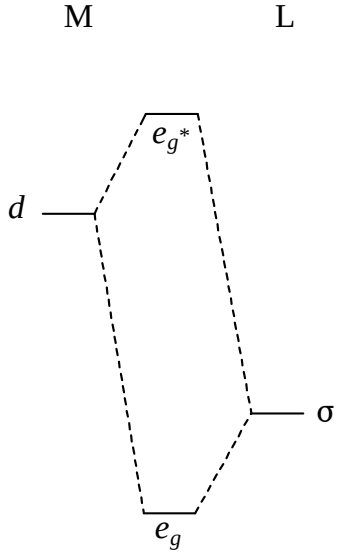
- As with the CFT model, both high and low spin ground states are possible for $d^4$ through $d^7$ metal ion configurations.

- In the MO scheme $\Delta_o$ 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

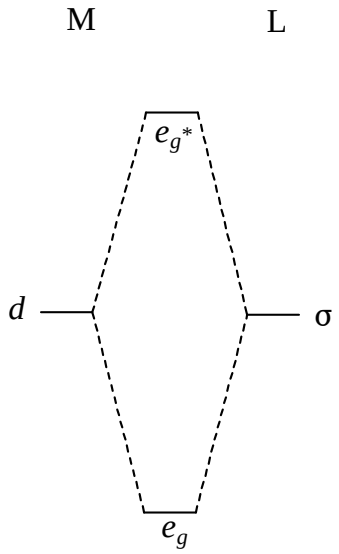
- We can make allowances for varying degrees of covalent interaction between the metal ion and ligands by adjusting the MO scheme.
  - No adjustment of the scheme can change the localized character of the $t_{2g}$ orbitals.
- Electrons occupying the $e_g$* MO will have more or less delocalization onto 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.

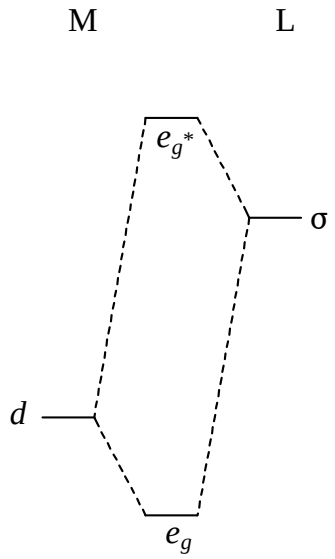
## Adjustments for Covalence

- 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

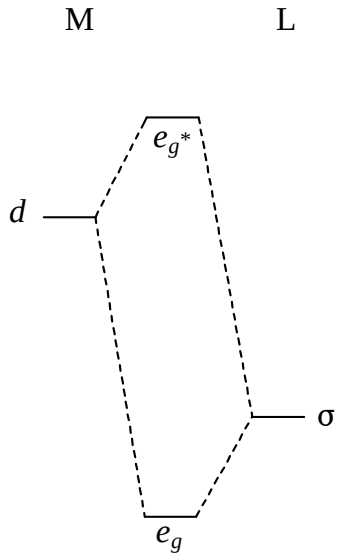
- If the ligand *sigma* orbitals were to lie significantly higher than the metal ion *d* orbitals, $e_g$* electron density would be predominantly localized on the ligands.



## 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 ($F^-$, $H_2O$, 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:




☞ 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.

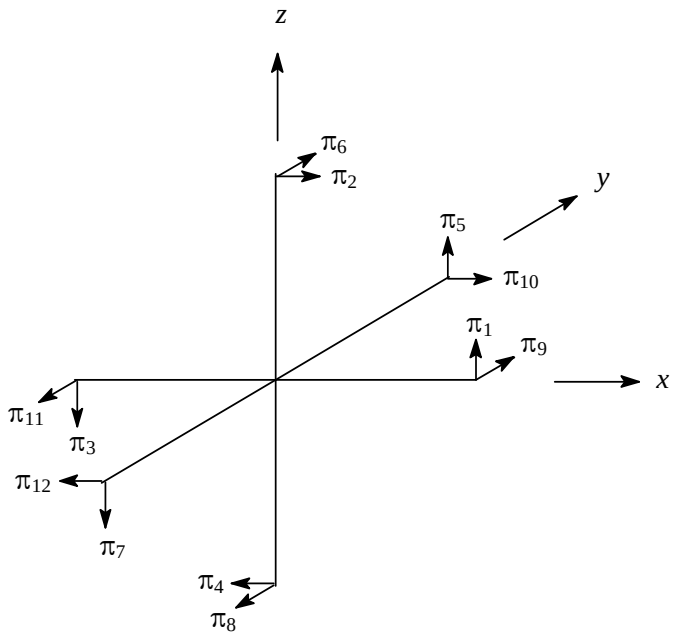
- Electron filling in the MO model in the highest occupied MOs is the same as in the CFT model:
  - Orbital symmetries are the same.
  - Orbital ordering is the same.
  - Electron filling is the same.
  - $\Delta_o$ is defined as the gap between the same symmetry orbital levels.

    ☞ 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.**

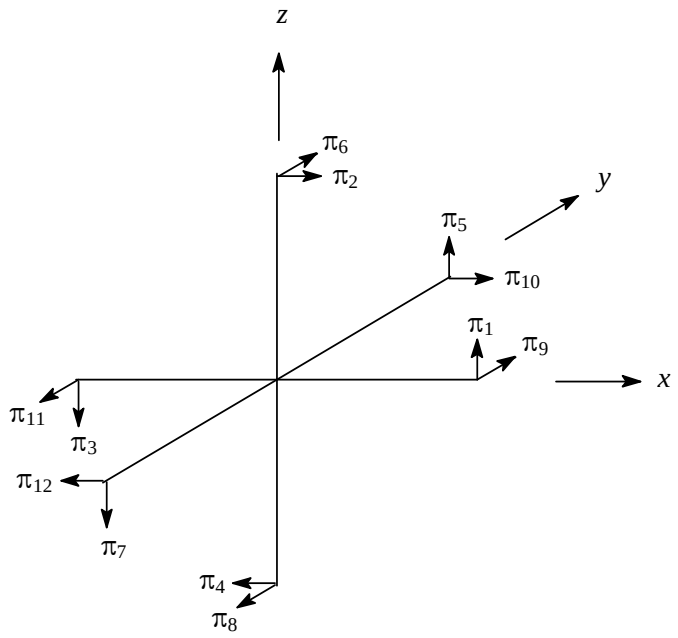
# $ML_6$ Complexes with Pi Bonding

To include *pi* bonding in our MO scheme for octahedral $ML_6$ 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 $CrX_6^{3-}$ (X = $F^-$, $Cl^-$).
    - These are classified as *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 $CN^-$ in complexes like $Cr(CO)_6$ and $[Fe(CN)_6]^{4-}$.
    - These are classified as *acceptor ligands*, since they receive electron density from the *pi* system.

# Representation for Pi-SALCs




| $O_h$ | $E$ | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2$ | $i$ | $6S_4$ | $8S_6$ | $3\sigma_h$ | $6\sigma_d$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_\pi$ | 12 | 0 | 0 | 0 | -4 | 0 | 0 | 0 | 0 | 0 |

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

## Matching $\Gamma_\pi$ with Metal AOs

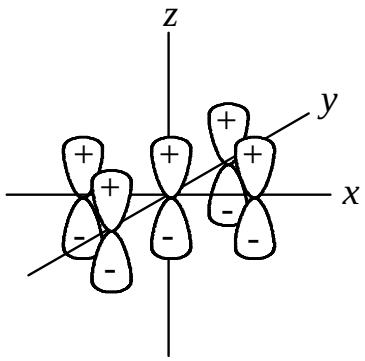
$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

**$T_{2g}$:** Can form *pi*-bonding and antibonding combinations between the $t_{2g}$ orbitals ($d_{xy}$, $d_{xz}$, $d_{yz}$) and $T_{2g}$ π-SALCs.

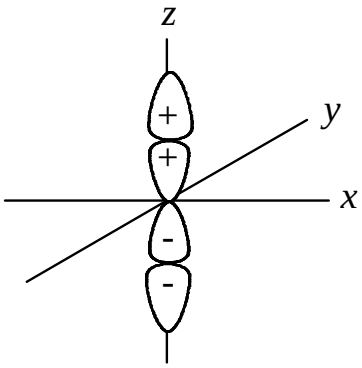
- This will change the character of the $t_{2g}$ level, which we previously had identified as nonbonding in the *sigma*-only MO scheme.

**$T_{1u}$:** 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 σ-MOs with the $T_{1u}$ σ-SALCs.
- The *sigma* interactions are likely to result in more effective overlaps




$np_z$ + $\Pi_z$



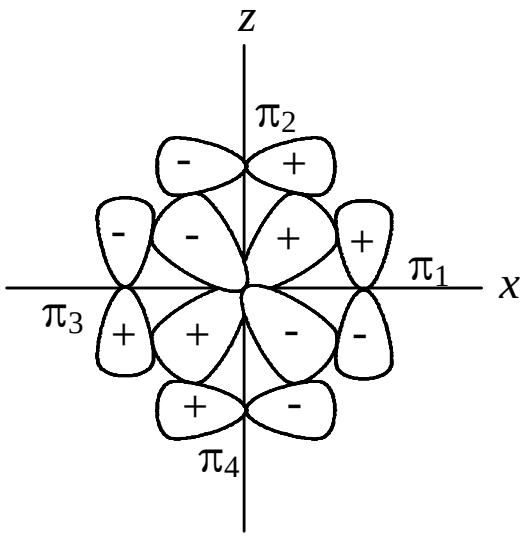

$np_z$ + $\Sigma_z$

☞ Assume that the *np* orbitals have only minimally effective interactions with the $T_{1u}$ π-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

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

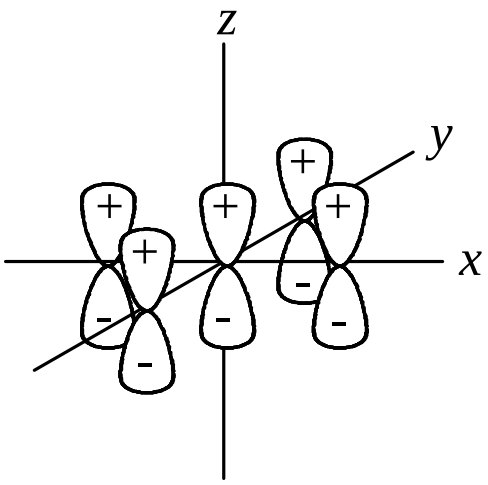



$$d_{xz} + \Pi_{xz}$$

Similar matches with the other two SALCs.

## Virtually Nonbonding $T_{1u}$ SALCs

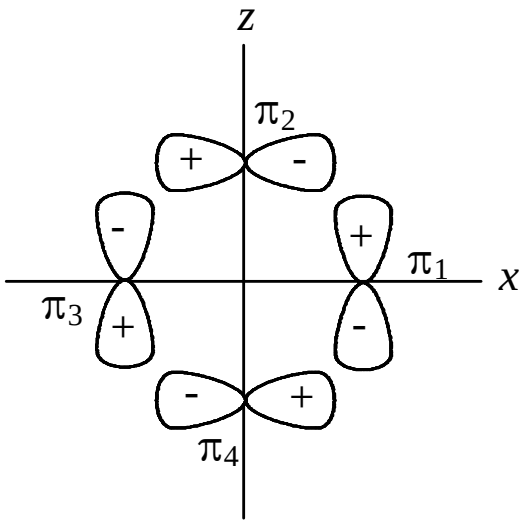
$$\Pi_z = \tfrac{1}{2}(\pi_1 - \pi_3 + \pi_5 - \pi_7)$$
$$\Pi_x = \tfrac{1}{2}(\pi_2 - \pi_4 + \pi_{10} - \pi_{12})$$
$$\Pi_y = \tfrac{1}{2}(\pi_6 - \pi_8 + \pi_9 - \pi_{11})$$




$p_z + \Pi_z$

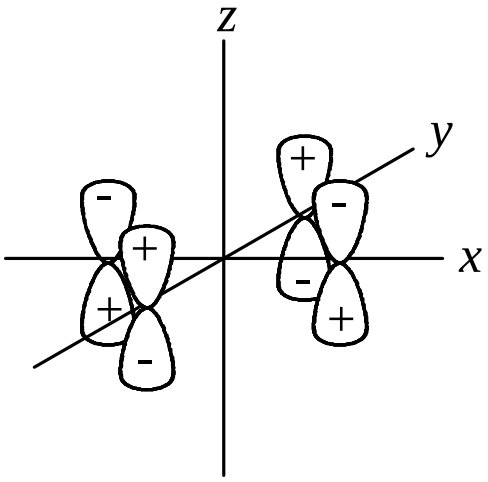
Similar matches with the other two SALCs.

## 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

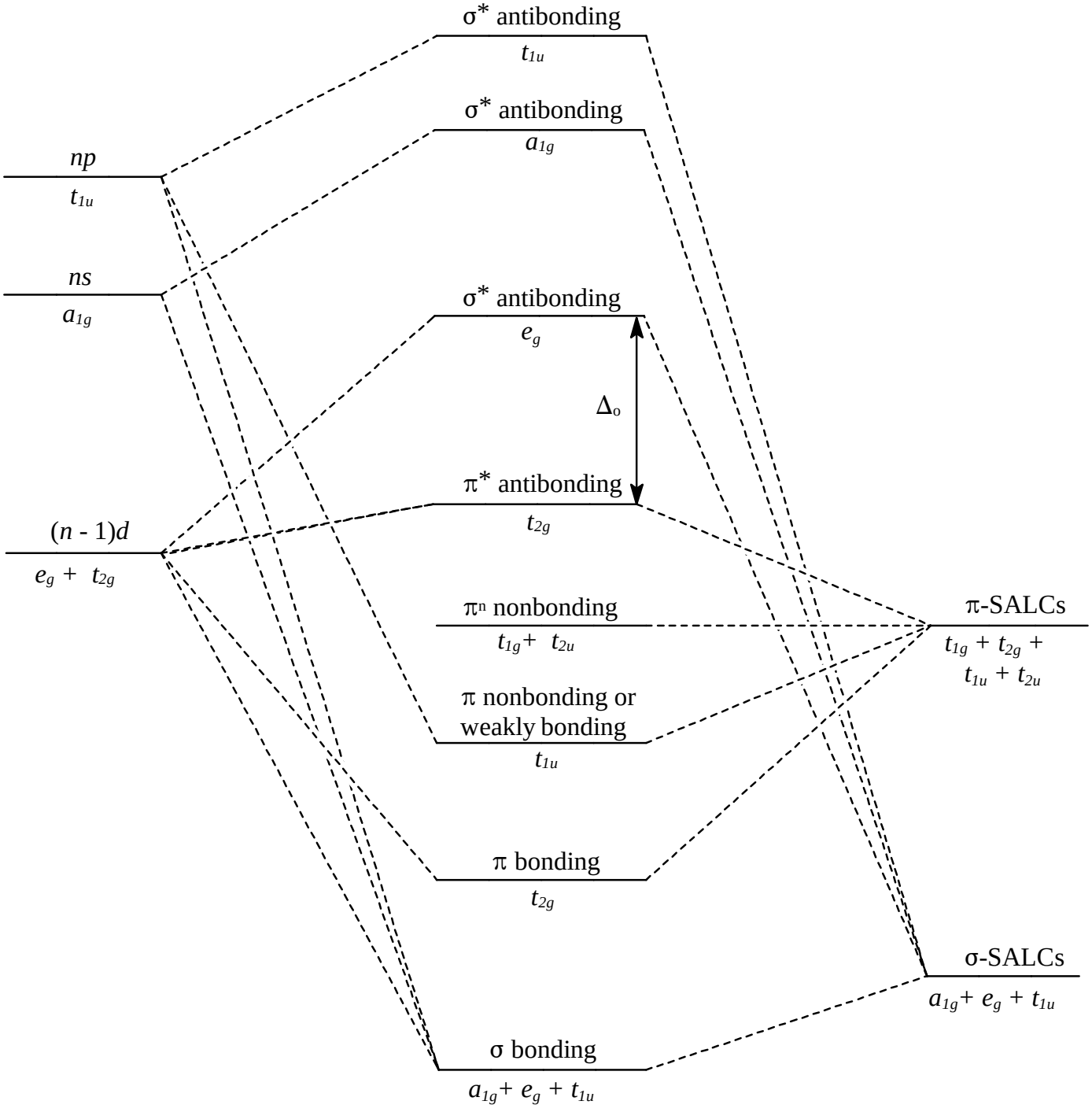
- The energy ordering and the nature of the MOs will be affected by the following factors:
  - Identity of the central metal ion
  - Identity of the ligands
  - Relative energies of the orbitals on metal and ligands
  - The nature and effectiveness of the *sigma* and *pi* orbital interactions
  - Electron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

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

☞ 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 $ML_6$



## Example: $CrF_6^{3-}$

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

- Assuming that the 2*s* 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

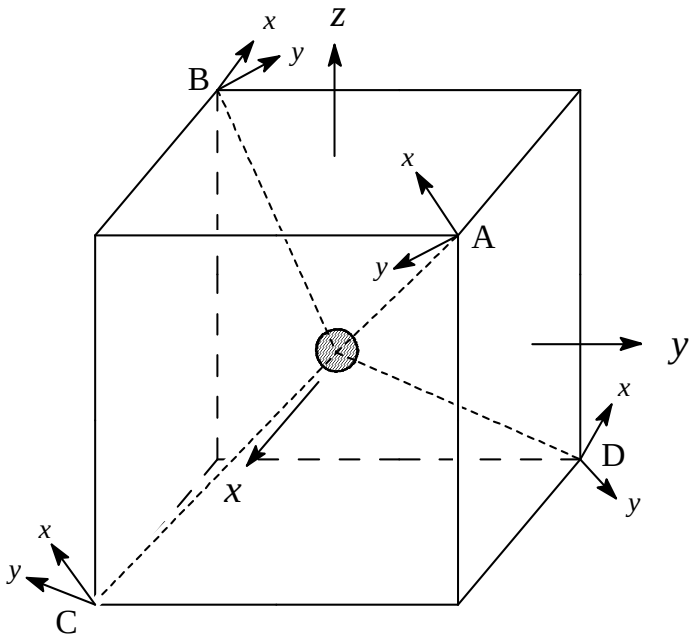
- Same as sigma SALCs of hydrogens in methane.

$$\Gamma_\sigma = A_1 + T_2$$

- The $A_1$ σ-SALC has appropriate symmetry to form *sigma* combinations with metal *ns* orbitals, although the effectiveness of the overlap may be limited.

- The $T_2$ σ-SALCs have appropriate symmetry to form *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 $t_2$ σ-MOs.
  - In constructing our MO scheme we will assume, for simplicity, that the $t_2$ σ-MOs are formed principally with the metal *np* orbitals, although *d-p* mixing may be appreciable in specific complexes.

# Pi SALCs Representation




- 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

| $T_d$ | $E$ | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ |
|---|---|---|---|---|---|
| $\Gamma_\pi$ | 8 | -1 | 0 | 0 | 0 |

$$\Gamma_\pi = E + T_1 + T_2$$

- 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.

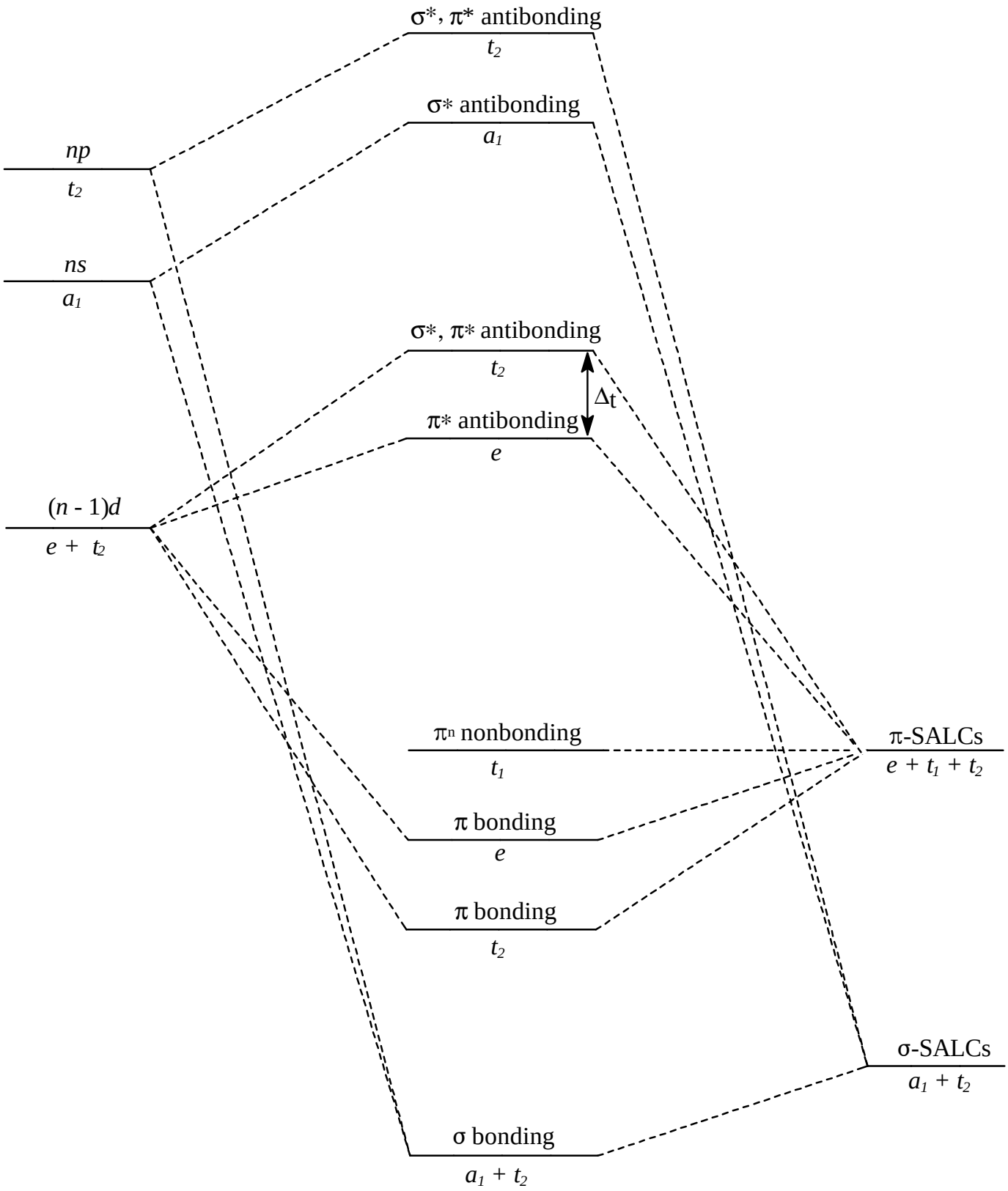
- The $T_2$ π-SALCs, like the $T_2$ σ-SALCs, can potentially form combinations with both $t_2$ ($n$ - 1)*d* and *np* orbitals on the metal atom, so the MOs that are formed may involve some degree of *d*-*p* mixing.

- We have assumed that the $t_2$ σ-MOs mainly use the *np* orbitals.
  - ☞ We will assume that the $t_2$ π-MOs are formed principally with the metal ($n$ - 1)*d* orbitals; i.e., $d_{xy}$, $d_{xz}$, $d_{yz}$ .

- The distinction between $t_2$ σ-MOs and $t_2$ π-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 $ML_4$ ($T_d$)



## 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.