

## Ligand Field Theory

- Quantitative results of CFT, based solely on electrostatic considerations, require correction to give satisfactory agreement with experiment.
  - When empirical corrections are added to CFT it is known as Ligand Field Theory (LFT).
- Need for corrections to CFT arise from metal-ligand orbital overlap, implying some degree of covalent M–L bonding.
  - Observed absorption spectra suggest there is less interaction between *d* electrons in a complex ion than in the free gaseous ion.
  - Covalent M–L interaction allows metal electrons to be somewhat delocalized onto the ligand.
  - This delocalization results in lesser energy separation between the Russell-Saunders term states in the complex than predicted for the ion in the crystal field environment.
  - On the basis of the CFT model, M→L interaction has the effect of "expanding" the *d* orbitals.

## The Nephelauxetic Effect

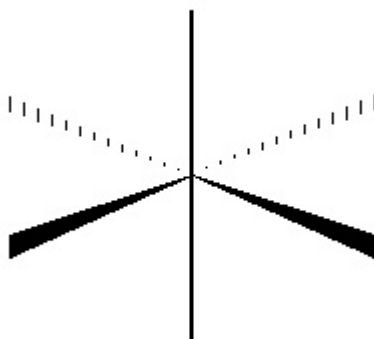
- The disparity between free-ion and complex-ion electronic state energies is the so-called *nephelauxetic effect* (Gk., *nephele* = cloud + *auxēsis* = growth; hence, “cloud-expanding”), which depends upon both the metal ion and ligand.
  - For a given metal ion, the ability of ligands to induce this cloud expanding increases according to a *nephelauxetic series*:



☞ 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:

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

☺ 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

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

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

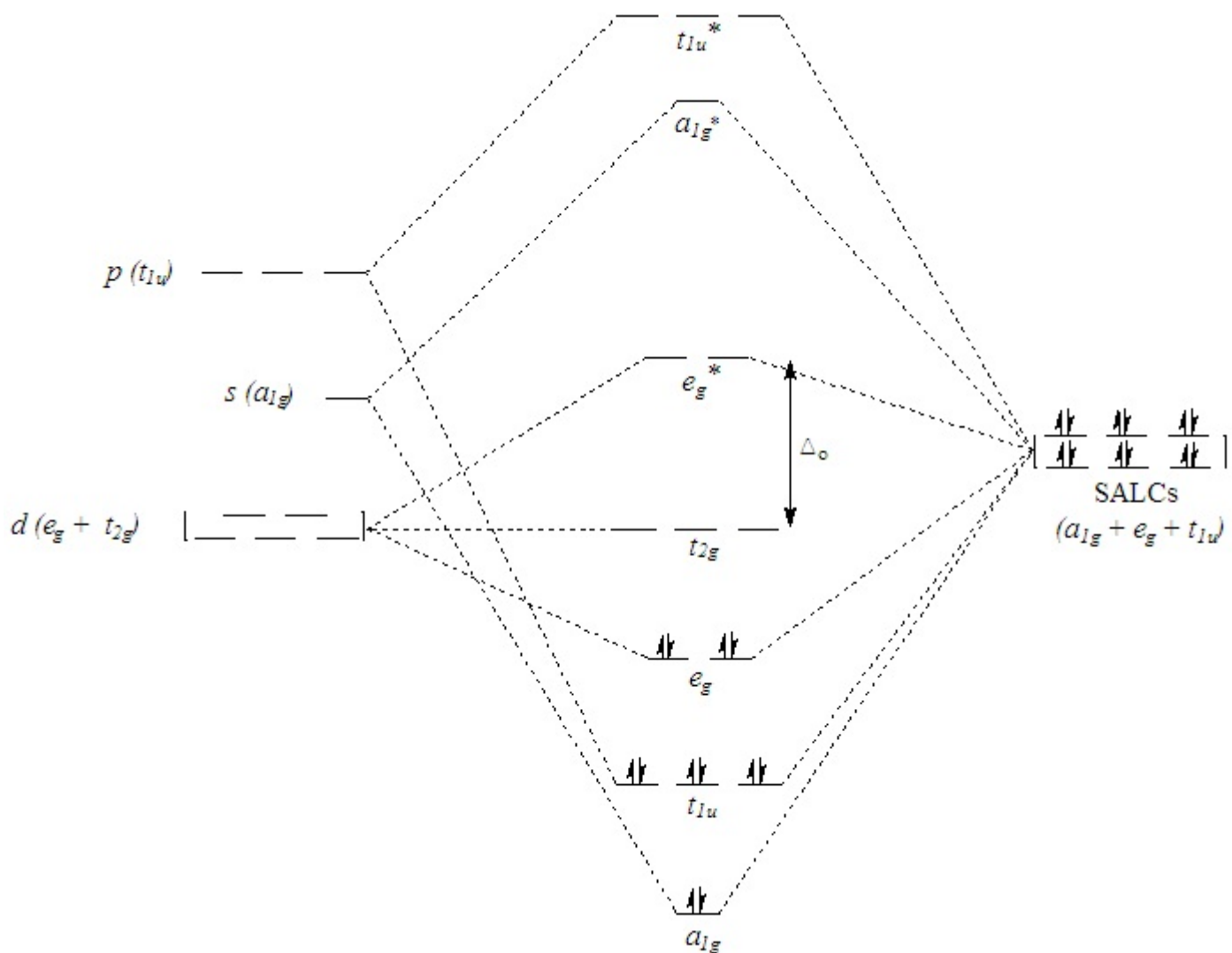
$$\Sigma_{x^2-y^2} = \frac{1}{2}(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$$

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

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

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

# ML<sub>6</sub> Sigma-Only MO Scheme

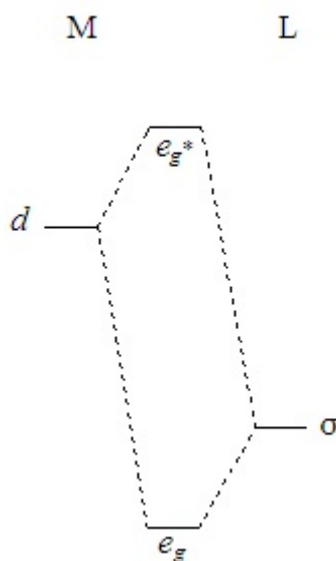


## Sigma-Only Model of $ML_6$

- 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

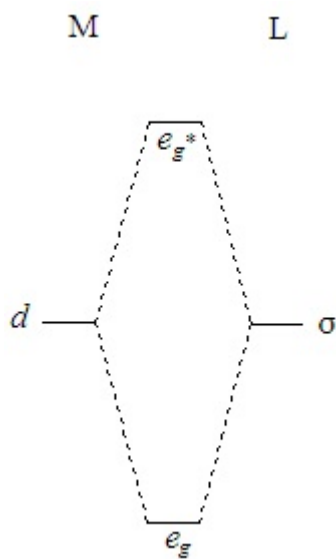
- We can make allowances for varying degrees of covalent interaction between the metal ion and ligands by adjusting the MO scheme.
  - No adjustment of the scheme can change the localized character of the  $t_{2g}$  orbitals.
- Electrons occupying the  $e_g^*$  MO will have more or less delocalization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

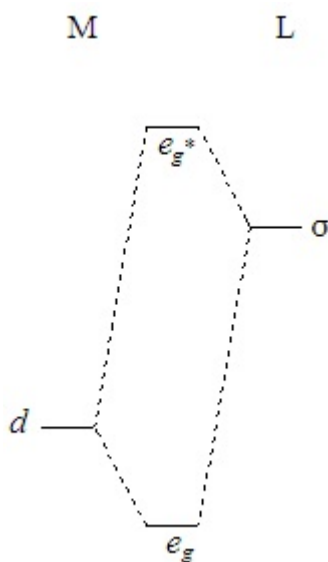
- As the energies of the metal ion  $d$  orbitals and the ligand  $\sigma$  orbitals become more comparable the degree of electron sharing (covalence) will become greater.
  - More of the  $e_g^*$  electron density will be delocalized toward the ligands.



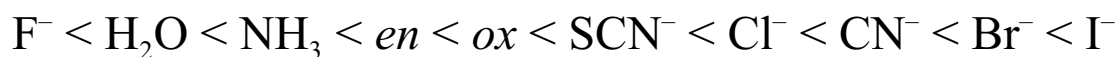


## Adjustments for Covalence

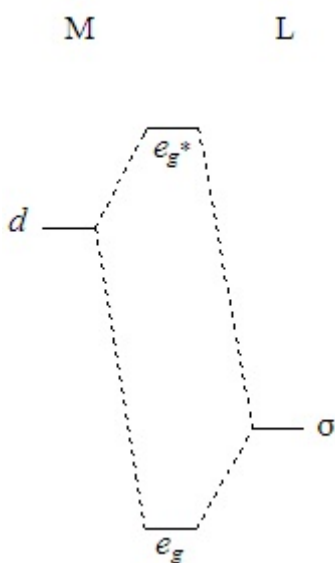
- If the ligand *sigma* orbitals were to lie significantly higher than the metal ion *d* orbitals,  $e_g^*$  electron density would be predominantly localized on the ligands.



## MO Interpretation of Nephelauxetic Effect Sigma-Only Case



- 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:



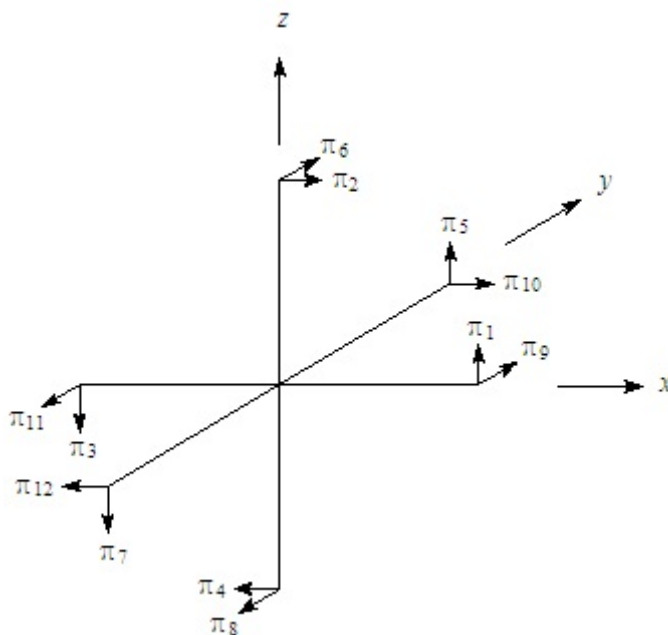
- ☞ For complexes with these ligands, both  $t_{2g}$  and  $e_g^*$  electron density is essentially localized in metal  $d$  orbitals, not unlike the assumptions of the CFT model.

## 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.**

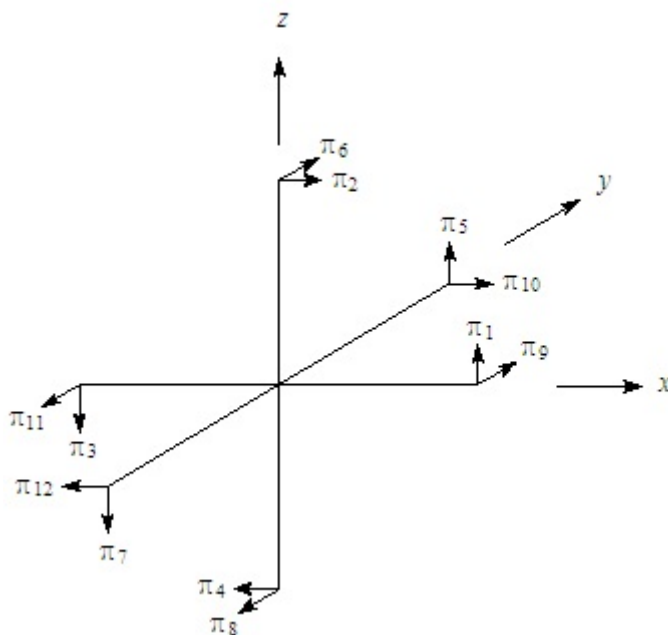
## ML<sub>6</sub> Complexes with Pi Bonding

To include *pi* bonding in our MO scheme for octahedral ML<sub>6</sub> 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  $\text{CrX}_6^{3-}$  ( $\text{X} = \text{F}^-, \text{Cl}^-$ ).
  - 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  $\text{CN}^-$  in complexes like  $\text{Cr}(\text{CO})_6$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ .
  - 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

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

Note: To understand how  $\chi = 0$  for  $C_4$ , consider the effect of the operation on the pair  $\pi_2$  and  $\pi_6$ , by which  $\pi_2 \rightarrow -\pi_6$  and  $\pi_6 \rightarrow \pi_2$ . In matrix notation this is

$$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \pi_2 \\ \pi_6 \end{bmatrix} = \begin{bmatrix} -\pi_6 \\ \pi_2 \end{bmatrix}$$

Therefore,  $\chi(C_4) = 0$  for the operator matrix for the pair. The result is the same for the pair  $\pi_4$  and  $\pi_8$ , or any other pairs perpendicular to the  $C_4$  axis.

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

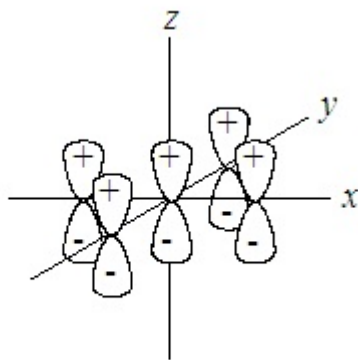
$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

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

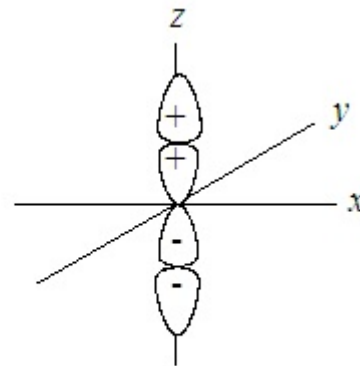
- This will change the character of the  $t_{2g}$  level, which we previously had identified as nonbonding in the *sigma*-only MO scheme.

**$T_{1u}$ :** 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



$np_z + \Pi_z$



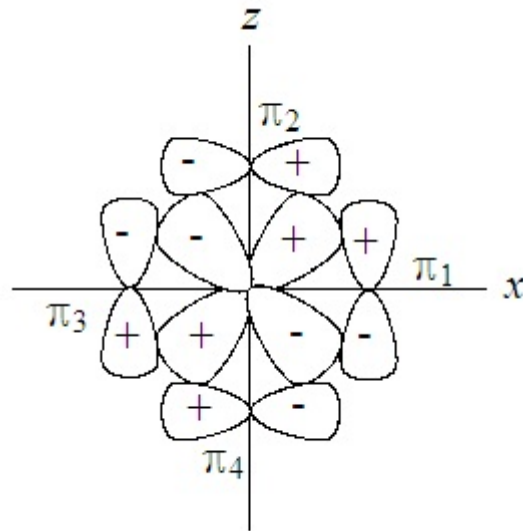
$np_z + \Sigma_z$

- ☞ 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

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

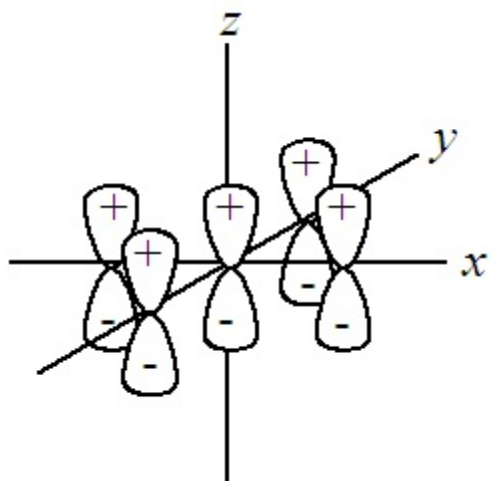


$$d_{xz} + \Pi_{xz}$$

Similar matches with the other two SALCs.

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

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

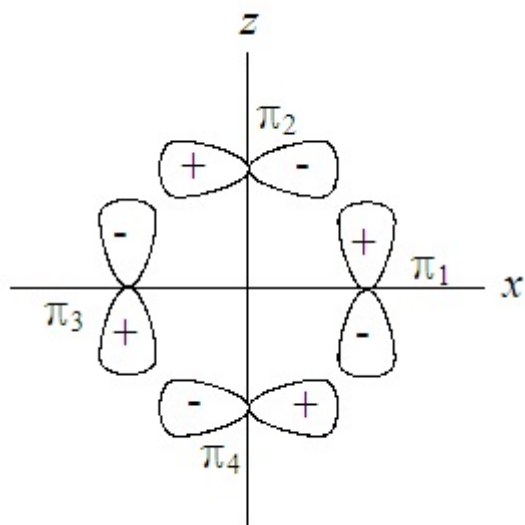


$$p_z + \Pi_z$$

Similar matches with the other two SALCs.

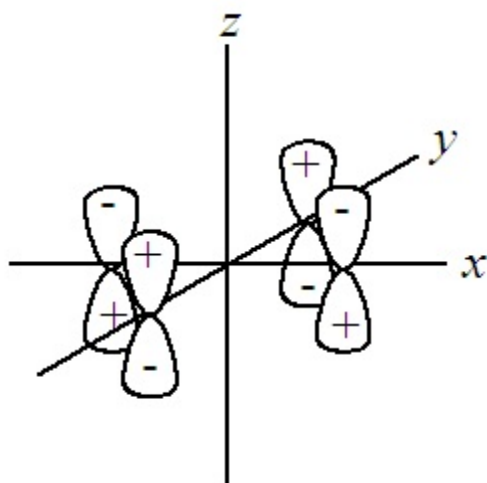


## Strictly Nonbonding $T_{1g}$ and $T_{2u}$ SALCs



$$T_{1g}(xz)$$

Similar form for the other two SALCs.



$$T_{2u}(z)$$

Similar form for the other two SALCs.

## Impediments to Forming a General MO Scheme

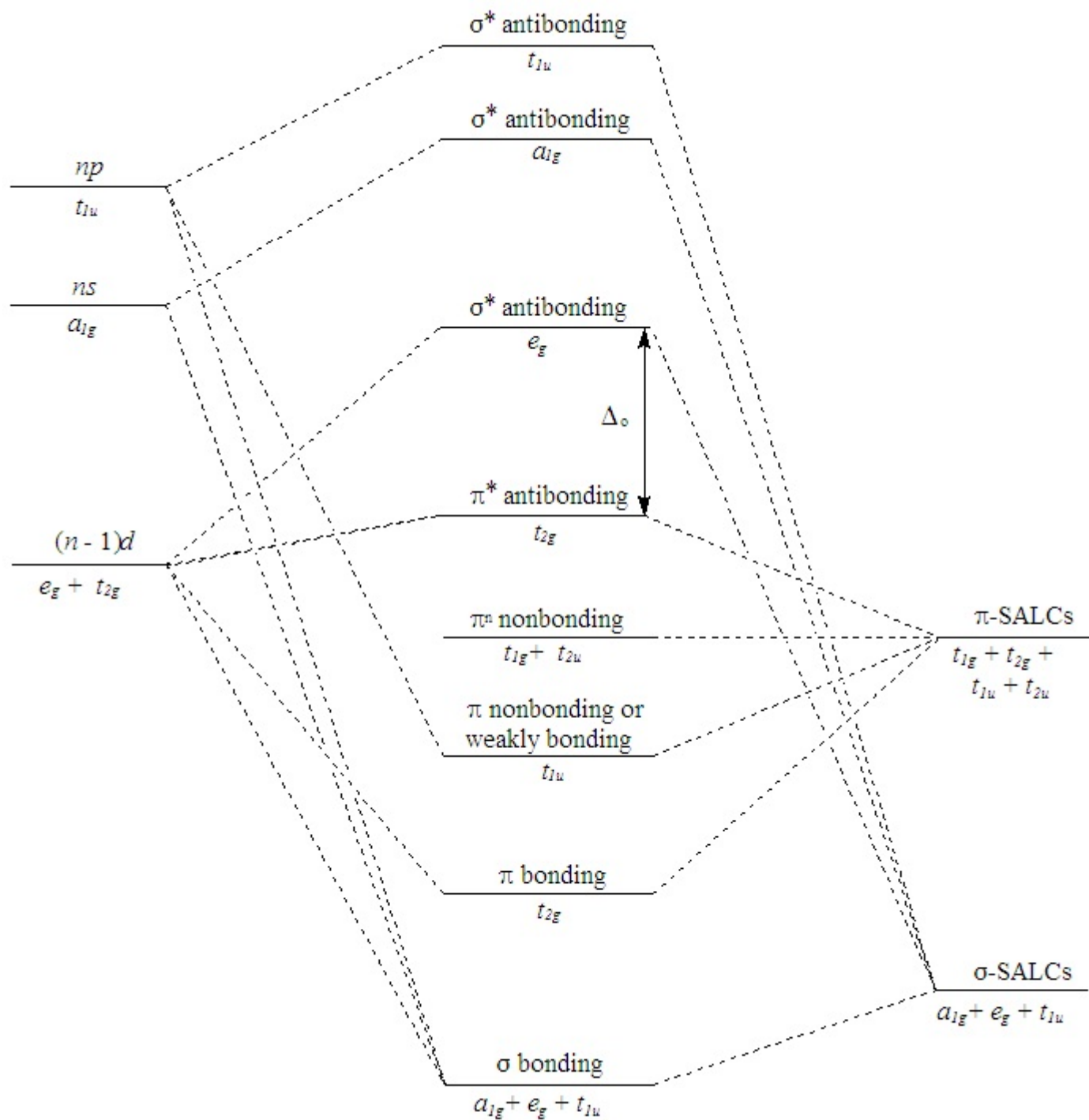
- The energy ordering and the nature of the MOs will be affected by the following factors:
  - Identity of the central metal ion
  - Identity of the ligands
  - Relative energies of the orbitals on metal and ligands
  - The nature and effectiveness of the *sigma* and *pi* orbital interactions
  - Electron 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 $ML_6$

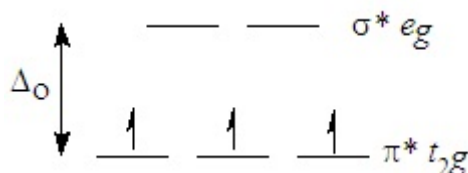


### Example: $\text{CrF}_6^{3-}$

- $\text{Cr}^{3+}$  ion has a  $d^3$  configuration, and therefore supplies three electrons.
- Assuming that the  $2s$  electrons are nonbonding, each  $\text{F}^-$  ion supplies six electrons, making a total of 36 electrons from ligands.

☞ Thus, we should fill our scheme with 39 electrons.

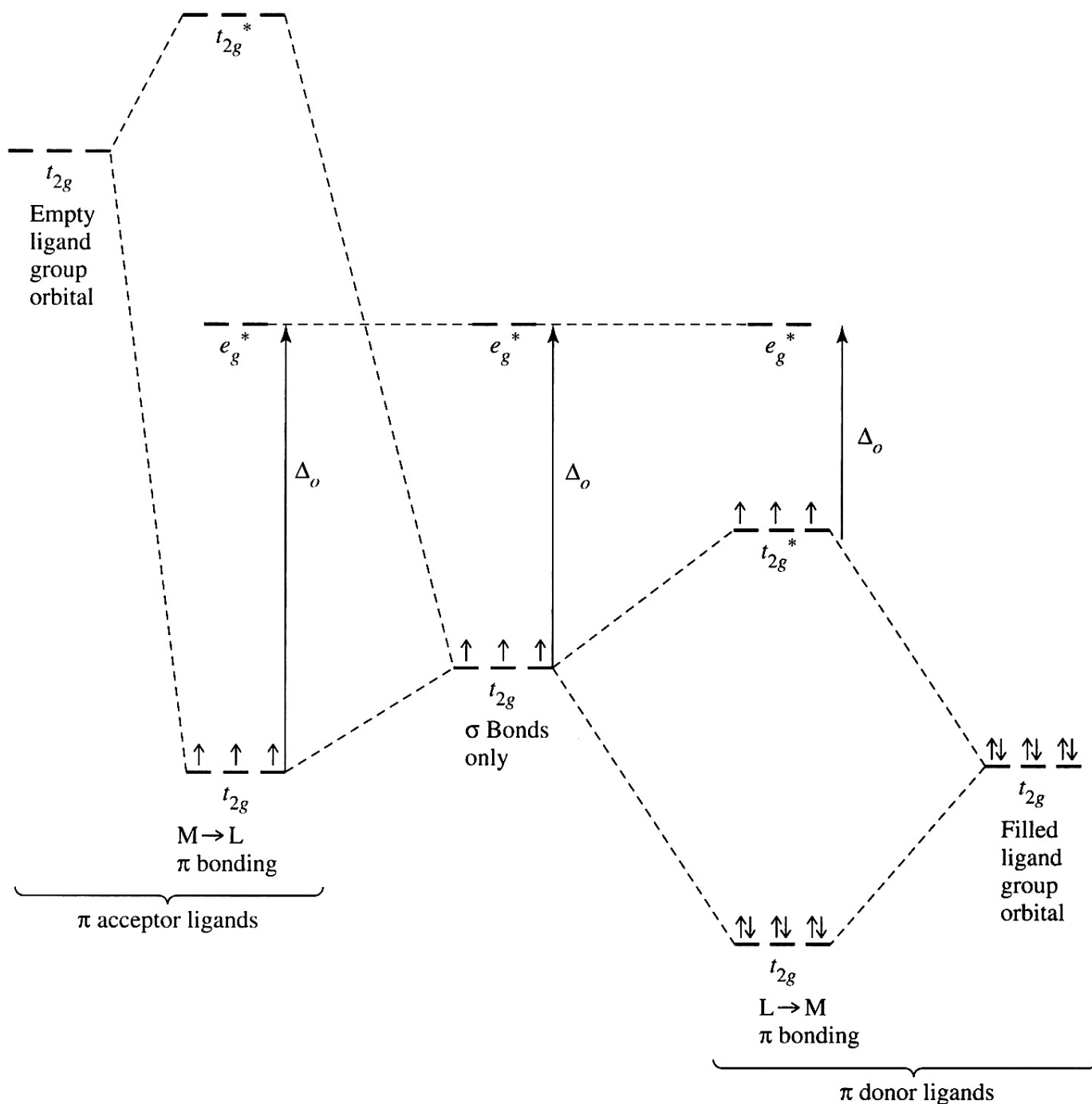
- Thirty-six electrons are sufficient to fill all levels through the nonbonding  $t_{1g}$  and  $t_{2u}$  MOs.
- The remaining three electrons occupy individual  $t_{2g} \pi^*$  MOs, resulting in a configuration  $(t_{2g}^*)^3$ , equivalent to the CFT model's configuration  $t_{2g}^3$ .



- $\Delta_o$  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.

## Effect of $\pi$ Interactions on $\Delta_o$

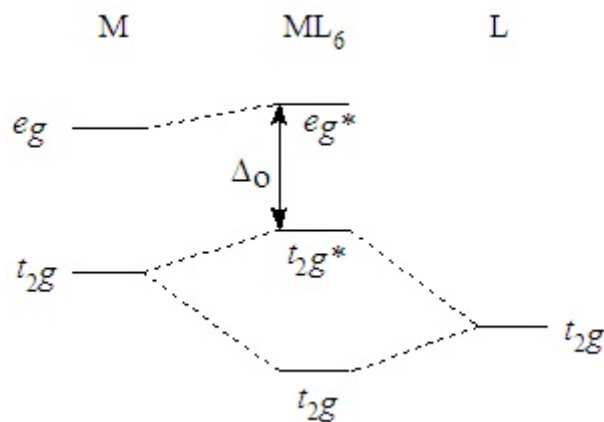
- The effect of  $\pi$  interactions on  $\Delta_o$  depends upon the energies of the ligand MOs relative to metal  $d$  orbitals, and also on whether the ligand  $\pi$  orbitals are filled or empty.



## Effect of $\pi$ Interactions on $\Delta_o - L \rightarrow M \pi$ Bonding

Case I:  $M d(t_{2g}) > L \pi\text{-SALC}(t_{2g})$  and ligand orbitals ( $t_{2g}$  bonding) filled ( $\pi$ -donor ligands). [above right]

- $\Delta_o = t_{2g}^* (\pi^*) \leftrightarrow e_g^* (\sigma^*)$
- $t_{2g}$   $\pi$ -bonding MOs are filled ( $6e$ ).
- $t_{2g}^* (\pi^*)$  and  $e_g^* (\sigma^*)$  filling corresponds to  $d$  filling in CFT model.

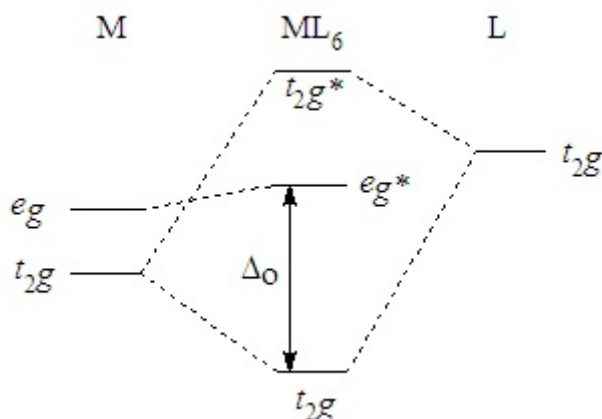


- As  $\pi$  interaction increases,  $t_{2g}$  bonding becomes more stable and  $t_{2g}^*$  is squeezed towards  $e_g^*$ , making  $\Delta_o$  smaller.
  - This is probably the situation with monatomic filled-subshell ligands such as  $O^{2-}$ ,  $F^-$ , etc.
  - This is described as ligand-to-metal ( $L \rightarrow M$ )  $\pi$  bonding.

## Effect of $\pi$ Interactions on $\Delta_o - M \rightarrow L \pi$ Bonding

Case II:  $M d(t_{2g}) < L \pi\text{-SALC}(t_{2g})$  and ligand orbitals ( $t_{2g}$  bonding) not filled ( $\pi$ -acceptor ligands). [above left]

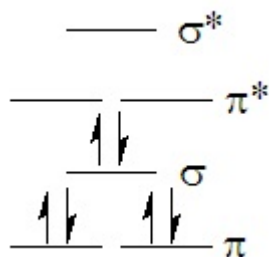
- $\Delta_o = t_{2g}(\pi) \leftrightarrow e_g^*(\sigma^*)$
- $t_{2g}$   $\pi$ -bonding MOs are filled as  $d$  filling in CFT model.
- $e_g^*$   $\sigma$ -antibonding MOs are filled (or empty) as  $d$  filling in CFT model.
- $t_{2g}^*$  antibonding MOs are not filled



- As  $\pi$  interaction increases,  $t_{2g}$   $\pi$ -bonding becomes more stable relative to  $e_g^*$   $\sigma$ -antibonding, making  $\Delta_o$  larger.
  - This is probably the situation with ligands such as  $\text{PH}_3$  and  $\text{AsH}_3$ , which use empty  $d$  orbitals on the central atom for  $\pi$  interactions.
- When both empty and filled ligand  $\pi$  orbitals are involved in the bonding the effect on  $\Delta_o$  is less predictable.

## CO, CN<sup>-</sup>, NO<sup>+</sup>, N<sub>2</sub> Ligands

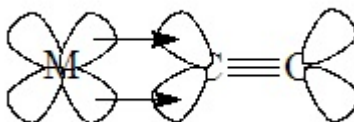
- CO, CN<sup>-</sup>, NO<sup>+</sup>, and N<sub>2</sub> are isoelectronic species that have both  $\sigma$  and  $\pi$  M-L interactions.
  - All have empty  $\pi^*$  MOs.



- The  $\sigma$  MO is the HOMO, which donates to the metal ion, forming L→M  $\sigma$  bonds ( $t_{1u}$   $\sigma$  MOs).



- Partially filled  $t_{2g}$  metal  $d$  orbitals "back-bond" to the  $\pi^*$  MO on the ligand, forming M→L  $\pi$  bonds ( $t_{2g}$   $\pi$  MOs).



- The back-bonding stabilizes the  $\pi$  bonding MOs of the complex, making large  $\Delta_o$ .
  - CO, CN<sup>-</sup>, NO<sup>+</sup>, and N<sub>2</sub> are strong-field ligands.
- Increased electron density in the ligand  $\pi^*$  MO weakens the C–O bond, causing a shift in the stretching vibration to lower frequency.

	CO	Ni(CO) <sub>4</sub>	Co(CO) <sub>4</sub> <sup>-</sup>	Fe(CO) <sub>4</sub> <sup>2-</sup>
$\nu_{\text{CO}}$ (cm <sup>-1</sup> )	2143	2060	1890	1790
$M^{n\pm}$	—	0	-1	-2



## 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<sub>z</sub>* orbitals for *sigma* interactions and *np<sub>x</sub>* and *np<sub>y</sub>* 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.

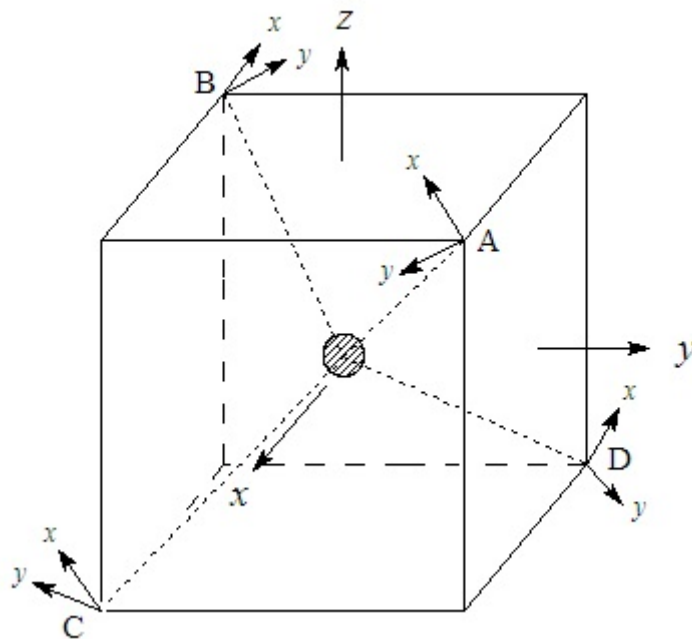
## Sigma SALC Representation and MOs

- Same as sigma SALCs of hydrogens in methane.

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

- The  $A_1$   $\sigma$ -SALC has appropriate symmetry to form *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 *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.

## 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

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

$$\chi(C_3) = -1$$

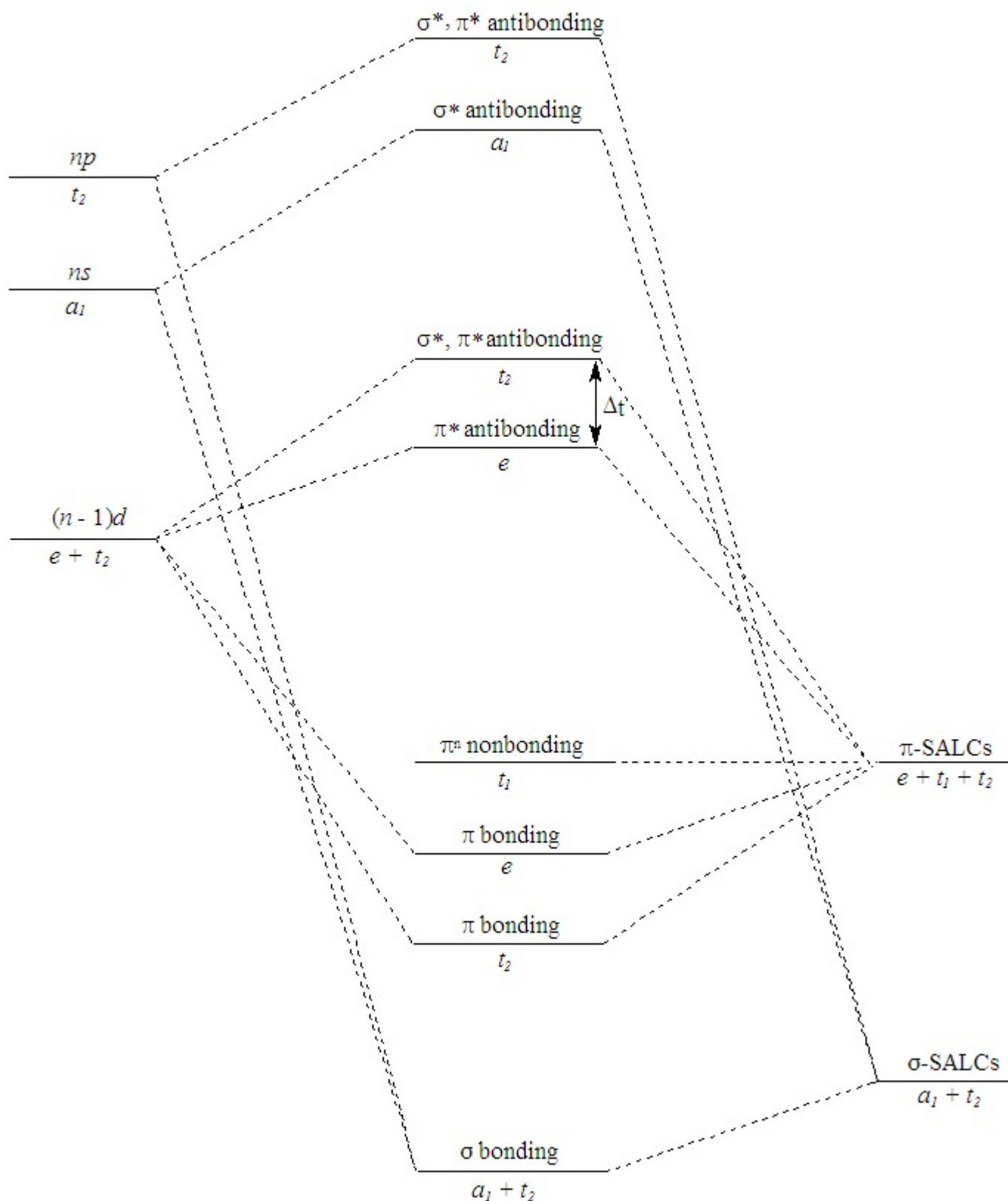
## Pi SALCs and MOs

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_\pi$	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  $T_2$   $\pi$ -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.
  - ☞ The  $\pi$ -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  $t_2$  orbitals is directed at ligands (the ideal orientation in *sigma* bonding).
  - None of the metal  $t_2$  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  $t_2$  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.