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., *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.

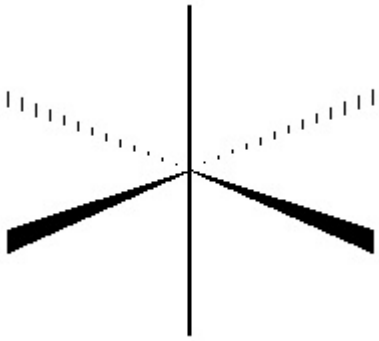
- By using empirically determined constants for both ligands and the central metal ion it is possible to reconcile the ligand field model of a complex with quantitative spectroscopic results.

    ☞ 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 ML_6 (O_h)



Pendant Atom SALCs:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_3$	$3\sigma_h$	$6\sigma_d$
Γ_σ	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

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

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

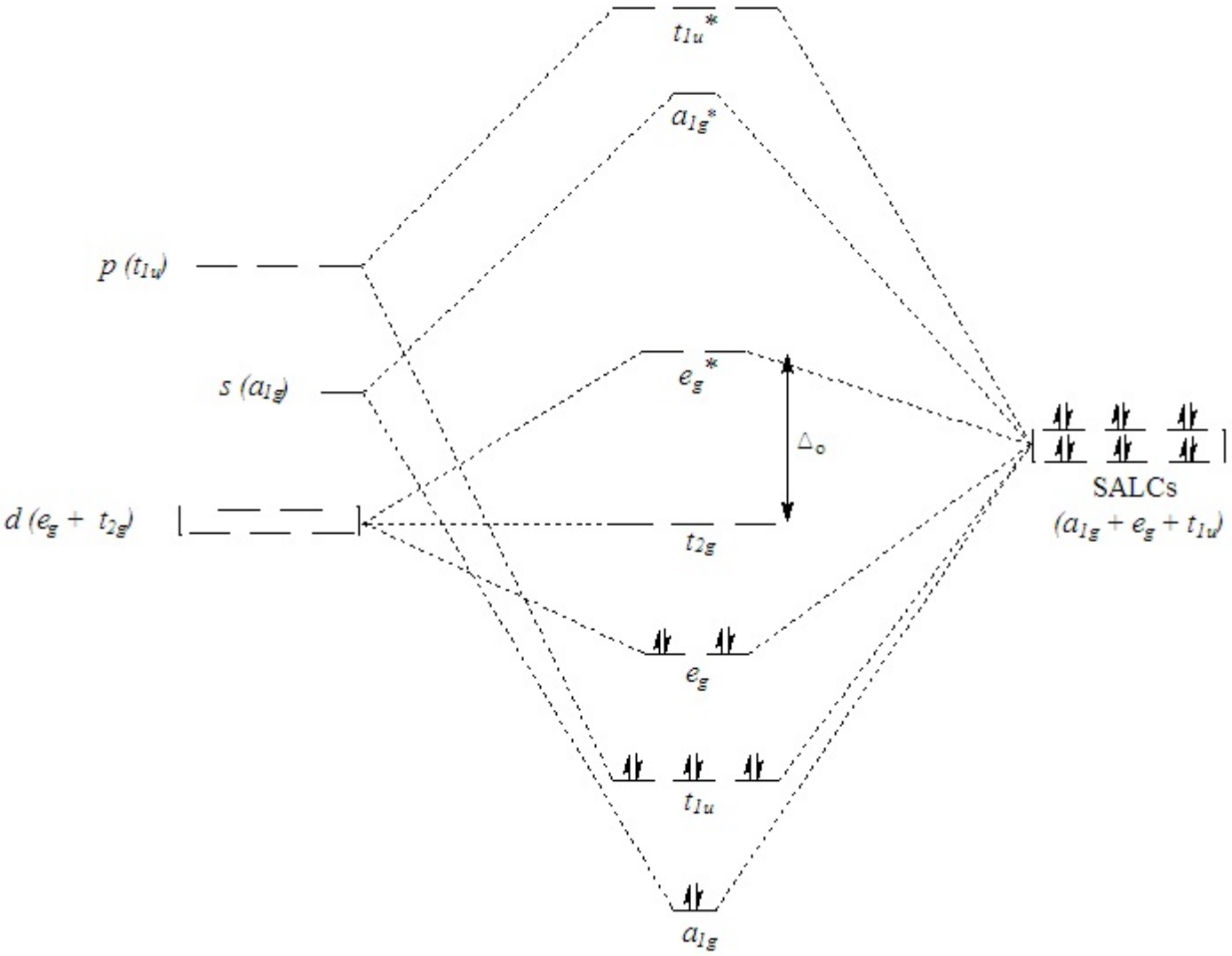
t_{1u}

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

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

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

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.

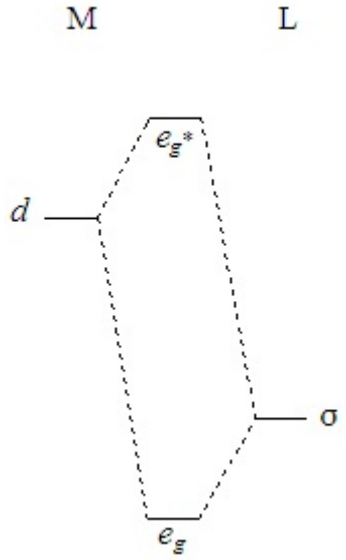
- As with the CFT model, both high and low spin ground states are possible for d^4 through d^7 metal ion configurations.

- In the MO scheme Δ_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

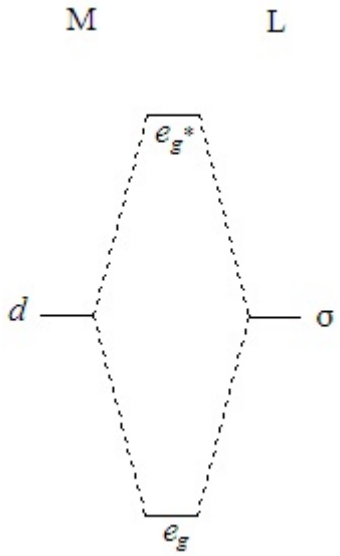
- We can make allowances for varying degrees of covalent interaction between the metal ion and ligands by adjusting the MO scheme.
  - No adjustment of the scheme can change the localized character of the t_{2g} orbitals.
- Electrons occupying the e_g* MO will have more or less delocalization onto the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

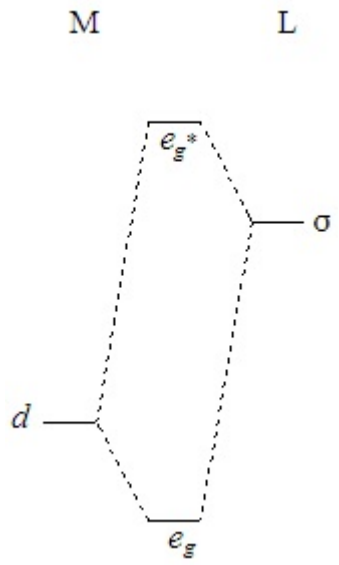
Adjustments for Covalence

- 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

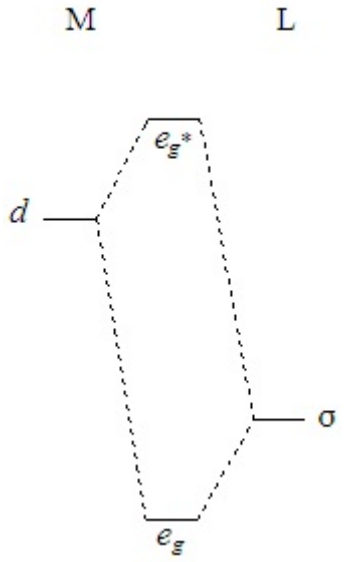
- If the ligand *sigma* orbitals were to lie significantly higher than the metal ion *d* orbitals, e_g* electron density would be predominantly localized on the ligands.



MO Interpretation of Nephelauxetic Effect
Sigma-Only Case

$$F^- < H_2O < NH_3 < en < ox < SCN^- < Cl^- < CN^- < Br^- < I^-$$

- 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.

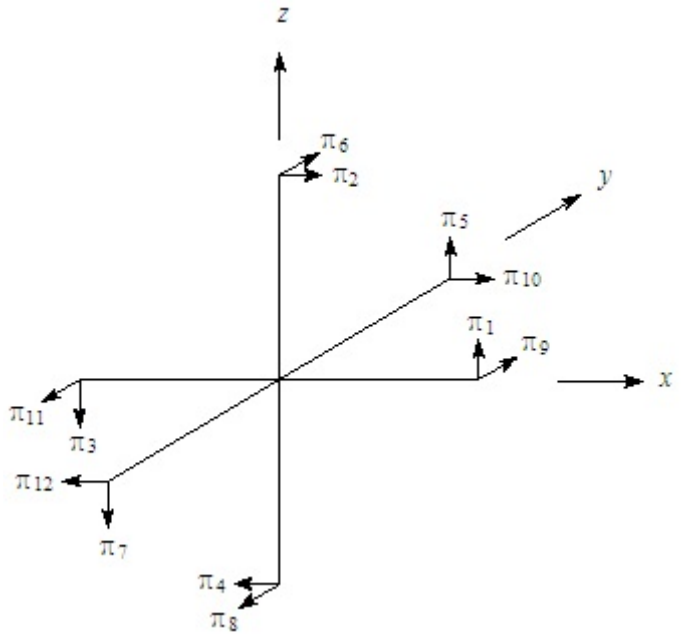
- Electron filling in the MO model in the highest occupied MOs is the same as in the CFT model:
  - Orbital symmetries are the same.
  - Orbital ordering is the same.
  - Electron filling is the same.
  - Δ_o is defined as the gap between the same symmetry orbital levels.

    ☞ 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.

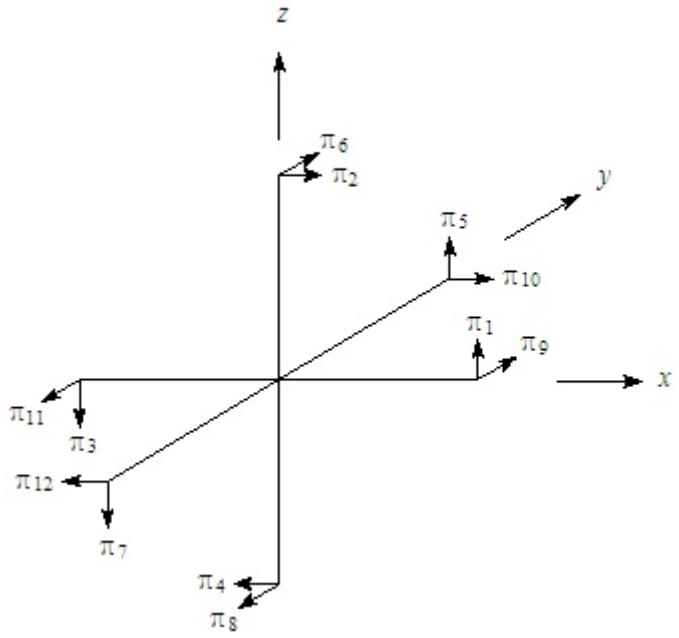


- These vectors might indicate

  - 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 π^* 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	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_π	12	0	0	0	-4	0	0	0	0	0

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

Matching Γ_π with Metal AOs

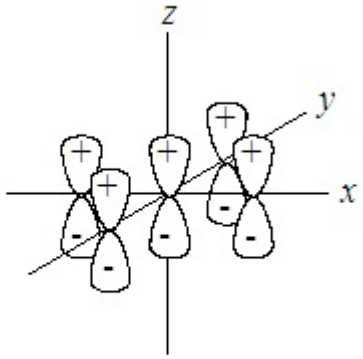
$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

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.

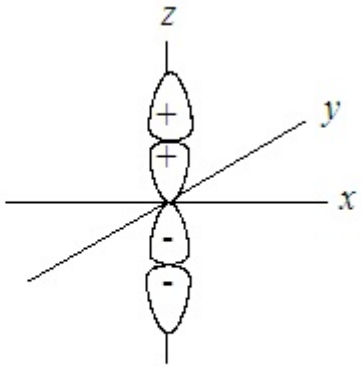
- This will change the character of the t_{2g} level, which we previously had identified as nonbonding in the *sigma*-only MO scheme.

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



$np_z + \Pi_z$



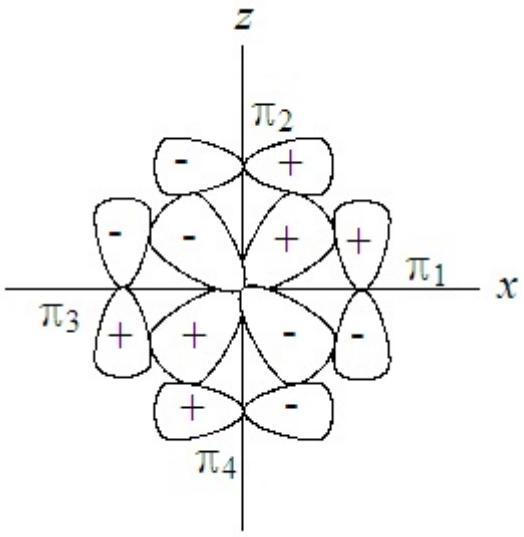
$np_z + \Sigma_z$

☞ 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

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

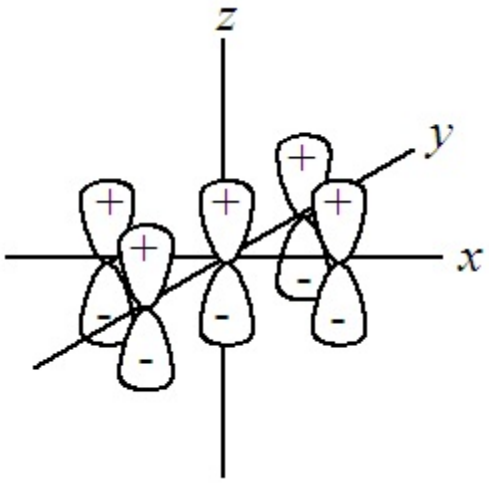


$$d_{xz} + \Pi_{xz}$$

Similar matches with the other two SALCs.

Virtually Nonbonding T_{1u} SALCs

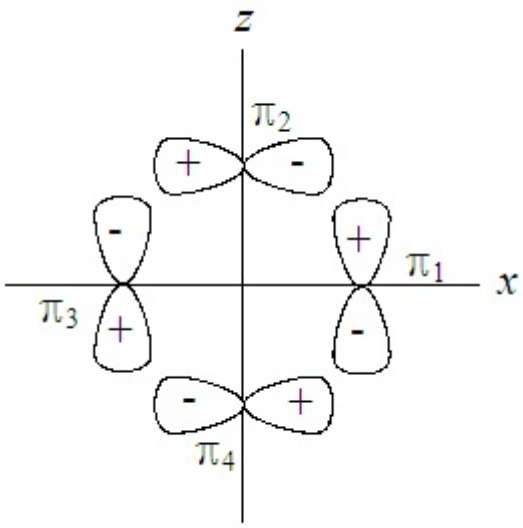
$$\Pi_z = \tfrac{1}{2}(\pi_1 - \pi_3 + \pi_5 - \pi_7)$$
$$\Pi_x = \tfrac{1}{2}(\pi_2 - \pi_4 + \pi_{10} - \pi_{12})$$
$$\Pi_y = \tfrac{1}{2}(\pi_6 - \pi_8 + \pi_9 - \pi_{11})$$



$$p_z + \Pi_z$$

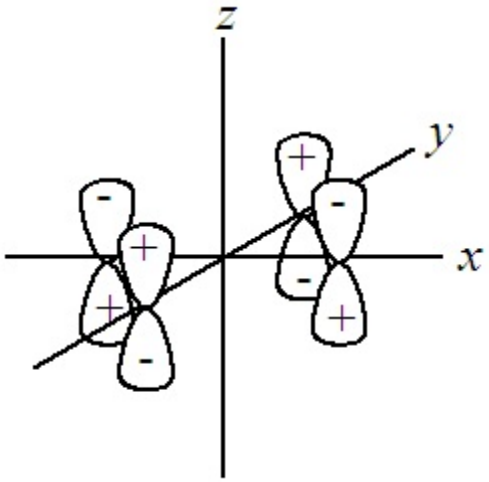
Similar matches with the other two SALCs.

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

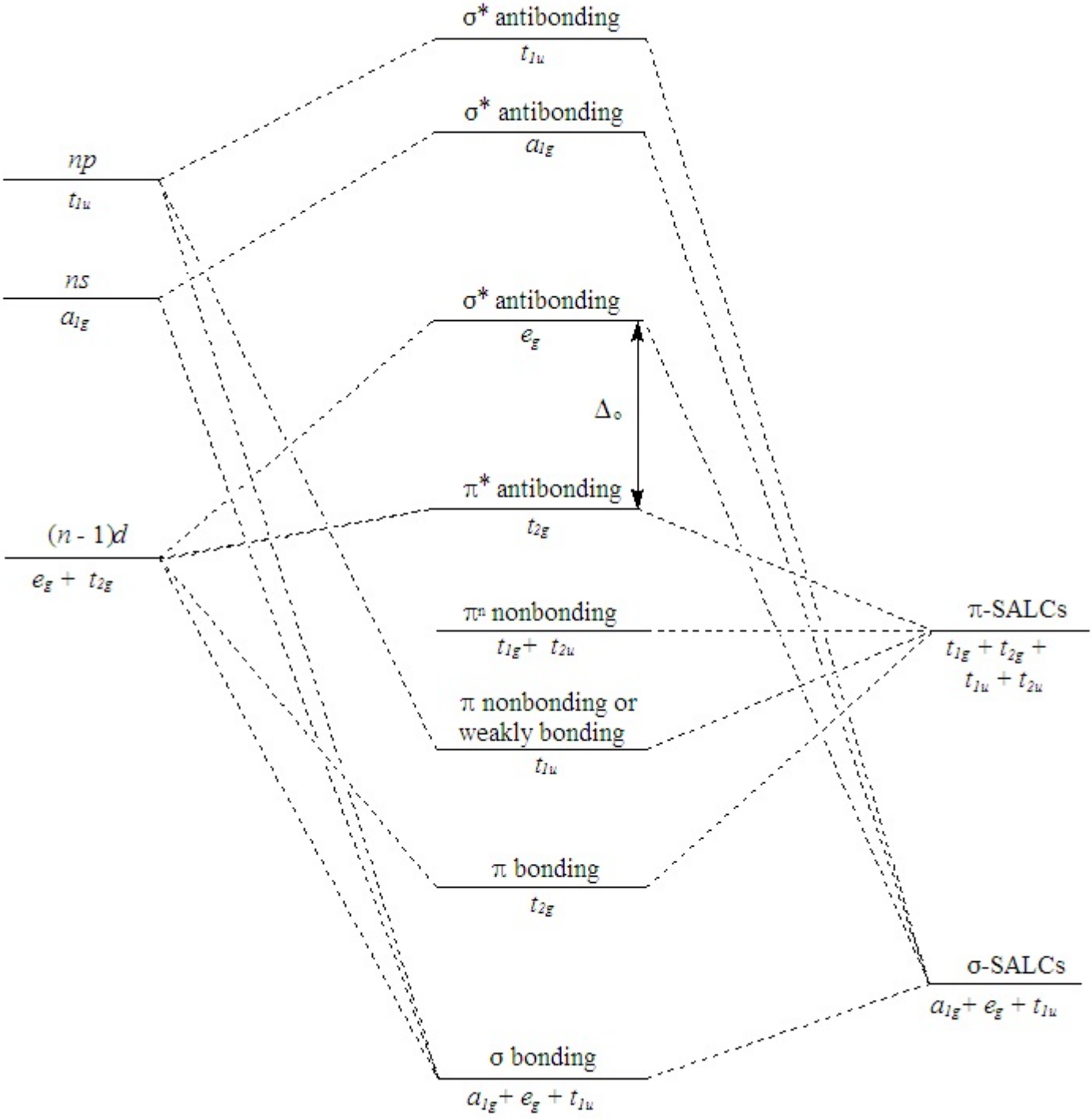
- The energy ordering and the nature of the MOs will be affected by the following factors:
  - Identity of the central metal ion
  - Identity of the ligands
  - Relative energies of the orbitals on metal and ligands
  - The nature and effectiveness of the *sigma* and *pi* orbital interactions
  - Electron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

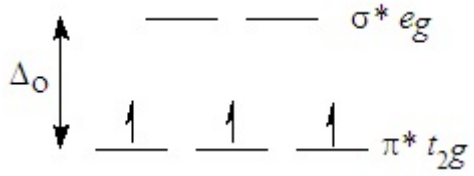
- Cr^{3+} ion has a d^3 configuration, and therefore supplies three electrons.

- 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} π* MOs, resulting in a configuration $(t_{2g}^*)^3$, equivalent to the CFT model's configuration t_{2g}^3.

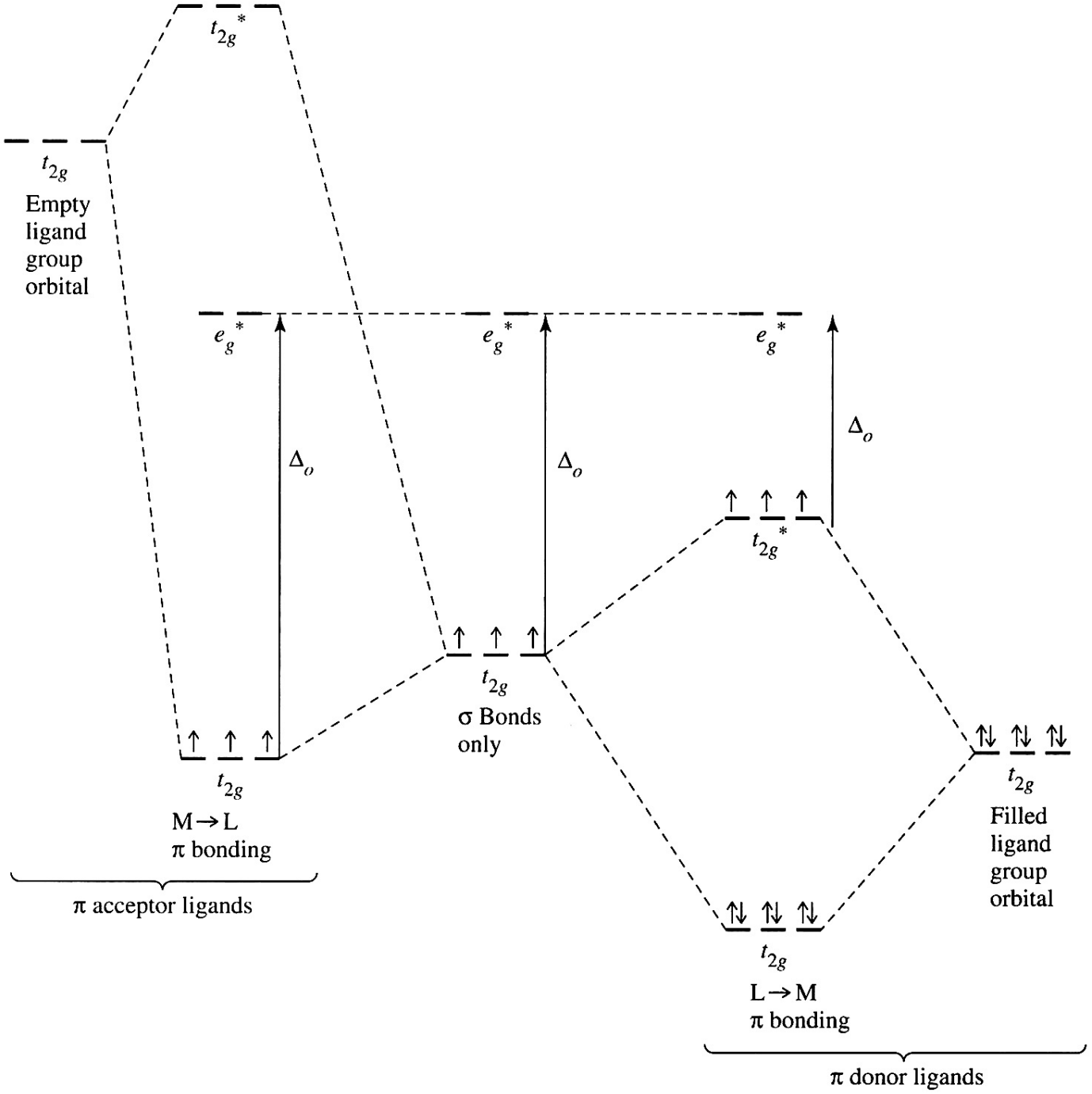


- Δ_o is defined as the energy gap between the *pi* antibonding t_{2g}* level and the *sigma* antibonding e_g* level.

- 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 Δ_o.
  - The relative abilities of a ligand to engage in *sigma* and *pi* bonding help determine its position in the spectrochemical series.

Effect of π Interactions on Δ_o

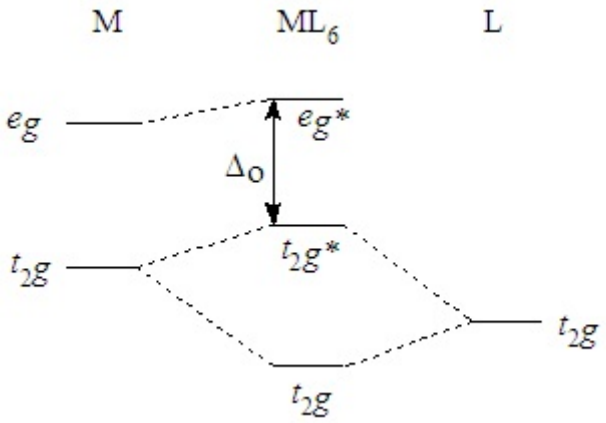
- The effect of π interactions on Δ_o depends upon the energies of the ligand MOs relative to metal *d* orbitals, and also on whether the ligand π orbitals are filled or empty.



Effect of π Interactions on Δ_o – L→M π Bonding

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

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

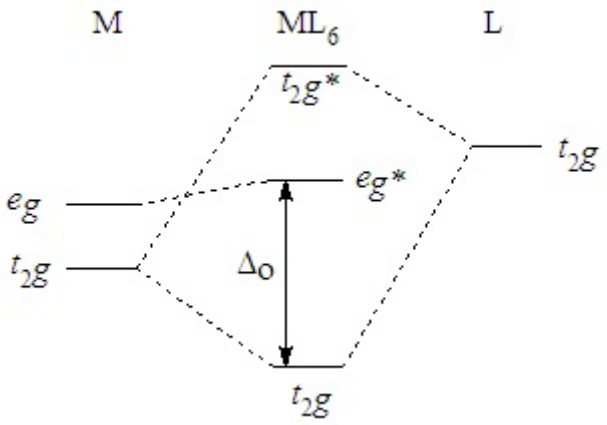


- As π interaction increases, t_{2g} bonding becomes more stable and t_{2g}^* is squeezed towards e_g^*, making Δ_o smaller.
  - This is probably the situation with monatomic filled-subshell ligands such as O^{2-}, F^-, etc.
  - This is described as ligand-to-metal (L→M) π bonding.

Effect of π Interactions on Δ_o – M→L π Bonding

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

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

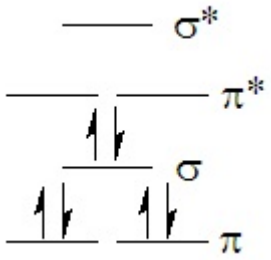


- As π interaction increases, t_{2g} π-bonding becomes more stable relative to e_g^* σ-antibonding, making Δ_o larger.
  - This is probably the situation with ligands such as PH_3 and AsH_3, which use empty *d* orbitals on the central atom for π interactions.

- When both empty and filled ligand π orbitals are involved in the bonding the effect on Δ_o is less predictable.

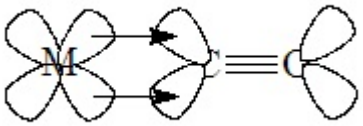
CO, CN^-, NO^+, N_2 Ligands

- CO, CN^-, NO^+, and N_2 are isoelectronic species that have both σ and π M–L interactions.
  - All have empty π* MOs.



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

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



- The back-bonding stabilizes the π bonding MOs of the complex, making large Δ_o.
  - CO, CN^-, NO^+, and N_2 are strong-field ligands.

- Increased electron density in the ligand π* MO weakens the C–O bond, causing a shift in the stretching vibration to lower frequency.

	CO	$Ni(CO)_4$	$Co(CO)_4^-$	$Fe(CO)_4^{2-}$
ν_{CO} (cm^{-1})	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_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

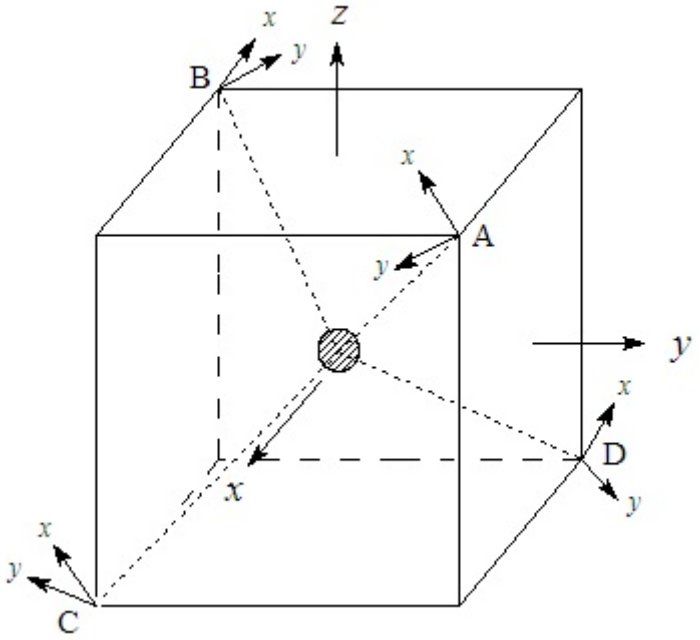
- Same as sigma SALCs of hydrogens in methane.

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

- 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 Γ_π.

- 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	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_π	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.

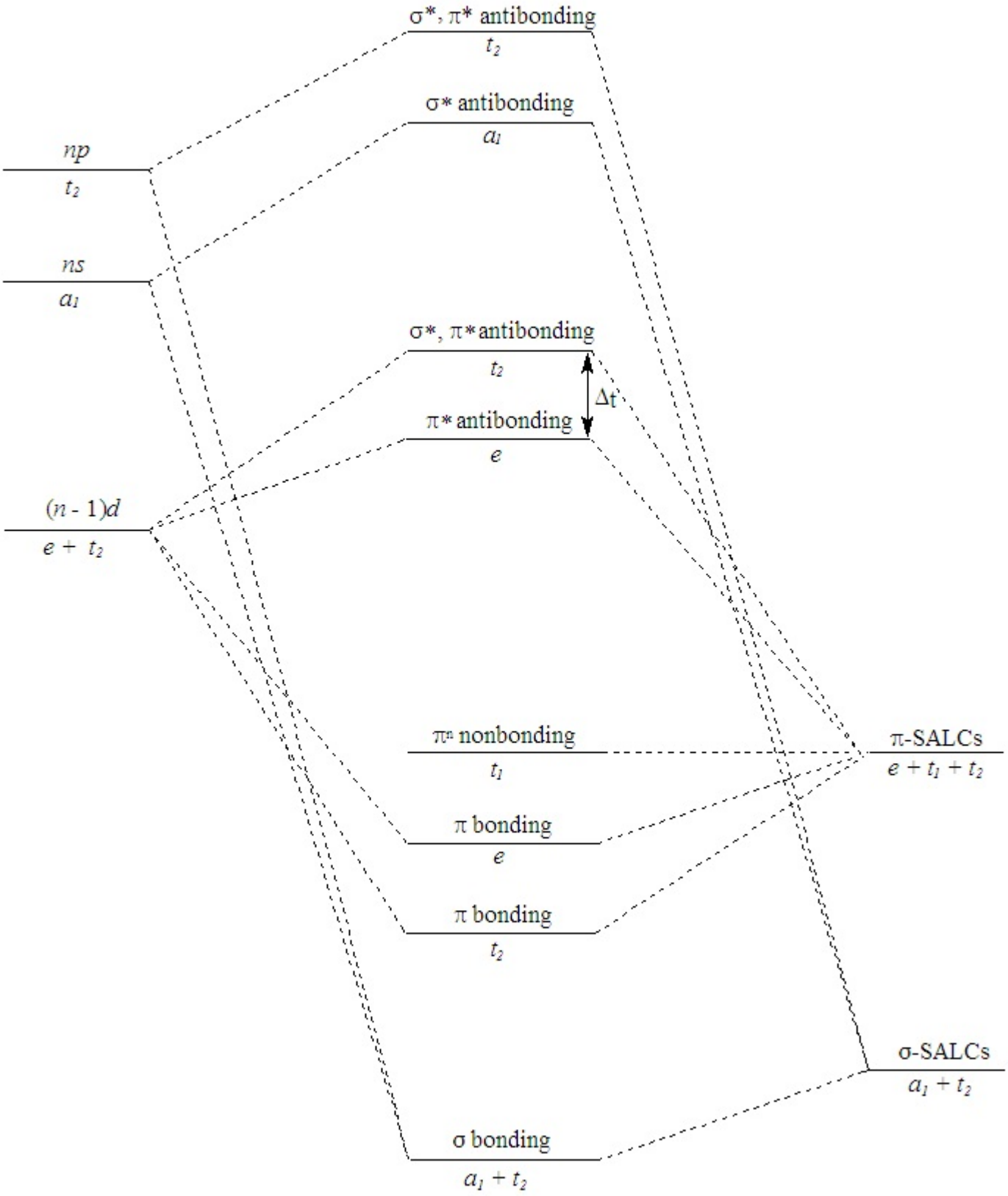
- The T_2 π-SALCs, like the T_2 σ-SALCs, can potentially form combinations with both t_2 (n - 1)d and np orbitals on the metal atom.
  - ☞ The π-MOs that are formed may involve some degree of *d-p* mixing.

- 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_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, Δ_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.