Free-Ion Terms to Ligand-field Terms

- Orbital term symbols for free atoms and ions are identical to symbols for irreducible representations in R_3.

  - The irreducible representations of R_3 include all possible degeneracies.

    ☞ There are no inherent symmetry restrictions on possible orbital degeneracies in R_3.

- In octahedral and tetrahedral crystal fields (O_h and T_d) the highest dimension irreducible representations are three-fold degenerate.

  ☞ For O_h and T_d complexes, free-ion terms with orbital degeneracies greater than three (*D*, *F*, *G*, ...) must split into new terms, each of which can have no higher than three-fold degeneracy.

  - In crystal fields of lesser symmetry (e.g., D_{4h}, D_3) free-ion orbital multiplicity terms with $(2L + 1) > 2$ must split as a result of the descent in symmetry from R_3 to the finite point group of the complex.

    ☞ Ligand-field terms can have no higher orbital degeneracy than allowed by the highest dimension irreducible representation of the complex's point group.

  - In any crystal field all the term symbols, including those that are not split, are redefined and newly designated with the appropriate Mulliken symbols of their corresponding irreducible representations in the point group of the complex.

Why Terms Split in a Ligand-field

- Lifting the degeneracy among the *d* orbitals can destroy the equivalences among microstates that give rise to a particular free-ion term.

  - Orbital assignments that were energetically equivalent in the free ion may now be quite distinct in the environment of the complex.

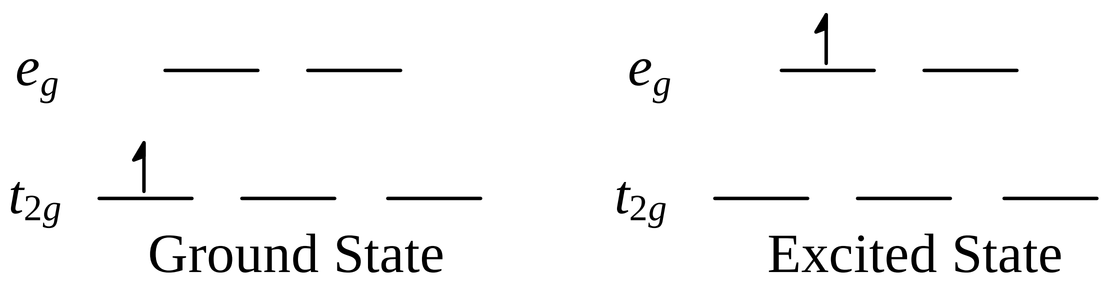
    - These differences result in new collections of equivalent microstates, each of which gives rise to a distinct *ligand-field term*.

    ☞ ***The total number of microstates for the configuration, as represented by D_t, remains the same.***

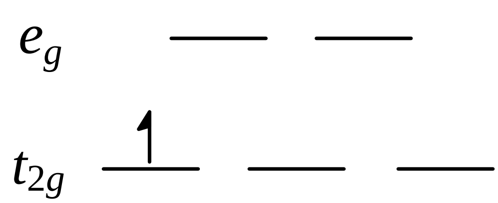
Example: Splitting of d^1 Terms in an O_h Field

- The 10 microstates for the free-ion configuration d^1 give rise to a ^2D term.

- In an octahedral field, the electron may have either the configuration t_{2g}^1 or e_g^1:



d^1 O_h Ground State Term



Ground State

- In the ground state, the electron can be in any of the three t_{2g} orbitals with either spin orientation ($m_s = \pm½$).
  - This makes six equivalent microstates.
  - There are three equivalent orbital assignments, so the overall orbital degeneracy (orbital multiplicity) is three.

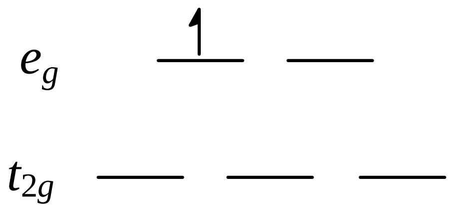
$$(2L + 1) = 3$$

  - There are only two overall spin orientations ($M_s = \pm½$), so the spin degeneracy (spin multiplicity) is two.

$$(2S + 1) = 2$$

☞ The resulting term is $^2T_{2g}$, in which the Mulliken symbol for the orbital term is appropriately three-fold degenerate.

d^1 O_h Excited State Term



Excited State

- In the excited state configuration $e_g^{\,1}$ the electron can be in either of the two e_g orbitals with either spin orientation ($m_s = \pm½$).
  - This makes four equivalent microstates.
  - There are two equivalent orbital assignments, so the overall orbital degeneracy (orbital multiplicity) is two.

$$(2L + 1) = 2$$

  - There are only two overall spin orientations ($M_s = \pm½$), so the spin degeneracy (spin multiplicity) is two.

$$(2S + 1) = 2$$

☞ The associated term is $^2\boldsymbol{E_g}$, in which the Mulliken symbol for the orbital term is two-fold degenerate.

Total Degeneracy, D_t, Remains Unchanged

- Note that the total degeneracy of each ligand-field term, equivalent to the number of microstates giving rise to it, is the product of its spin degeneracy times its orbital degeneracy.

$$D_t \text{ (term)} = (2L + 1)(2S + 1)$$

  - For $^2T_{2g}$ we have

$$D_t\,(^2T_{2g}) = (2)(3) = 6$$

  - For ^2E_g we have

$$D_t\,(E_g) = (2)(2) = 4$$

☞ The sum of total degeneracies of the ligand-field terms is equivalent to D_t for the free-ion configuration d^1.

$$D_t\,(d^1) = D_t\,(^2T_{2g}) + D_t\,(^2E_g) = 6 + 4 = 10$$

Determining Ligand-Field Terms from Free-ion Terms

- The fate of any free-ion term in the point group of a complex can be determined by applying equations by which the characters for an irreducible representation in R_3 can be calculated:

$$\chi(E) = 2j + 1$$

$$\chi[C(\theta)] = \frac{\sin(j + 1/2)\theta}{\sin\theta/2}$$

$$\chi(i) = \pm(2j + 1)$$

$$\chi[S(\theta)] = \pm\frac{\sin(j + 1/2)(\theta + \pi)}{\sin(\theta + \pi)/2}$$

$$\chi(\sigma) = \pm\sin(j + 1/2)\pi$$

Making Free-ion Terms the Basis for a Representation

- It is possible to apply these equations to both the spin and orbital terms (*S* and *L* states), but the field does not interact directly on the electron spin in a chemical environment such as a complex ion.

  - The new ligand-field terms will retain the original spin multiplicities of the free-ion terms from which they originate.

  - We only apply these equations to the *L* state of a free-ion term to determine the identities of the terms that result from splitting in the ligand field.

- In the last three equations with variable sign (±), the positive sign is used with *gerade* functions and the negative sign is used with *ungerade* functions.

  ☞ **We will be concerned solely with terms arising from configurations of *d* electrons, which are inherently *gerade*. Therefore we will choose the positive expression in all cases.**

  - Nonetheless, in noncentrosymmetric point groups (e.g., T_d, D_{3h}) the resulting Mulliken symbol for the new state will not have a *g* subscript notation, which would be inappropriate in such groups.

{If terms arising from *p* or *f* configurations are to be considered, use the negative sign equations, because states arising from these are inherently *ungerade*.}

Splitting of d^n Free-ion Terms *S*, *P*, *D*, and *F* in O_h

- ***S* state**, for which $L = 0$, is nondegenerate.

  - As with an *s* orbital, it has no angular dependence and no orientation in space.

  - Without using the equations, we conclude that ***in any point group*** an *S* term will not be split and will bear the Mulliken symbol for the totally symmetric representation.

☞ **In O_h, $S \rightarrow A_{1g}$**

Splitting of d^n Free-ion Terms *S*, *P*, *D*, and *F* in O_h

- ***P* state**, for which $L = 1$, is triply degenerate.

  - Substituting $L = 1$ into the equations for the operations of O_h gives the following representation.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_P	3	0	-1	1	-1	3	1	0	-1	-1

  - Inspection of the character table shows that $\Gamma_P \equiv T_{1g}$.

☞ **In O_h, $P \rightarrow T_{1g}$**

  - A *P* term is not split, but becomes a triply degenerate T_{1g} term.

{Recall that the three-fold degenerate *p* orbitals transform as T_{1u} in O_h, but as we now see a *P* state transforms as T_{1g}. The transformations are different because the *p* orbitals are inherently *ungerade*, but the *P* state arising from a *d* configuration is inherently *gerade*.}

Splitting of d^n Free-ion Terms *S*, *P*, *D*, and *F* in O_h

- ***D* state**, for which $L = 2$, is five-fold degenerate.

  - Substituting $L = 2$ into the equations for the operations of O_h gives the following representation.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_D	5	-1	1	-1	1	5	-1	-1	1	1

  - This is identical to the reducible representation we obtained for *d* orbitals.

☞ **In O_h, $D \rightarrow E_g + T_{2g}$**

  - The five-fold degeneracy of the *D* free-ion term is lifted to become a doubly degenerate term and a triply degenerate term because of the restrictions on maximum degeneracy in O_h.

Splitting of d^n Free-ion Terms S, P, D, and F in O_h

- ***F* state**, for which $L = 3$, is seven-fold degenerate.
  - Substituting $L = 3$ into the equations for the operations of O_h gives the following representation.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_F	7	1	-1	-1	-1	7	-1	1	-1	-1

  - This reduces as $\Gamma_F = A_{2g} + T_{1g} + T_{2g}$.

☞ **In O_h, $F \rightarrow A_{2g} + T_{1g} + T_{2g}$**

Splitting of Higher Terms

- The splitting of other states (*G*, *H*, *I*, etc.) can be determined in similar manner, giving the following results:

Free-ion Term	Terms in O_h
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

Example: Splitting of d^2 Free-Ion Terms in O_h

- The free-ion terms for the configuration nd^2, in order of increasing energy are

$$^3F < {}^1D < {}^3P < {}^1G < {}^1S$$

  - Each of these terms will split into the ligand filed terms we have just identified.

Free-ion terms	^3F	^1D	^3P	^1G	^1S
Octahedral terms	$^3A_{2g}$	^1E_g	$^3T_{1g}$	$^1A_{1g}$	$^1A_{1g}$
	$^3T_{1g}$	$^1T_{2g}$		^1E_g	
	$^3T_{2g}$			$^1T_{1g}$	
				$^1T_{2g}$	
Microstates	21	5	9	9	1

$$D_t = 21 + 5 + 9 + 9 + 1 = 45$$

Ligand-Field Terms in Other Fields

- The splittings of free-ion terms and the Mulliken symbols for the ligand-field terms in other point groups can be obtained in similar manner by making them bases for representations in the appropriate point group.
  - It is usually more efficient to use the correlation tables
  - For example, inspection of the correlation table for O_h and T_d shows that the splittings are identical in both groups, except for the omission of the subscript *g* for the tetrahedral states.
  - Correlations with other groups (e.g., D_{4h}, D_3, D_{2d}) are not as trivial, but are equally straightforward.

Correlation Diagrams for Ligand Field Splitting

☞ What is the energy order of the ligand field terms?

☞ How will the energies of the terms change with changing Δ_o?

- Group theory alone, cannot provide quantitative answers.

- It is possible to address the problem at least qualitatively with a *correlation diagram*, which shows how the energies of terms change as a function of the ligand field strength, measured as Δ_o.

- To construct the correlation diagram, we look at two extremes:

  - **Left side:** A ***weak field***, just strong enough to lift the R_3 free-ion term degeneracies.

    - On the left side of the diagram we show the energies of the free-ion terms and the Mulliken symbols for the terms into which they are split in a weak octahedral field.

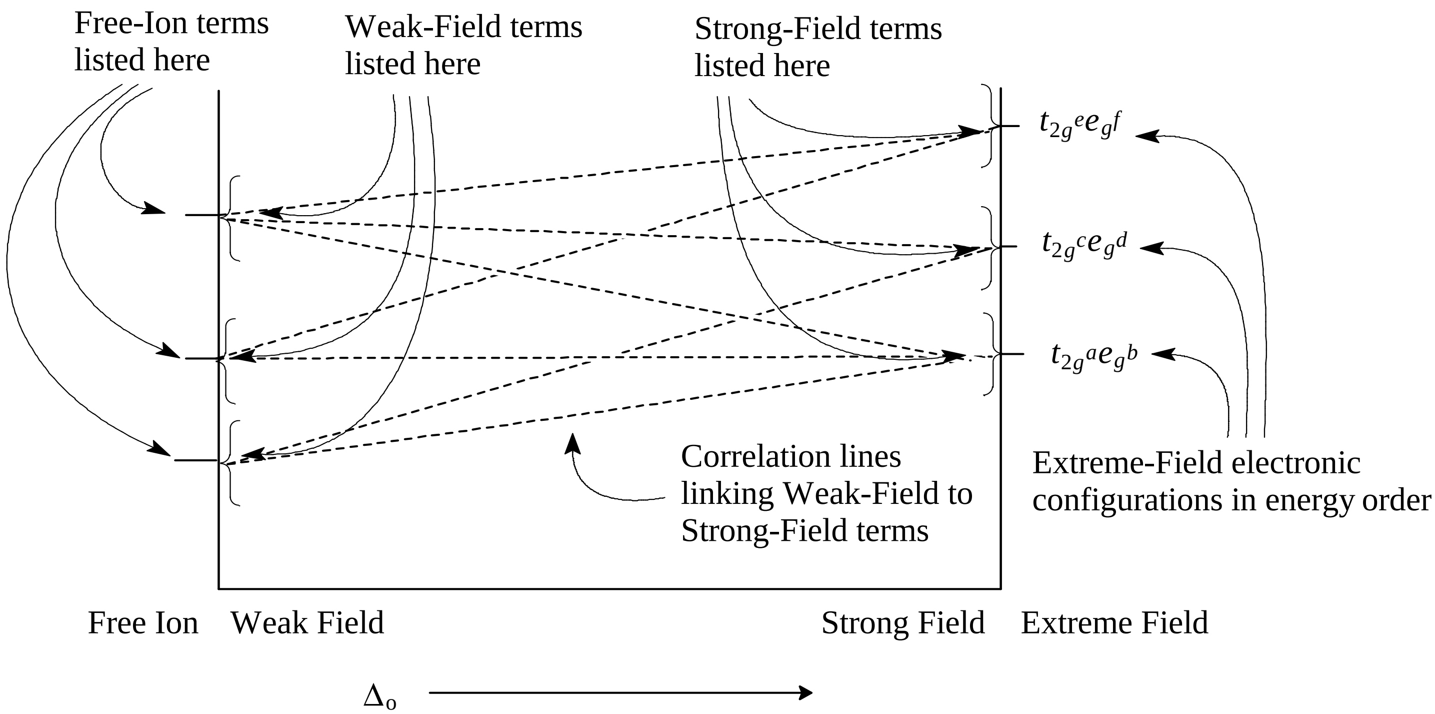
  - **Right side:** A ***hypothetical extremely strong field***.

    - At the limit of an extremely large Δ_o separation between t_{2g} and e_g orbitals, we assume that interactions between electrons in separate orbitals are negligible.

    - At this limit we can assess the energy order of the possible electronic configurations for the ground state and all excited states.

    - We can then identify the terms that will emerge from each of these configurations in a slightly less strong field, where electronic interactions begin to be felt.

Layout of a Term Splitting Correlation Diagram



Constructing A Correlation Diagram for d^2

☞ The job of constructing the diagram amounts to determining the correlations between terms in the weak field and the terms in the strong field.

- General Approach - The Method of Descending Symmetry (Bethe).
  - Rigorous, generally applicable, but tedious.
- We will take a somewhat less systematic approach to d^2, which will illustrate the principles.
  - Concentrate primarily on identifying the triplet states arising from the allowed d^2 configurations in the strong-field case and correlate them with the appropriate terms for the weak field case.
    - These terms have the same spin multiplicity as the ground state term for d^2 (^3F).
    - These are of primary importance to understanding the visible spectra of transition metal complexes.
    - Also, taking this approach in this case will reveal the correlations for all the terms, both singlets and triplets.

Weak Field Splitting of d^2 Terms
(Left Side of Correlation Diagram)

- The free-ion terms for nd^2 are listed below in order of increasing energy (left to right):

Free-ion terms	^3F	^1D	^3P	^1G	^1S
Octahedral terms	$^3A_{2g}$	^1E_g	$^3T_{1g}$	$^1A_{1g}$	$^1A_{1g}$
(weak field)	$^3T_{1g}$	$^1T_{2g}$		^1E_g	
	$^3T_{2g}$			$^1T_{1g}$	
				$^1T_{2g}$	

- These free-ion terms and the ligand-field terms into which they split will be listed in order of increasing energy of the free-ion terms, running up the left side of the correlation diagram we will construct .

Principles for Correlating Weak-Field Terms to Strong-Field Terms

1. Only terms of the same spin state are linked in both weak and strong fields.

   Example: A triplet term will not correlate to a singlet or vice versa.

2. A term does not change its orbital identity as a result of the field strength.

   Example: A T_{1g} term in the weak field remains a T_{1g} term in the stronger field.

3. The ***Noncrossing Rule*** is observed: Correlation lines for states of the same symmetry and same multiplicity do not cross, but rather repel one another, thereby increasing their relative energy separation beyond a certain minimum as field strength increases.

   Example: The ${}^3T_{1g}$ from ${}^3F$ and the ${}^3T_{1g}$ from ${}^3P$ will not have crossing correlation lines when linking the weak field side to the strong field side of the diagram.

Extremely Strong Field States

- At this hypothetical extreme we can have the following three configurations:

e_g	___ ___	↑ ___	↑ ↑
t_{2g}	↑ ↑ ___	↑ ___ ___	___ ___ ___

  - In the absence of interelectronic interactions, we can assume that the ground state is t_{2g}^{2}.

  - The configuration $t_{2g}^{1}e_g^{1}$ puts one electron in an orbital that lies Δ_o higher, so the energy of this state lies higher by Δ_o.

  - The configuration e_g^{2} promotes both electrons by Δ_o, so the energy of this state is higher than the ground state configuration by $2\Delta_o$.

Terms in a Slightly Less Strong Field

- If we now relax the field a little, so that the electrons just begin to interact, each of the strong-field configurations will give rise to a number of energy states, depending upon how electrons with specific spins occupy specific orbitals.

  - Each of these new terms is uniquely associated with a collection of microstates.

- The total degeneracy over all new states must be the same as for d^2; i.e.,

$$D_t = 45$$

  - By our expression for D_t ,

$$D_t(t_{2g}^2) = 15$$

    There are 15 ways of arranging the two electrons by individual spins and orbital assignments within the t_{2g} orbitals.

    - Some of these microstates will have the electrons with the same spin and some will have the electrons with opposite spins.

      ☞ Both singlet and triplet terms arise from this configuration.

  - For the configuration e_g^2,

$$D_t(e_g^2) = 6$$

    There are six ways of arranging the two electrons in the two e_g orbitals, each resulting in a microstate.

    ☞ Again, both singlet and triplet states will arise from this configuration.

Terms in a Slightly Less Strong Field

- The configuration $t_{2g}^1 e_g^1$ involves two nonequivalent electrons.

  - There are six ways of arranging one electron in the three t_{2g} orbitals (three possible orbital assignments with two possible spin orientations); i.e.,

    $$D_t(t_{2g}^1) = 6$$

  - There are four ways of arranging one electron in the two e_g orbitals (two possible orbital assignments with two possible spin orientations); i.e.,

    $$D_t(e_g^1) = 4$$

  - The two electrons are in separate degenerate sets of orbitals, so the possible microstates are not restricted by the Pauli exclusion principle.

    $$D_t(t_{2g}^1 e_g^1) = D_t(t_{2g}^1) \times D_t(e_g^1) = 6 \times 4 = 24$$

    ☞ Here, too, we can have both singlet and triplet states arising from the configuration.

- Altogether these three configurations account for 45 microstates, equal to the total degeneracy for a d^2 configuration.

$$D_t(d^2) = D_t(t_{2g}^2) + D_t(e_g^2) + D_t(t_{2g}^1 e_g^1) = 15 + 6 + 24 = 45$$

Orbital Term Symbols for The Slightly Less Strong Field

- We need to know the term symbols arising from these 45 microstates in the slightly relaxed strong-field case.

- We can determine the Mulliken symbols for the orbital part of the term symbols by taking the direct products of the irreducible representations of the individual electrons in the three configurations.

- For the ground state configuration t_{2g}^2 we take the direct product $t_{2g} \times t_{2g}$, which yields the following representation:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma(t_{2g}^2)$	9	0	1	1	1	9	1	0	1	1

$$\Gamma(t_{2g}^2) = A_{1g} + E_g + T_{1g} + T_{2g}$$

☞ The orbital terms arising from t_{2g}^2 in a strong but not extreme field are $A_{1g} + E_g + T_{1g} + T_{2g}$.

Spin States for the t_{2g}^2 Terms

- We also need to know the spin multiplicities of these terms to make the correlations with the weak-field terms.

  - We can begin to sort out the spin multiplicities by recalling that the total degeneracy of a configuration is equal to the sum of the products of the spin degeneracies times the orbital degeneracies over all terms.

    - Here, $D_t = 15$, so we may write for the terms $A_{1g} + E_g + T_{1g} + T_{2g}$

$$(a)(1) + (b)(2) + (c)(3) + (d)(3) = 15$$

      where the unknown coefficients are either 1 or 3.

    - This is satisfied if either T_{1g} or T_{2g} is a triplet and the other two terms are singlets, or if both A_{1g} and E_g are triplets and the other two terms are singlets.

      ☞ At this point any one of the following assignments is possible:

$$^1A_{1g} + {}^1E_g + {}^1T_{1g} + {}^3T_{2g}$$
$$^1A_{1g} + {}^1E_g + {}^3T_{1g} + {}^1T_{2g}$$
$$^3A_{1g} + {}^3E_g + {}^1T_{1g} + {}^1T_{2g}$$

Narrowing the Possible Spin States for $A_{1g} + E_g + T_{1g} + T_{2g}$

- We can narrow the choices slightly by considering the possible orbital arrangements of two unpaired electrons (a triplet state) for the configuration t_{2g}^2:

t_{2g} ↿ ↿ ___ ↿ ___ ↿ ___ ↿ ↿

  - There are three orbital arrangements for two unpaired electrons, so the triplet state must have a triply degenerate orbital term (either $^3T_{1g}$ or $^3T_{2g}$ in this case).

    ☞ This means we have either

$$^1A_{1g} + {}^1E_g + {}^1T_{1g} + {}^3T_{2g}$$
$$^1A_{1g} + {}^1E_g + {}^3T_{1g} + {}^1T_{2g}$$

    i.e., we can rule out the third listed choice.

  - Both remaining assignments satisfy the total degeneracy of the configuration, so we will need to gather more information before deciding which of these is correct.

Orbital Term Symbols for e_g^2

- In similar manner, to determine the orbital terms for the configuration e_g^2 we take the direct product $e_g \times e_g$ and obtain the representation

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma(e_g^2)$	4	1	0	0	4	4	0	1	4	0

$$\Gamma(e_g^2) = A_{1g} + A_{2g} + E_g$$

☞ The orbital terms arising from e_g^2 in a strong but not extreme field are $A_{1g} + A_{2g} + E_g$.

Narrowing the Possible Spin States for e_g^2 Terms

- The total degeneracy for this configuration is 6, so

$$(a)(1) + (b)(1) + (c)(2) = 6$$

  - Clearly $c \neq 3$, so either $a = 3$ or $b = 3$ and the other two coefficients are 1.

  - Therefore we have either

$$^3A_{1g} + {}^1A_{2g} + {}^1E_g$$
$$^1A_{1g} + {}^3A_{2g} + {}^1E_g$$

- We can come to the same conclusion by looking at how we could arrange two unpaired electrons in two degenerate orbitals:

$$e_g \ \underline{\ \ \uparrow\ \ } \quad \underline{\ \ \uparrow\ \ }$$

  - There is only one choice, so the orbital term for the triplet state must be nondegenerate (either A_{1g} or A_{2g} in this case).

  - Again, we will need to obtain other information before deciding which possible assignment is correct.

Orbital Term Symbols and Spin States for $t_{2g}^1e_g^1$

- The orbital terms for $t_{2g}^1e_g^1$ are found by taking the direct product $t_{2g} \times e_g$:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma(t_{2g}^1e_g^1)$	6	0	0	0	-2	6	0	0	-2	0

$$\Gamma(t_{2g}^1e_g^1) = T_{1g} + T_{2g}$$

☞ The orbital terms arising from $t_{2g}^1e_g^1$ in a strong but not extreme field are $T_{1g} + T_{2g}$.

- The electrons in this configuration are unrestricted by the Pauli exclusion principle and may have the same or opposite spins with all possible orbital assignments.

  ○ This means that both terms occur as both singlets and triplets.

  ○ The total degeneracy for $t_{2g}^1e_g^1$ is $D_t = 24$, which is uniquely satisfied by the assignment

$$^1T_{1g} + {}^1T_{2g} + {}^3T_{1g} + {}^3T_{2g}$$

Beginning to Construct the Correlation Diagram

- Although we have not unambiguously decided all the spin multiplicities we can proceed to make the correlations.
    - At this point the terms on the weak field side (left) and strong field side (right) have been identified, and some information about the possible spin states of the strong field terms has been obtained.
    - Proceeding with the correlations will actually help determine the correct spin states for the strong field terms.

Template for the Correlation Diagram