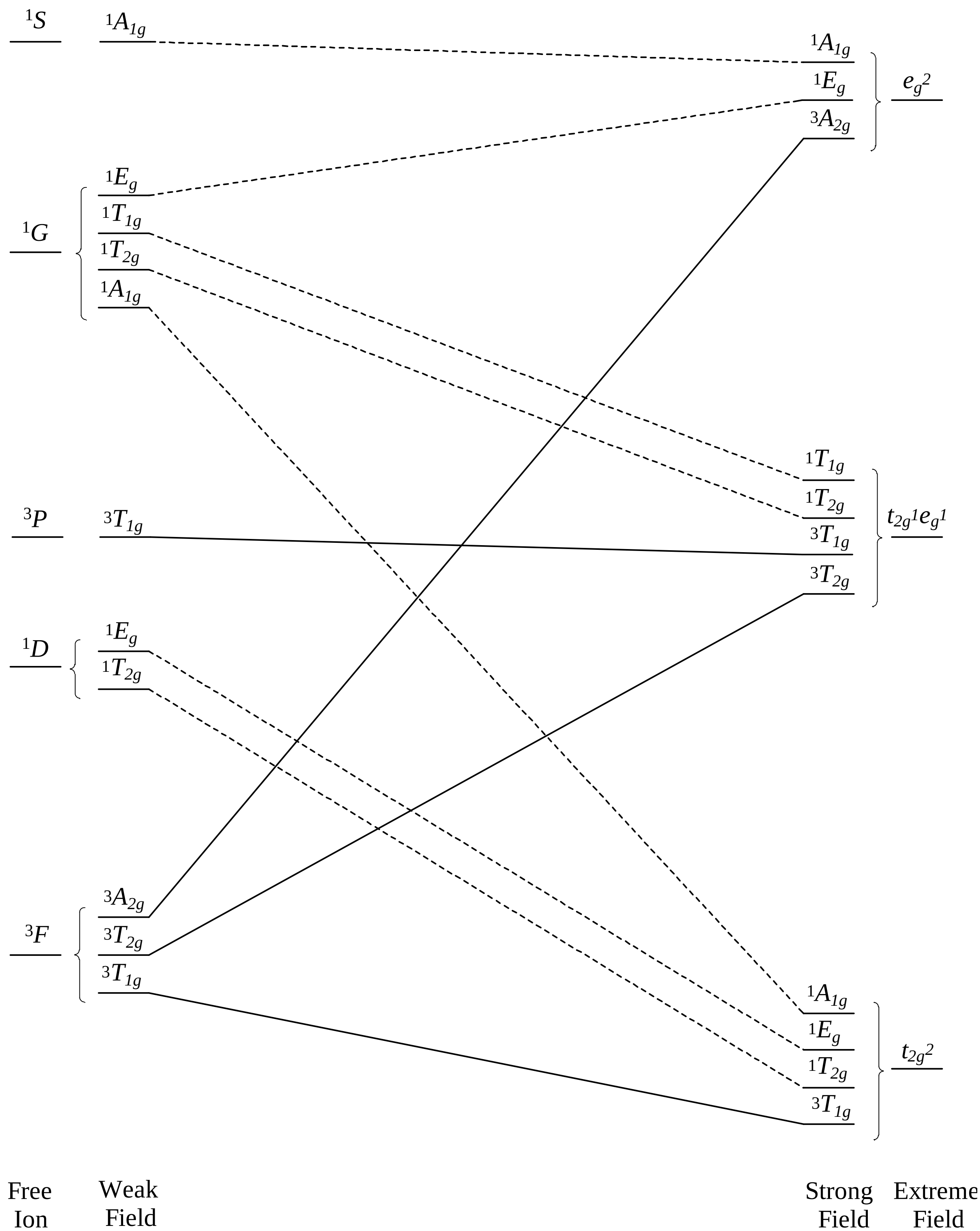
d^2 Correlation Diagram



Other Configurations and Other Fields

- In principle, we can construct the correlation diagram for any d^n configuration in an octahedral or other field by the Bethe's method of descending symmetry or similar *de novo* methods.

  - As the number of microstates and terms increases with the number of electrons, the labor of constructing the correlation diagrams "from scratch" becomes considerably more onerous.

  - Fortunately, some general relationships between configurations, terms, and ligand environments minimize the needed effort.

Ligand Field Splitting for d^n and d^{10-n} Terms

- Free-ion terms for a configuration d^n and a configuration d^{10-n} are the same.

  - Each free-ion term splits into a specific collection of terms in any ligand field.

    ☞ The splitting of terms for a configuration d^n is identical to that for the configuration d^{10-n}.

- However, ***the order of splitting of a given d^n term will show the reverse pattern of that of a d^{10-n} configuration in the same ligand field.***

  - The same ligand-field term that becomes more stable (moves to lower energy) for a d^n ion will become less stable (moves to higher energy) for a d^{10-n} ion as Δ_o changes.

Term Splitting of d^1 and d^9
d^1 Correlation Diagram

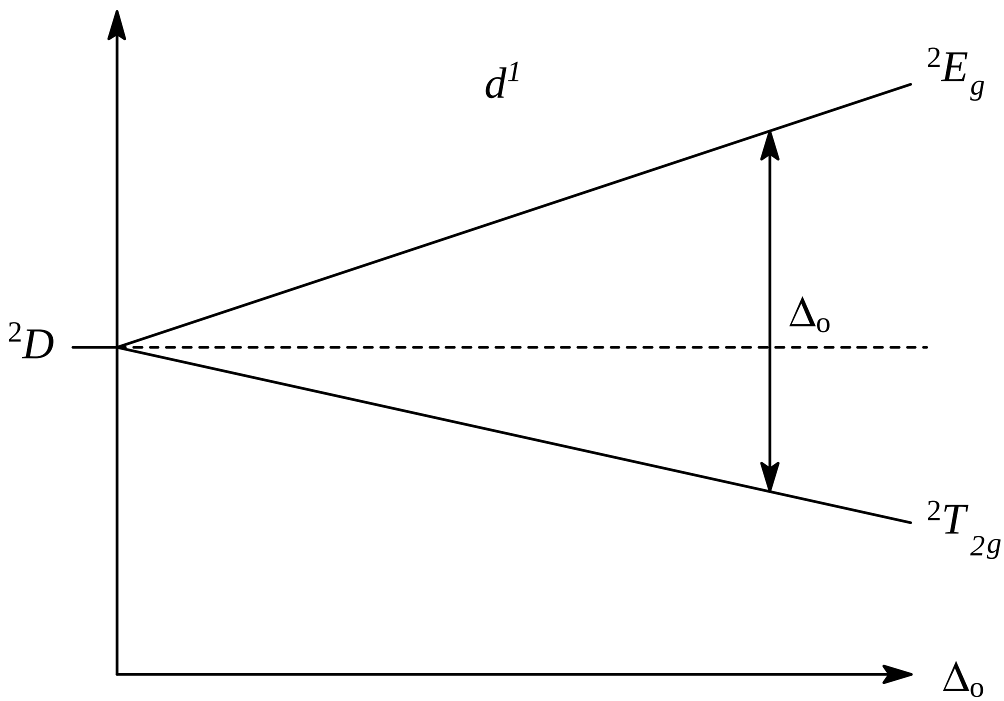
- Both configurations give rise to a ^2D free-ion term, which is split into ^2E_g and $^2T_{2g}$ terms in an octahedral field.

- In the d^1 case, the two terms in the octahedral field arise from the following configurations

t_{2g}^1 ground state = $^2T_{2g}$ | e_g^1 excited state = ^2E_g

- As the Δ_o gap between t_{2g} and e_g orbitals increases with increasing field strength the $^2T_{2g}$ term will become more stable and the ^2E_g term will become less stable.
  - Thus, the separation between the two states will increase.
  - The separation is numerically equal to Δ_o, the magnitude of the field.
  - Relative to the energy of the ^2D free-ion term, the $^2T_{2g}$ term will be stabilized by $-(2/5)\Delta_o$ and the ^2E_g term will be destabilized by $+(3/5)\Delta_o$.

d^1 Correlation Diagram



Term Splitting of d^1 and d^9
d^9 Correlation Diagram

- The same terms will arise from the ^2D free-ion term of a d^9 configuration, but they now correspond to the following two configurations in the octahedral field:

e_g	●●	●○		●●	●●	
t_{2g}	●●	●●	●●	●●	●●	●○

$t_{2g}^6 e_g^3$ — ground state = ^2E_g

$t_{2g}^5 e_g^4$ — excited state = $^2T_{2g}$

(◦ = hole = absence of an electron in an orbital)

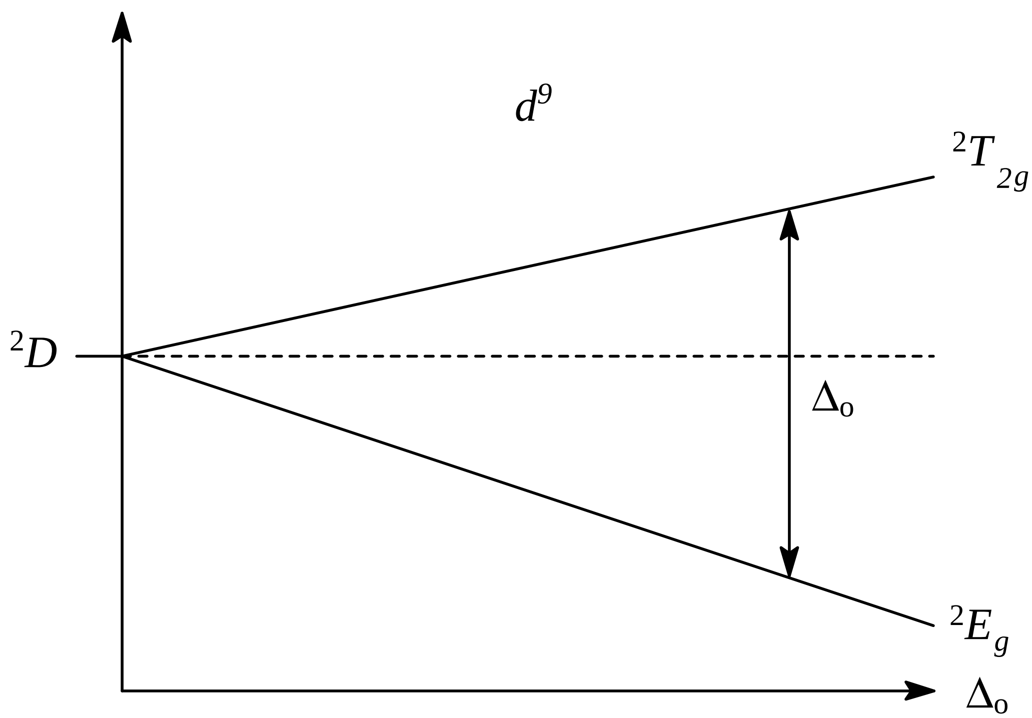
- ○ Using the hole as a marker, note that the ground state $t_{2g}^6e_g^3$ configuration consists of two equivalent orbital assignments and therefore must correspond to the ^2E_g term.

- ○ Likewise, the three possible orbital assignments for the hole in the $t_{2g}^5e_g^4$ configuration show that it gives rise to the $^2T_{2g}$ term.

☞ Thus, the energy ordering of the terms for d^9 is the reverse of the d^1 case.

- ○ For the d^9 (O_h) case the ^2E_g term is stabilized by $-(3/5)\Delta_o$ and the $^2T_{2g}$ term is destabilized by $+(2/5)\Delta_o$.

d^9 Correlation Diagram



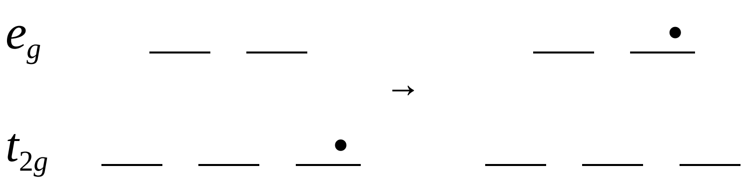
Hole Formalism

- The relationship between d^{n} and d^{10-n} term splittings in the same symmetry ligand field is sometimes called the *hole formalism*.

  - The name comes from seeing d^{n} as a configuration of n electrons and d^{10-n} as a configuration of n positive holes (equivalent to positrons).

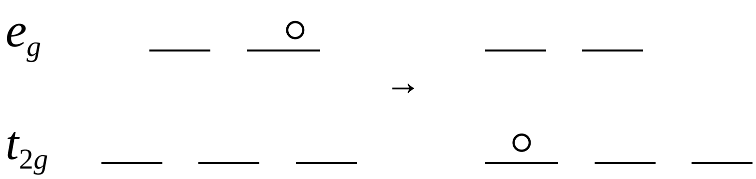
  - A configuration of n electrons will interact with a ligand field in the same way as a configuration of n positrons, except that repulsions in the former case become attractions in the latter case.

Example: For a d^{1} ion in an octahedral field a transition from the ground state to the excited states involves promoting the electron by Δ_o.



electron promotion

The same kind of transition for a d^{9} ion involves demoting the hole by Δ_o.



hole demotion

- The correlation diagram for d^{10-n} can be obtained by reversing the order of the sets of terms for the various $t_{2g}e_g$ configurations on the strong field side of the d^{n} diagram, relabeling for the appropriate d^{10-n} configurations, and redrawing the connecting lines, paying attention to the noncrossing rule.

Relationship Between Octahedral and Tetrahedral Fields

- Ligand-field term symbols for the states in a tetrahedral field arising from any d^n free-ion term are the same as those in an octahedral field, except the labels for the tetrahedral terms omit the subscript *g* notation.

- The energies of the new terms in the tetrahedral field have an inverted order.

  - Analogous to the splitting of *d* orbitals into *e* and t_2 levels in a tetrahedral field, which is the inverse of the splitting into t_{2g} and e_g levels in an octahedral field.

  - The tetrahedral and octahedral fields have similar but opposite effects on the *d* orbitals.

    - The same is true for the terms arising from d^n configurations.

Relationship Between Octahedral and Tetrahedral Correlation Diagrams

- The correlation diagram for d^n (T_d) can be obtained by reversing the order of the sets of terms for the various $t_{2g}e_g$ configurations on the strong field side of the d^n (O_h) diagram, relabeling for the appropriate d^n tetrahedral configurations, omitting the subscript g notations from all terms, and redrawing the connecting lines, paying attention to the noncrossing rule.

  - This is essentially the same process we have seen for configurations related by hole formalism.

  - The correlation diagram for d^n (T_d) is qualitatively the same as that for d^{10-n} (O_h), except for minor changes in labels of configurations and term symbols.

☞ For example, the d^2 (O_h) correlation shown is essentially the same as the correlation for d^8 (T_d).

☞ The d^8 (O_h) correlation shown is essentially the same as the correlation for d^2 (T_d).

Tanabe-Sugano Diagrams

- Most chemists refer to a more detailed set of semi-empirical diagrams for octahedral complexes, originally developed by Yukito Tanabe and Satoru Sugano in 1954.

  - A complete set of these diagrams for octahedral complexes of metal ions with the configurations d^2 through d^8 is shown in Appendix D.

- Tanabe-Sugano diagrams plot term energy versus field strength.

  - Energies of all states are plotted relative to the energy of the ground state term; i.e., the ground state energy forms the abscissa of the plot.

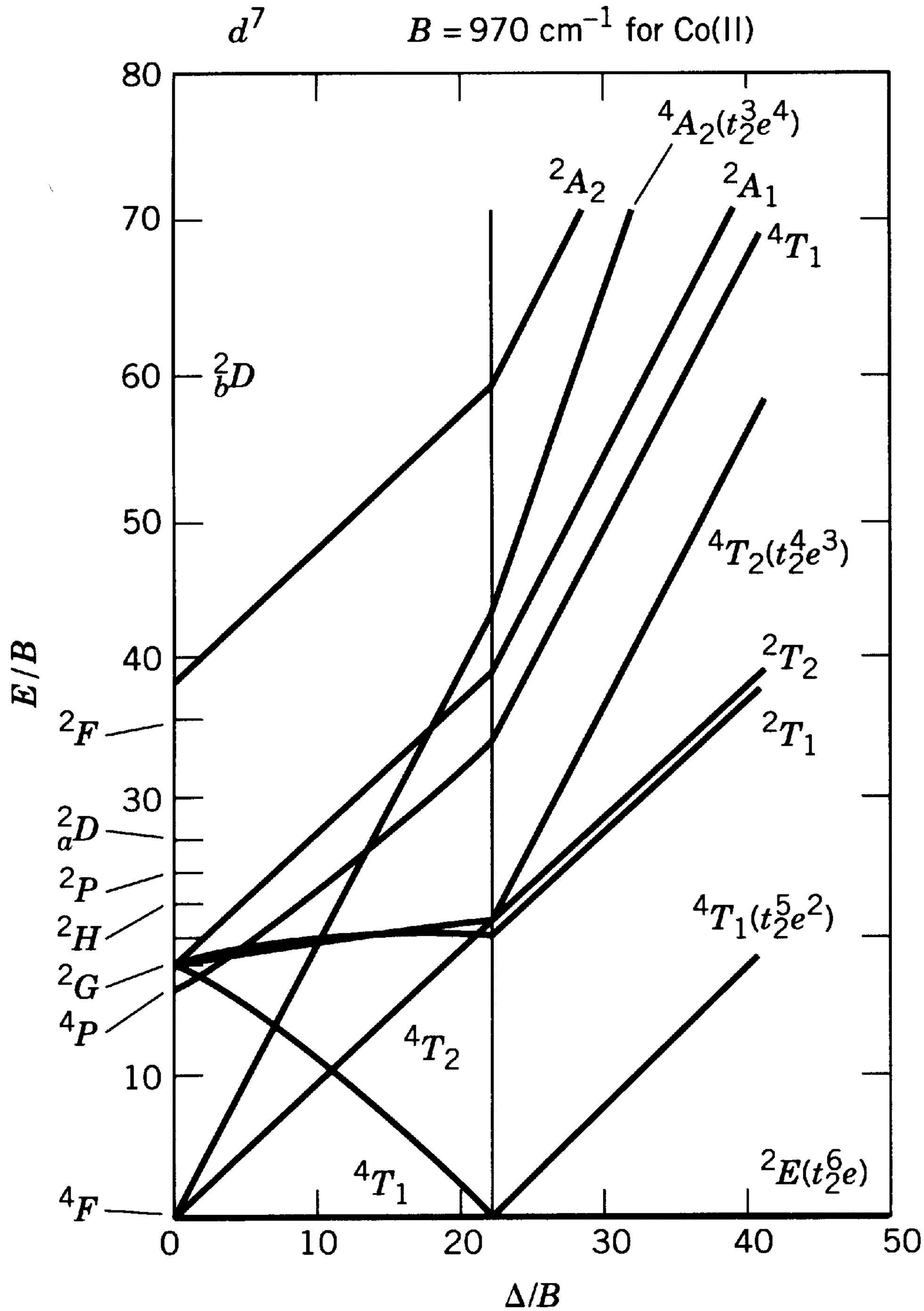
  - Term energies and field strengths are expressed as the variables E/B and Δ/B, respectively, where B is the *Racah parameter*.

    - The Racah parameter is a measure of the interelectronic repulsion and is used to measure the energy difference between states of the same spin multiplicity.

      Example: Co^{2+}, $3d^7$, has a difference between the ^4F and ^4P free-ion terms of $15B \approx 14{,}500\ cm^{-1}$.

    - By using the appropriate values of the Racah parameter, the Tanabe and Sugano diagrams can be used with a variety of metal ions and complexes.

Tanabe-Sugano Diagram for d^7



Notes on d^7 Tanabe-Sugano Diagram

- The d^7 diagram, like all such diagrams for configurations that may be either high spin or low spin, has a perpendicular line near the middle marking the change in spin state.

  - To the left of the line (low field strength, high spin), the ground state is $^4T_1$, emerging from the free-ion ^4F term.

  - To the right of the line (high field strength, low spin), the ground state is ^2E, and therefore becomes the abscissa beyond the spin-state crossover point.

  - The high-spin ^2E ground state is a continuation of the line for the low-spin excited state ^2E term, which emerges from the ^2G free-ion term.

  - The line for the former high-spin ground state $^4T_1$ term ascends as an excited state on the low-spin (right) side of the diagram.

Making Sense of the Confusion

- Sometimes it can be difficult to trace back the free-ion origin of some of the octahedral terms, particularly on the diagrams for high-spin/low-spin configurations.

- Remember: ***the spin multiplicities of the split terms must match those of the free-ion terms***.

  - Failure to recognize this has caused some texts to erroneously render the d^6 diagram with the low-spin ground state $^1A_1$ term originating from the ^3D free-ion term, rather than the correct ^1I term.