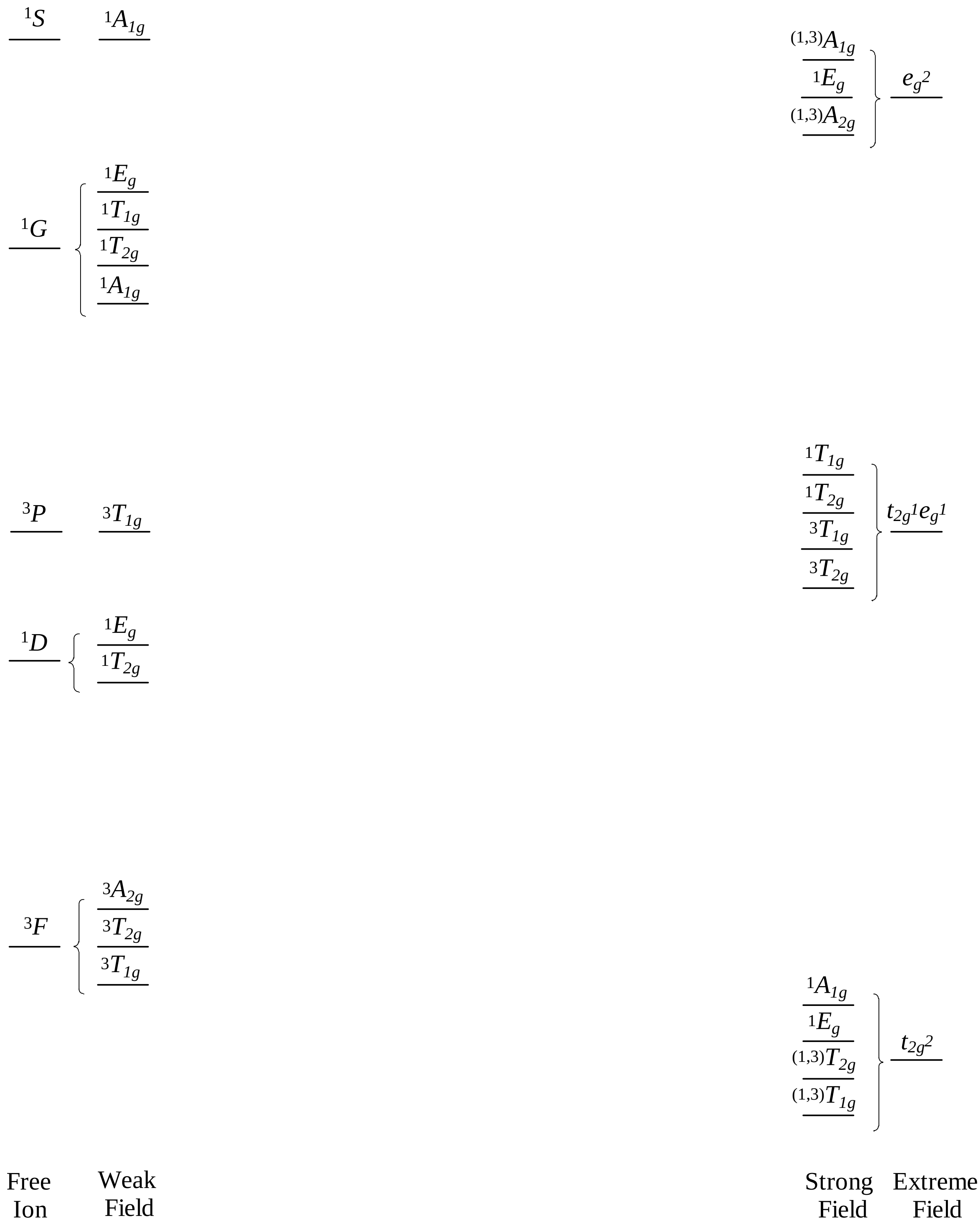
Template for the d^2 Correlation Diagram



Making the Correlations for Triplet States
Correlation for the $^3A_{2g}$ Term from ^3F

- We begin by examining the split terms from the ^3F free-ion term on the left of the diagram.

  - The $^3A_{2g}$ term is unique among the weak-field terms, and it must correlate with the unique A_{2g} term from e_g^2 on the strong-field side.

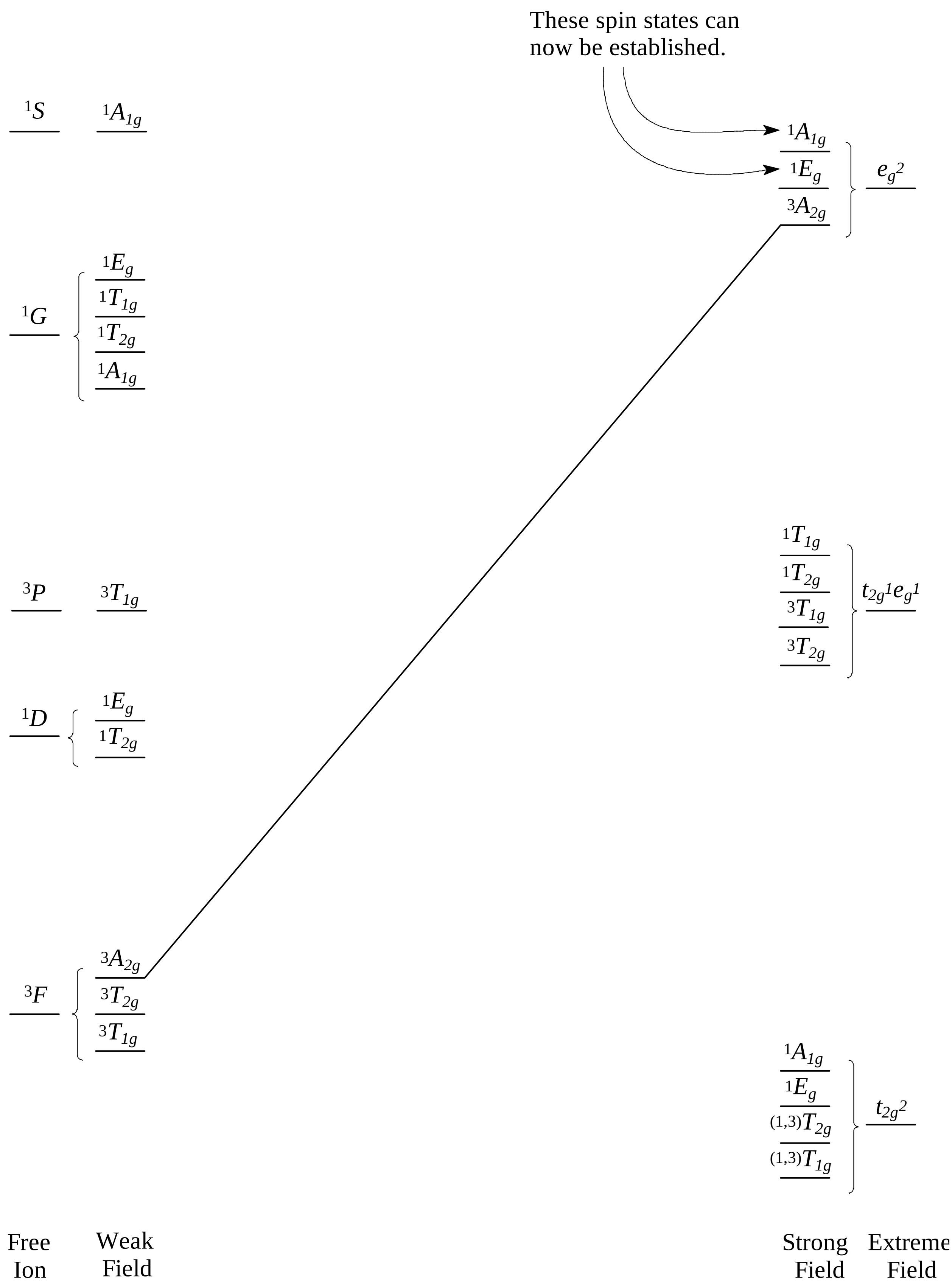
    ☞ The strong-field A_{2g} term must also must be a triplet.

    ☞ It now becomes evident that our choice of spin multiplicities for the terms from e_g^2 must be

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

- We can draw the correlation line for the $^3A_{2g}$ term and remove the ambiguous spin state notation for the A_{1g} and E_g terms for e_g^2 on the strong-field side of the diagram.

Correlation for $^3A_{2g}$ Added



Making the Correlations for Triplet States
Correlation for the $^3T_{2g}$ Term from ^3F

- We turn now to the $^3T_{2g}$ term arising from ^3F.

  ○ This is the only triplet T_{2g} term on the weak-field side (the two other T_{2g} terms are singlets).

  ☞ There can be only one such term on the strong-field side.

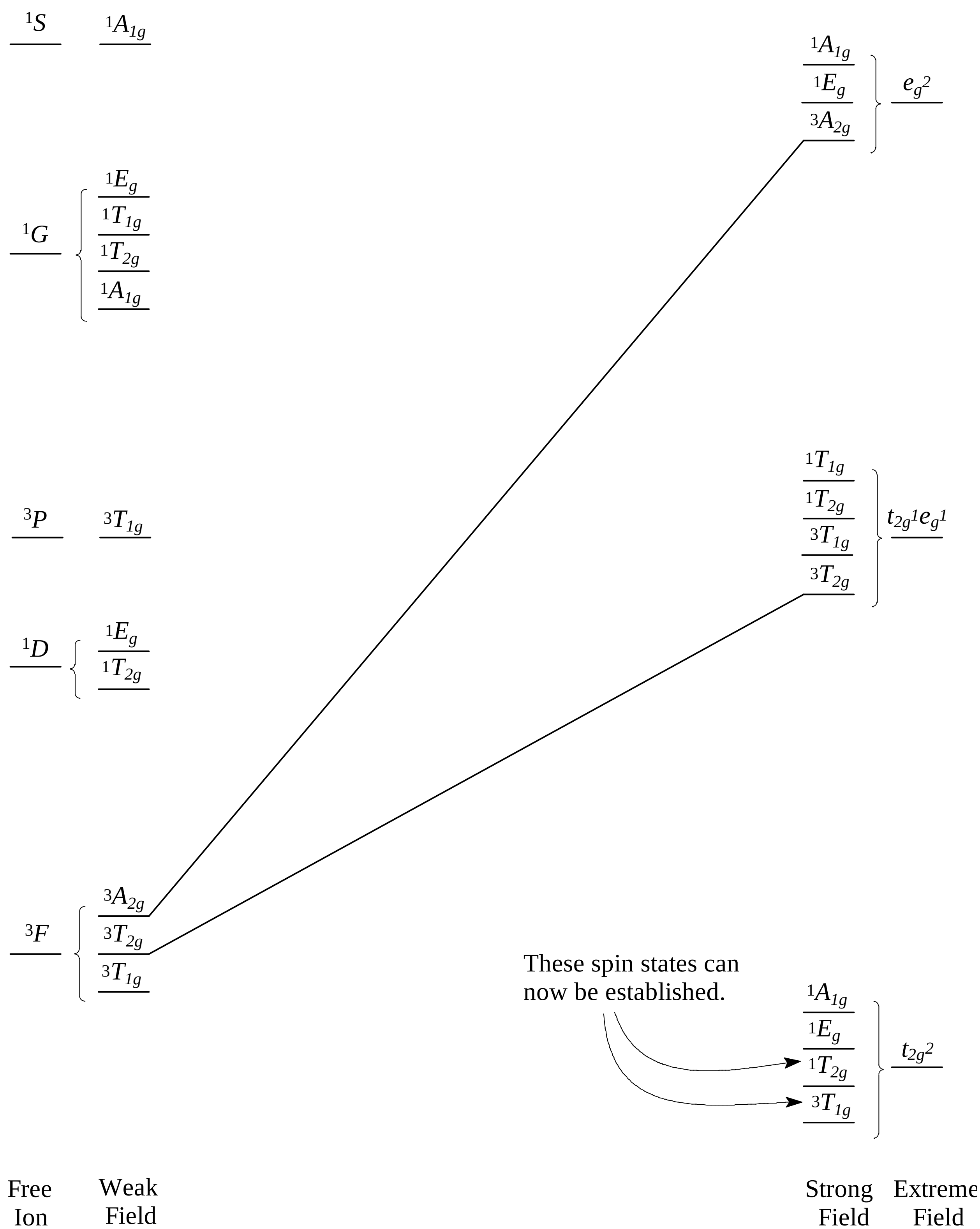
  ○ We have already identified a $^3T_{2g}$ term from $t_{2g}{}^1e_g{}^1$ on the strong-field side, which must correlate with the $^3T_{2g}$ term from ^3F.

  ☞ This means that the T_{2g} term from $t_{2g}{}^2$ on the strong field side must be a singlet.

  ☞ From this it follows that the spin multiplicities for terms from $t_{2g}{}^2$ must be

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

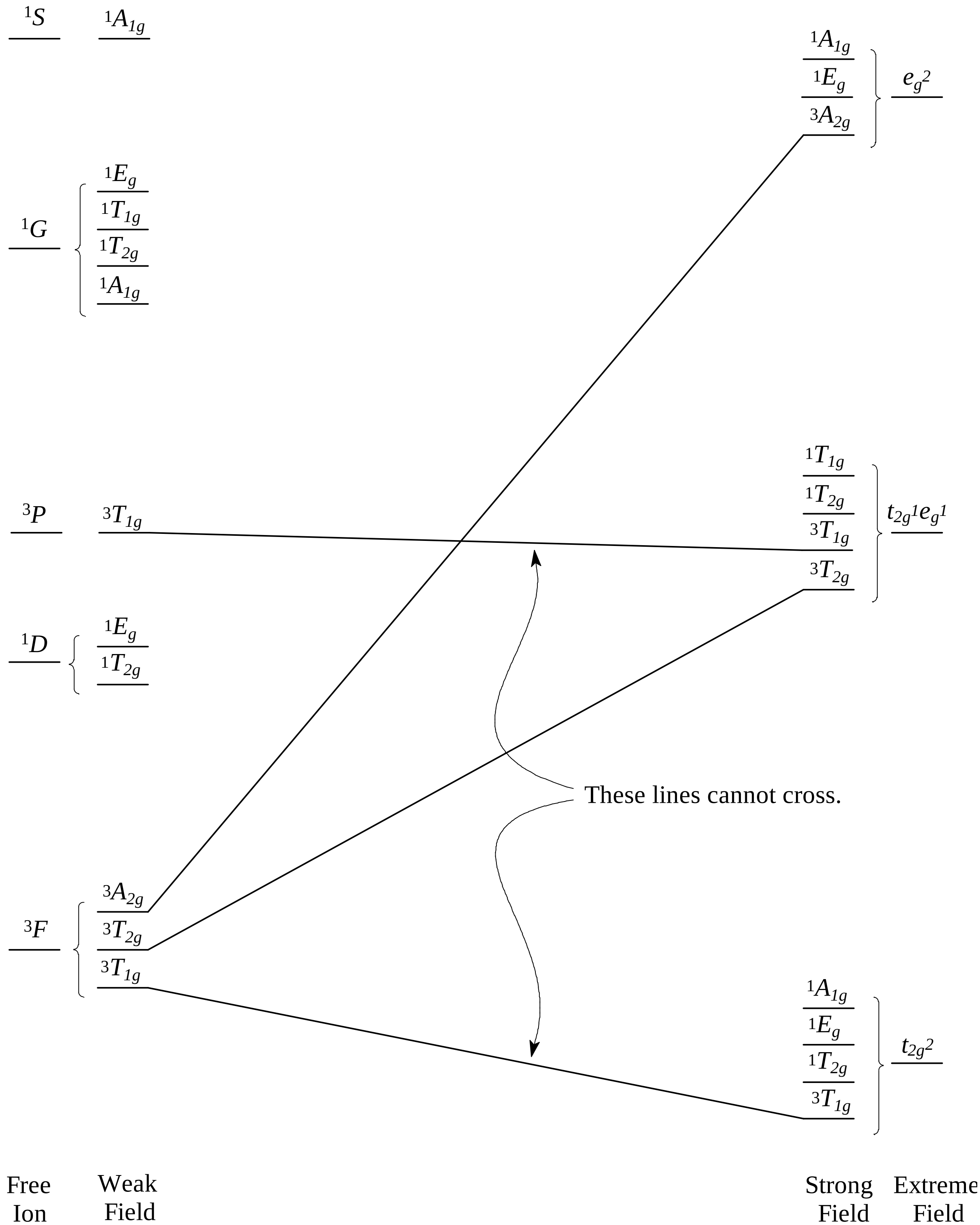
Correlation for $^3T_{2g}$ Added



Making the Correlations for Triplet States
Correlation for the $^3T_{1g}$ Terms from ^3F and ^3P

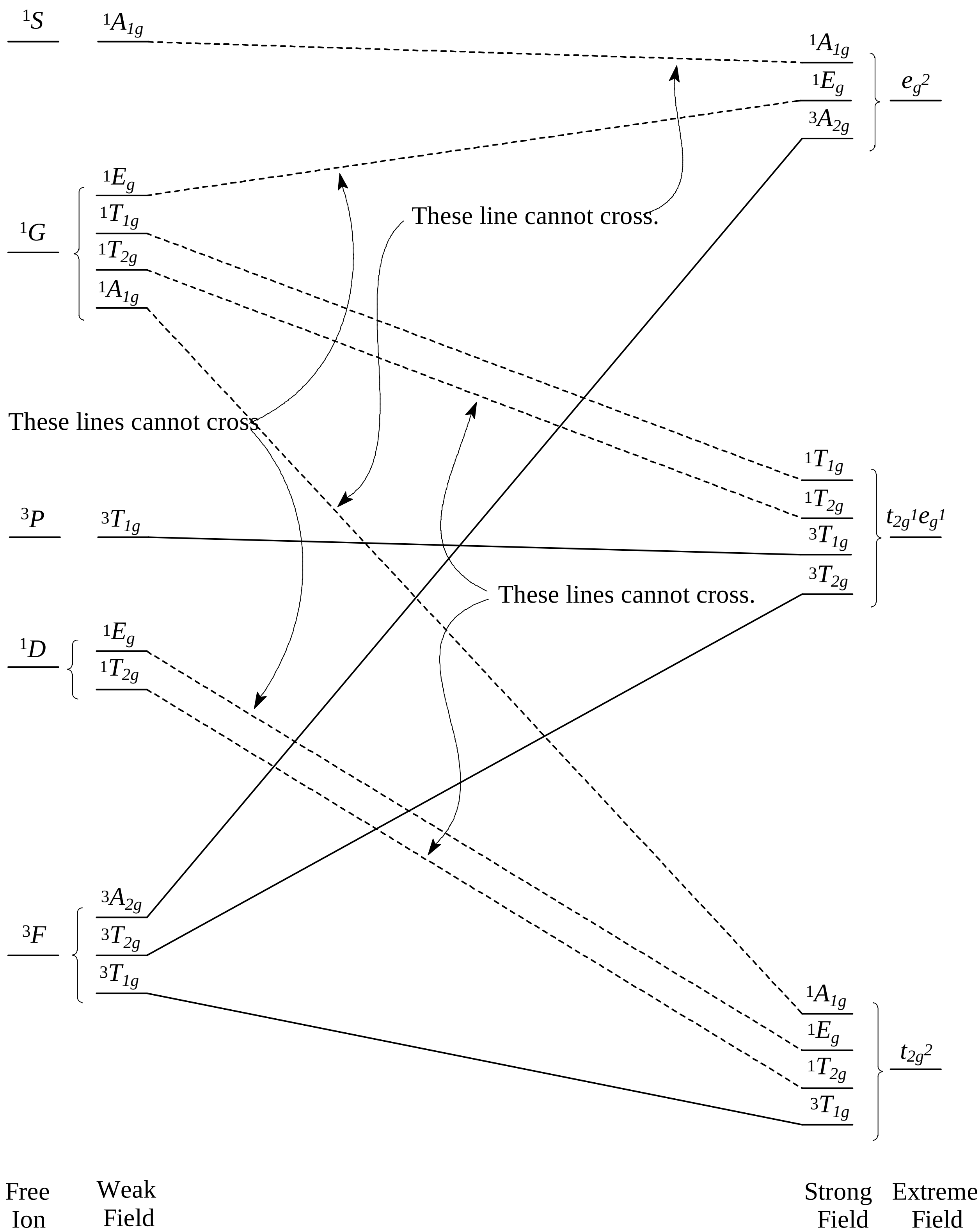
- We now can make the correlation for the remaining two triplet terms on the weak-field side; viz., $^3T_{1g}$ (F) and $^3T_{1g}$ (P).
  - From the ***noncrossing rule*** we conclude that
    - $^3T_{1g}$ (F) connects with $^3T_{1g}$ from t_{2g}^2
    - $^3T_{1g}$ (P) connects with $^3T_{1g}$ from $t_{2g}^1e_g^1$

Adding the $^3T_{1g}$ Correlations

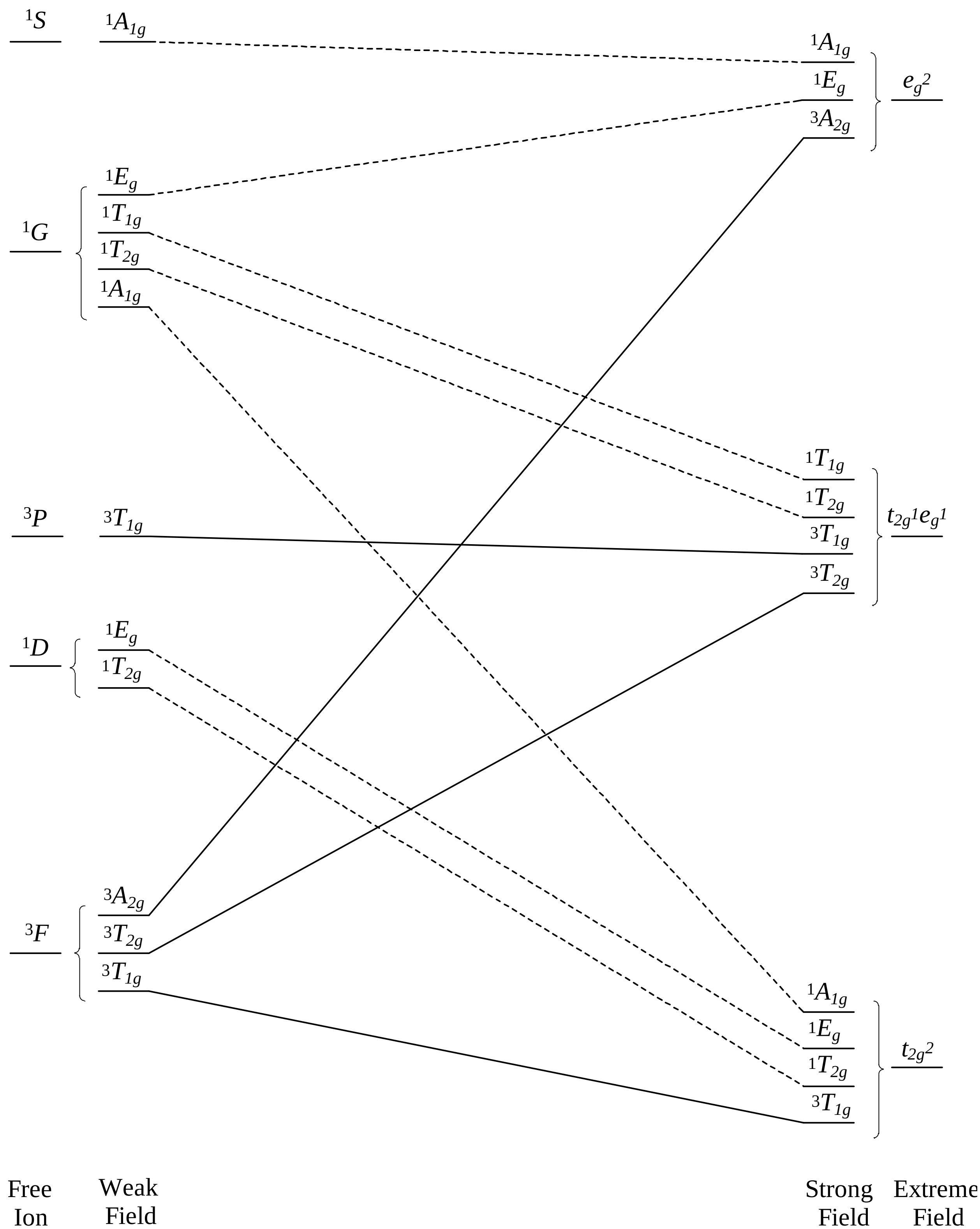


- The remaining correlations between singlet states on both sides can now be made by applying the noncrossing rule.

Adding the Singlet State Correlations



The Complete d^2 Correlation Diagram



Other Configurations and Other Fields

- In principle, we could construct the correlation diagram for any d^n configuration in an octahedral or other field by taking an approach similar to what we have shown here for the d^2 case.

    - 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

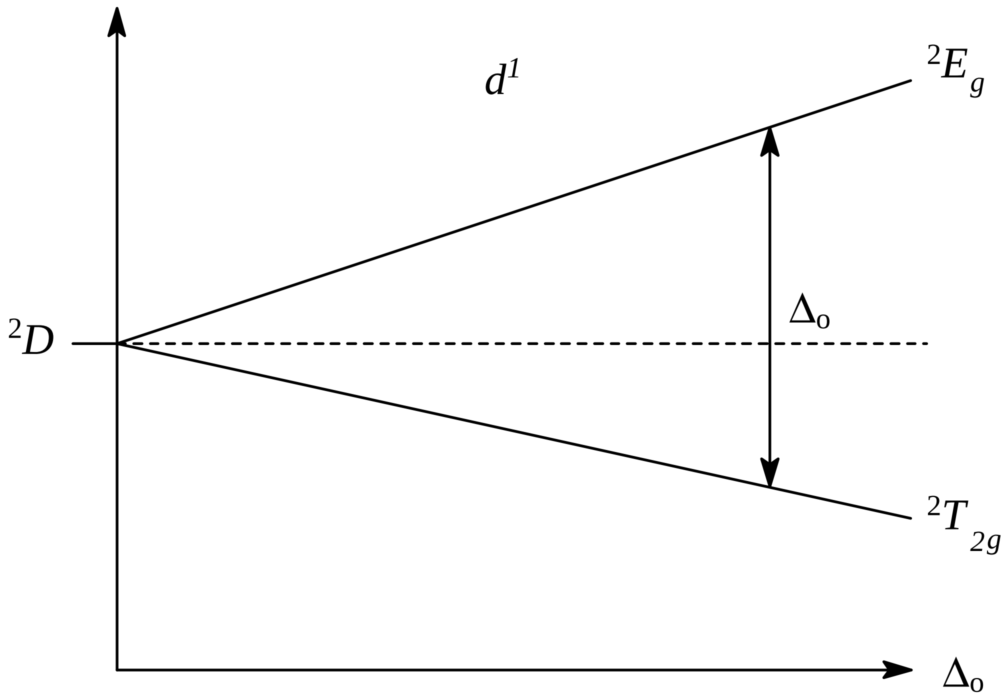
- Both configurations give rise to a ^2D free-ion term, which is split into ^2E_g and $^2T_{2g}$ terms in an octahedral field.

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

e_g	___ ___	•___ ___
t_{2g}	•___ ___ ___	___ ___ ___
	t_{2g}^1	e_g^1
	ground state = $^2T_{2g}$	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}	•• •• ••	•• •• •○
	$t_{2g}^6\ e_g^3$	$t_{2g}^5\ e_g^4$
	ground state = ^2E_g	excited state = $^2T_{2g}$

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

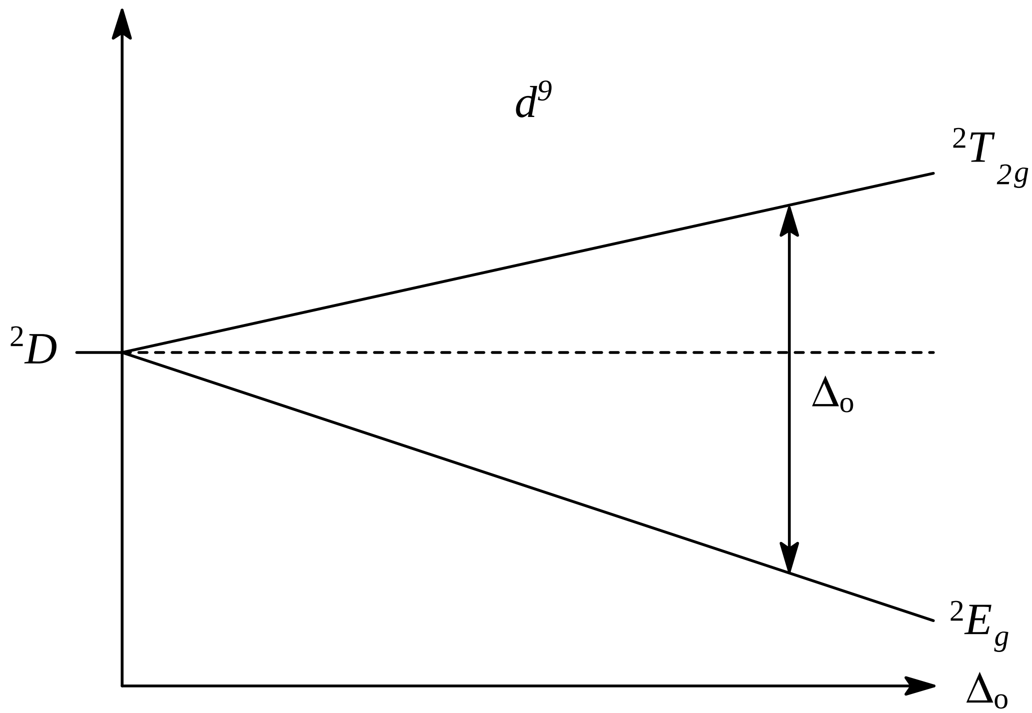
- ○ Using the hole as a marker, note that the ground state $t_{2g}^6e_g^3$ configuration consists of two equivalent orbital assignments and therefore must correspond to the ^2E_g term.

- ○ 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 $+(2/5)\Delta_o$.

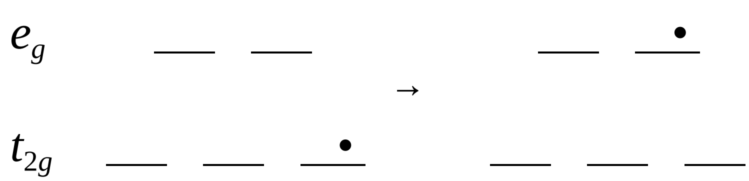
d^9 Correlation Diagram



Hole Formalism

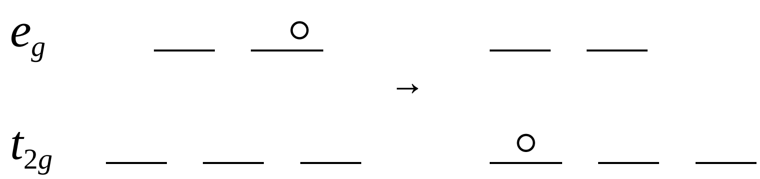
- The relationship between d^n and d^{10-n} term splittings in the same symmetry ligand field is sometimes called the *hole formalism*.
    - The name comes from seeing d^n as a configuration of n electrons and d^{10-n} as a configuration of n positive holes (equivalent to positrons).
    - A configuration 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

Applying Hole Formalism to Correlation Diagrams

- The correlation diagram for $d^{10\text{-}n}$ 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 $d^{10\text{-}n}$ configurations, and redrawing the connecting lines, paying attention to the noncrossing rule.

- We can use this principle with our d^2 O_h correlation diagram to obtain the d^8 correlation diagram.

  - Note that in the d^2 diagram the sets of terms for the three $t_{2g}e_g$ configurations on the strong-field (right) side are ordered

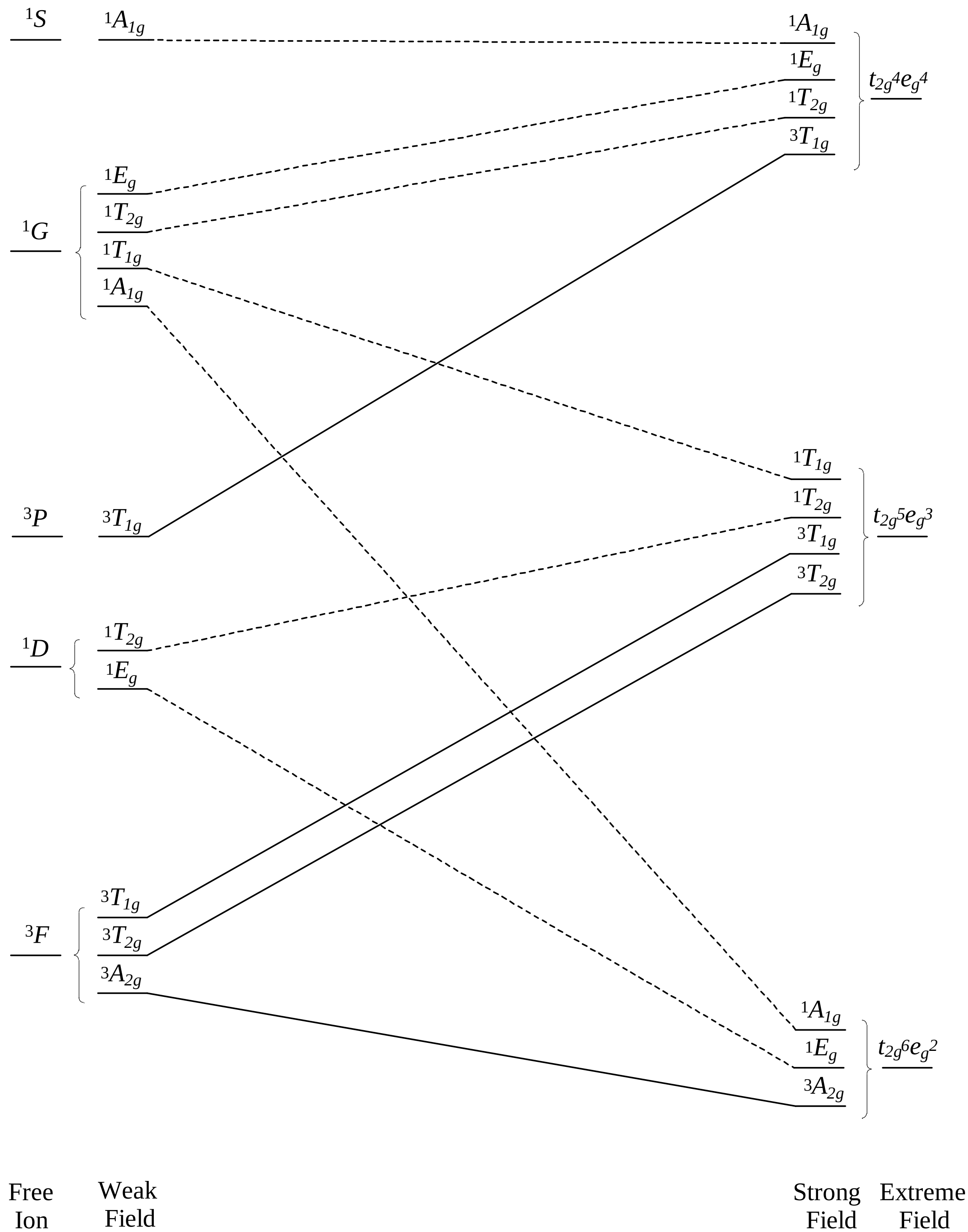
    $$[^3T_{1g},\ ^1T_{2g},\ ^1E_g,\ ^1A_{1g}] < [^3T_{2g},\ ^3T_{1g},\ ^1T_{2g},\ ^1T_{1g}] < [^3A_{2g},\ ^1E_g,\ ^1A_{1g}]$$

  - The order will be reversed for the d^8 diagram:

    $$[^3A_{2g},\ ^1E_g,\ ^1A_{1g}] < [^3T_{2g},\ ^3T_{1g},\ ^1T_{2g},\ ^1T_{1g}] < [^3T_{1g},\ ^1T_{2g},\ ^1E_g,\ ^1A_{1g}]$$

  - The ordering of ligand-field terms within each set is arbitrarily chosen for convenience in drawing the diagrams and has no significance regarding relative energies within the set.

d^8 O_h Correlation Diagram



☞ Note that the connections between certain weak field terms and their strong field counterparts have changed as a result of 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.

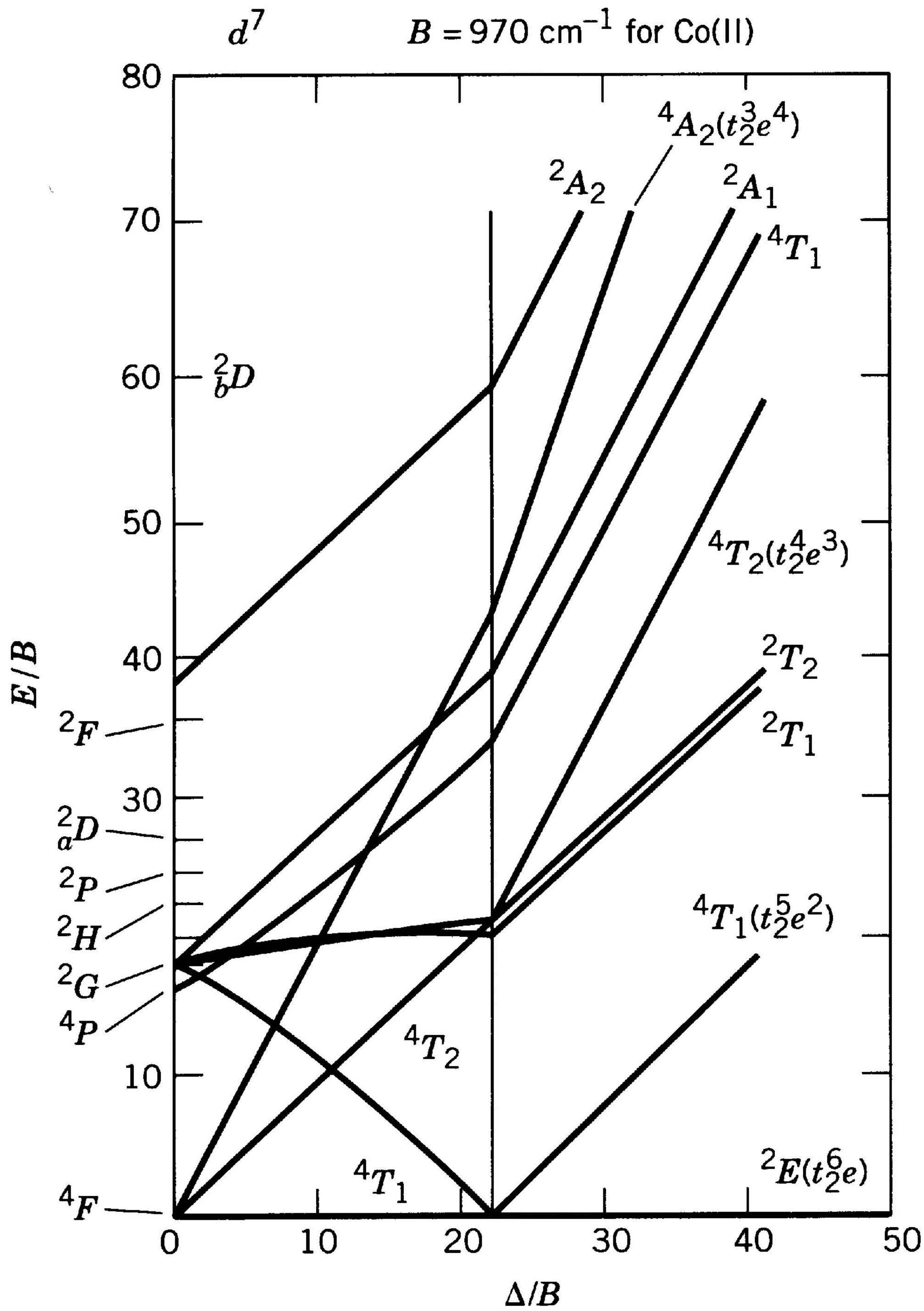
  - Term energies and field strengths are expressed as the variables E/B and Δ/B, respectively, where B is the *Racah parameter*.

    - 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 $15B \approx 14{,}500\ \text{cm}^{-1}$.

    - 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.