

Terms of Free Ions with d^n Configurations

- The usual notation for electronic configurations (e.g., $3d^2$) does not tell us which specific orbitals are occupied, except when a degenerate set of orbitals is half filled or fully filled.
- Except for a fully filled subshell, we rarely presume to know which of the two possible spin states individual electrons have ($m_s = \pm 1/2$).

Example: There are ten ways of arranging the single electron in the configuration nd^1 ($n = 3, 4, 5, \dots$)

$m_l = -2$	$m_l = -1$	$m_l = 0$	$m_l = +1$	$m_l = +2$
1				
	1			
		1		
			1	
				1
↓				
	↓			
		↓		
			↓	
				↓

- The number of possible arrangements increases greatly with additional electrons.

Electron Arrangements for nd^2 (Same Spins)

- Consider the 20 possible ways of arranging electrons for the configuration nd^2 ($n = 3, 4, 5, \dots$), in which the two electrons have the same spins (both $m_s = +1/2$ or $m_s = -1/2$) :

$m_l = -2$	$m_l = -1$	$m_l = 0$	$m_l = +1$	$m_l = +2$
1	1			
1		1		
1			1	
1				1
	1	1		
	1		1	
	1			1
		1	1	
		1		1
			1	1
↓	↓			
↓		↓		
↓			↓	
↓				↓
	↓	↓		
	↓		↓	
	↓			↓
		↓	↓	
		↓		↓
			↓	↓

Electron Arrangements for nd^2 (Opposite Spins)

- There are 25 additional configurations with opposite spins.

$m_l = -2$	$m_l = -1$	$m_l = 0$	$m_l = +1$	$m_l = +2$
↑	↓			
↑		↓		
↑			↓	
↑				↓
	↑	↓		
	↑		↓	
	↑			↓
		↑	↓	
		↑		↓
			↑	↓
↓	↑			
↓		↑		
↓			↑	
↓				↑
	↓	↑		
	↓		↑	
	↓			↑
		↓	↑	
		↓		↑
			↓	↑
↑↓				
	↑↓			
		↑↓		
			↑↓	
				↑↓

Microstates

- Each set of individual m_l and m_s values constitutes a *microstate* of the configuration.
- Some microstates may be allowable arrangements in the ground state, and others may be allowable arrangements in some higher-energy excited state.
- With additional electrons the number of microstates rises dramatically.
- For any allowed number of electrons in a set of degenerate orbitals (called *equivalent electrons*), the number of possible microstates is given by

$$D_t = \frac{(2N_o)!}{(2N_o - N_e)!N_e!}$$

D_t = number of possible microstates = *total degeneracy* of the configuration

N_o = number of degenerate orbitals in the set or subshell

N_e = number of electrons in the configuration

Example: nd^2

$$D_t = \frac{(2 \times 5)!}{[(2 \times 5) - 2]!2!} = \frac{10!}{8! \times 2!} = \frac{3628800}{(40320)(2)} = 45$$

Microstates for nd^{1-10}

configuration	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
microstates	10	45	120	210	252	210	120	45	10	1

- ☞ The number of microstates (the total degeneracy) for a configuration nd^x is the same as for nd^{10-x} .

Microstates and Terms

- In any microstate both the individual orbital magnetic moments (related to m_l) and spin magnetic moments (related to m_s) will interact with one another, resulting in an energy state or *term* for the configuration.
- Except for a fully filled configuration, no one microstate uniquely gives rise to a particular energy for the configuration.
- A number of microstates generally contribute to a single term.
- Terms are usually degenerate according to the number of microstates giving rise to them.
- In a ligand field, degeneracies among all the microstates comprising a particular free-ion term may be partially lifted.

Russell-Saunders Coupling Scheme

- The ways in which individual m_l and m_s values interact are not easily evaluated for a real atom or ion.
- In fact, the notion that we can assign individual m_l and m_s values to the electrons and assess their interactions on that basis is really an extreme extension of the one-electron wave mechanical model.
- The Russell Saunders coupling scheme is a reasonably good first approximation for assessing the origins of the term energies in many cases in terms of summations of individual electron m_l and m_s values.
- The Russell-Saunders coupling scheme can be applied successfully to interpreting the term energies of first and second row transition metals
 - Less successful with the third row transition elements
 - Hopelessly inadequate with f -block transition elements (i.e., lanthanides and actinides).

Free-Ion Term Symbols

- The various terms that can exist for a particular configuration are indicated by a *term symbol* of the form

$$^{2S+1}L$$

- L is related to the overall orbital angular momentum for the system of electrons.
 - Values of L may be 0, 1, 2, ...
 - S is related to the overall spin angular momentum for the system of electrons.
 - Values of S may be 0, 1/2, 1, 3/2, ...
 - L and S are analogous to the quantum numbers l and s for single electrons.
- The left superscript number $2S + 1$ is the *multiplicity* of the term.

The J Quantum Number

- A third quantum number, J , is often added to term symbols as a right subscript.

$$^{2S+1}L_J$$

- J relates to the total angular momentum arising from spin-orbital coupling.
- Allowed J values are $L + S, L + S - 1, L + S - 2, \dots, |L - S|$.
- For a given L value, the various values of J represent closely spaced energy sublevels of the term energy.
- $2S + 1$ equals the number of J values (and hence the number of sublevels) for the particular L value when $L > S$.
- When $L = 0$ or $L < S$ the number of J values is $2L + 1$.
- For a given L value the energy differences between the sublevels of various J values are small and can be ignored for our purposes.

☞ We will omit the J values from our term symbols.

- The multiplicity indicated by the superscript $2S + 1$ is retained, because it relates directly to the spin state (and hence the number of unpaired electrons) of the term.

☞ $2S + 1$ is often called the *spin multiplicity* and used without reference to J .

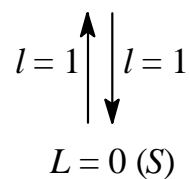
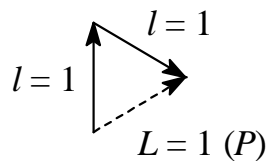
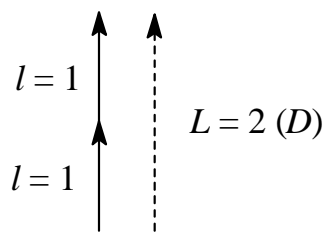
Relationship of L to Resultant Orbital Angular Momentum and Resultant Orbital Magnetic Moment

L = Overall orbital angular momentum quantum number
= Resultant orbital quantum number

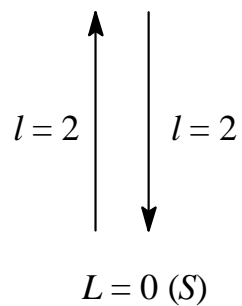
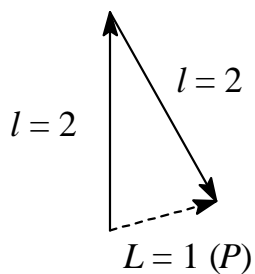
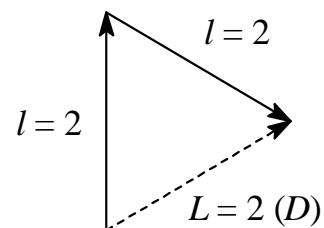
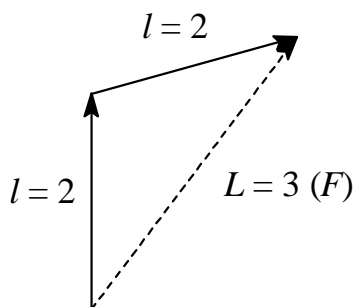
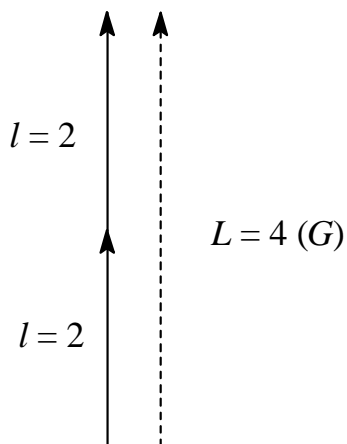
- L is related to the *resultant orbital angular momentum* and to the *resultant orbital magnetic moment* of the system, obtained by vectorial addition of the vectors related to the l quantum numbers of the individual electrons.
 - The orbital angular momentum for individual electrons has a *magnitude* of $[l(l + 1)]^{1/2}(h/2\pi)$
 - Likewise the resultant orbital angular momentum has a *magnitude* of $[L(L + 1)]^{1/2}(h/2\pi)$.
- There are a variety of ways in which the individual l values can add vectorially, so a variety of L values can result for a given configuration of electrons.
 - This is true even when all electrons have the same individual l values.

Vector Addition of Individual l Vectors to Give L Values for Configurations p^2 and d^2

p^2



d^2



Term Symbol Notation

<i>L</i> value	0	1	2	3	4	5	6	7	...
State	<i>S</i>	<i>P</i>	<i>D</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>	<i>K</i>	...

- Capital letter designations follow orbital notations (*s*, *p*, *d*, *f*)
- After $L = 2$ notation proceeds alphabetically (with the omission of *J*, to avoid confusion with the total angular momentum quantum number, *J*).

Example:

Configuration p^2 gives rise to the terms *S*, *P*, and *D*

Example:

Configuration d^2 gives rise to the terms *S*, *P*, *D*, *F*, and *G*

Relationship Between L and M_L

- For a given term the magnitude of the resultant orbital angular momentum is fixed as $[L(L + 1)]^{1/2}(h/2\pi)$.
 - However, the vector for the momentum can have a number of allowed orientations in space relative to an applied magnetic field, which defines the z direction of the system.
 - The various allowed orientations are associated with the *overall orbital magnetic quantum number*, M_L , which can take on the $2L + 1$ values

$$M_L = L, L - 1, \dots, 1 - L, -L$$

- $2L + 1$ may be regarded as the *orbital multiplicity* or *orbital degeneracy* of the term.
- Each orientation has a projection on z whose magnitude is $M_L(h/2\pi)$.

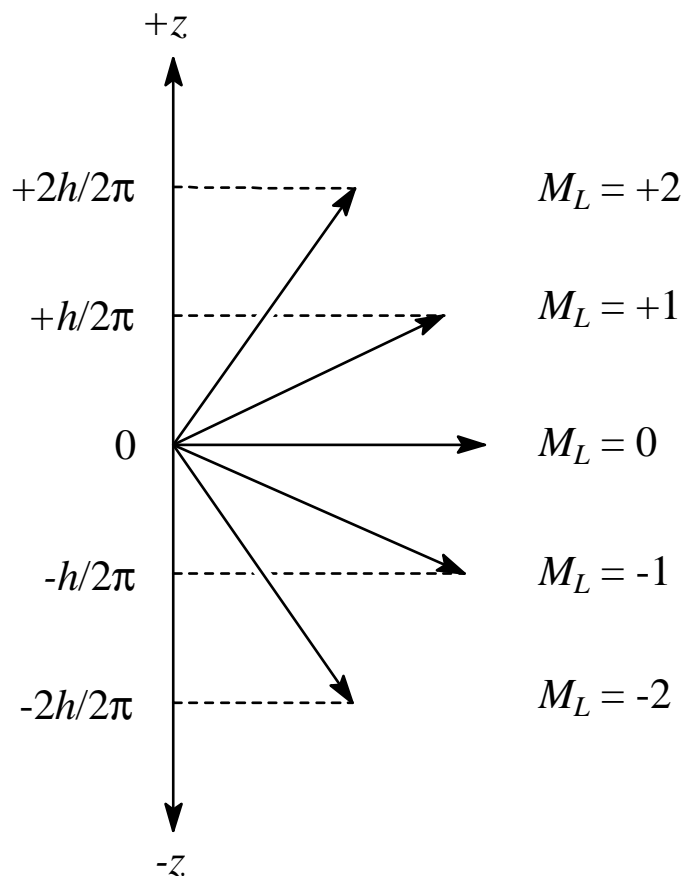
Example: M_L Orientations for a D Term

- A D term ($L = 2$, $2L + 1 = 5$) has five possible orientations corresponding to $M_L = +2, +1, 0, -1, -2$.
- The magnitude of the resultant orbital angular momentum is

$$[L(L + 1)]^{1/2}(h/2\pi) = [(2)(2+1)]^{1/2}(h/2\pi) = \sqrt{6} (h/2\pi)$$

- Each orientation of the resultant orbital angular momentum has a projection on z whose magnitude is

$$M_L(h/2\pi) = +2h/2\pi, +h/2\pi, 0, -h/2\pi, -2 h/2\pi$$



Relationship Between M_L and m_l

- In the Russell-Saunders coupling scheme values of M_L can be obtained as the sum of the m_l values of the individual electrons; i.e.,

$$M_L = \Sigma m_l.$$

- Thus it is possible to assign an M_L value for each and every microstate of a configuration.
- Since M_L represents the possible orientations of the orbital angular momentum vector, it follows that a given L value must arise from a complete set of microstates with the $2L + 1$ values $M_L = L, L - 1, \dots, 1 - L, -L$, which identify these orientations.

Overall Spin Quantum Number, S

- The *overall spin quantum number*, S , defines the spin state of the term, and $2S + 1$ defines the spin multiplicity.

S	$2S + 1$	State Multiplicity
0	1	singlet
1/2	2	doublet
1	3	triplet
3/2	4	quartet (quadruplet)
...

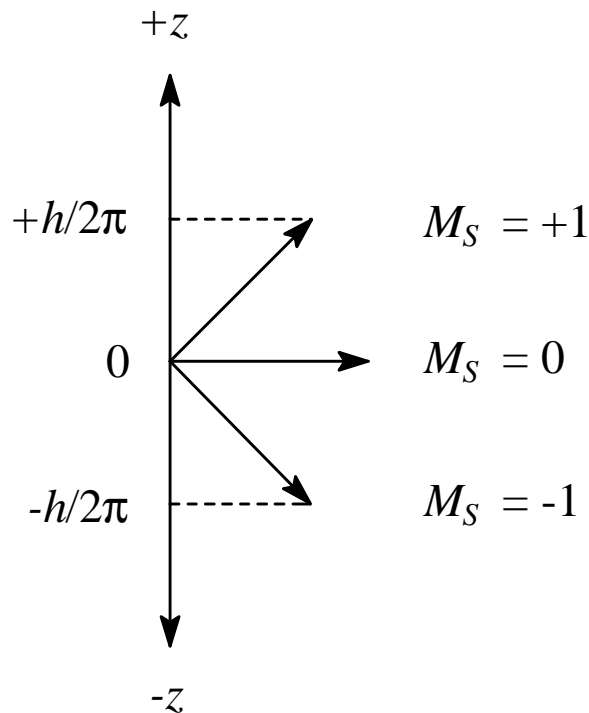
- S is related to the *resultant spin angular momentum* and to the *resultant spin magnetic moment* of the system.
- S can be obtained by vectorial addition of the spin angular momentum vectors related to the s quantum numbers of the individual electrons.
- The magnitude of the resultant spin angular momentum is
$$[S(S + 1)]^{1/2}(h/2\pi)$$
- S is related to an *overall spin magnetic quantum number*, M_S , whose allowed values are

$$M_S = S, S + 1, \dots, 1 - S, -S$$

Allowed Orientations of the Spin Angular Momentum

- The $2S + 1$ values indicate the allowed orientations of the spin angular momentum vector relative to an applied magnetic field, which defines the z direction of the system.
- The spin multiplicity, given as $2S + 1$, represents the *spin degeneracy* of a particular spin state.
- For a given spin state the magnitude of the spin angular momentum is fixed as $[S(S + 1)]^{1/2}(h/2\pi)$, but its projections on the z axis in the allowed orientations are given by $M_S(h/2\pi)$.

Example: $S = 1$, $M_S = -1, 0, +1$



Relationship Between M_S and m_s

- In the Russell-Saunders scheme we assume that M_S is the sum of m_s values of the individual electrons; i.e.,

$$M_S = \sum m_s$$

where $m_s = \pm 1/2$.

- Each microstate can be assigned a value of M_S .
- Since M_S represents the possible orientations of the spin angular momentum vector, it follows that a given S value must arise from a complete set of microstates with the $2S + 1$ values $M_S = S, S - 1, \dots, 1 - S, -S$.

Relationship Between M_L and M_S of Microstates and L and S of Terms

- ☞ A term having particular values of both L and S must arise from the set of microstates that has the necessary $2L + 1$ values of M_L and also the necessary $2S + 1$ values of M_S .
- This means that one can identify all the allowed terms of a configuration by systematically arranging all microstates in such a way as to be able to cull the sets of M_L and M_S values with the appropriate ranges that define the various terms.
- This is a straightforward but tedious process, especially for configurations with large numbers of microstates.
- ☺ We will not concern ourselves with the mechanics of this task, except to note that a variety of techniques have been developed to carry out the labor.¹

¹Two good methods have been described by K. E. Hyde, *J. Chem. Educ.*, **1975**, 52, 87 and E. R. Tuttle, *Amer. J. Phys.*, **1967**, 35, 26.

Equivalent Electrons Have Fewer Possible Terms

Example: d^2

- We have seen by vector addition that the configuration d^2 gives rise to the terms

$$S, P, D, F, G$$

- The only possible spin states are $S = 0$ (paired) and $S = 1$ (unpaired).
 - Thus, the spin multiplicities of the terms can only be singlets and triplets.
 - If the two electrons are in different subshells (e.g., $3d^1 4d^1$) all terms will occur as both singlets and triplets.
 - If we stipulate that the two electrons are equivalent, meaning a configuration nd^2 within the same subshell, the Pauli exclusion principle will limit the possible combinations of m_l and m_s , so only certain terms can be singlet or triplets.
 - For the configuration nd^2 the allowed terms are

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

Relationship Between Total Degeneracy and Term Degeneracies

Example: $nd^2 \Rightarrow {}^1S, {}^3P, {}^1D, {}^3F, {}^1G$

- We know that the terms for two *equivalent d* electrons arise from 45 microstates.
- Therefore the sum of the degeneracies of all these terms must equal this number.

☞ *The degeneracy of each term, equivalent to the number of microstates giving rise to it, is the product of its spin degeneracy times its orbital degeneracy; i.e.,*

$$(2S + 1)(2L + 1).$$

- For the set of terms for nd^2 we have

Term	1S	3P	1D	3F	1G	D_t
Degeneracy	$(1)(1) = 1$	$(3)(3) = 9$	$(1)(5) = 5$	$(3)(7) = 21$	$(1)(9) = 9$	45

Terms for Free Ion d^n Configurations

d^n	Free Ion Terms	D_t
d^0, d^{10}	1S	1
d^1, d^9	2D	10
d^2, d^8	$^1S, ^1D, ^1G, ^3P, ^3F$	45
d^3, d^7	$^2P, ^2D(2), ^2F, ^2G, ^2H, ^4P, ^4F$	120
d^4, d^6	$^1S(2), ^1D(2), ^1F, ^1G(2), ^1I, ^3P(2), ^3D, ^3F(2), ^3G, ^3H, ^5D$	210
d^5	$^2S, ^2P, ^2D(3), ^2F(2), ^2G(2), ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$	252

☞ Note that in each case the total degeneracy of terms is equal to the calculated value of D_t .

- The ground state term can be identified by applying Hund's rules.
- In general the actual energies of the terms, and hence their relative ordering, must be determined from analysis of spectroscopic data.