

BOX 20.5

CHEMICAL AND THEORETICAL BACKGROUND

Term symbols for free atoms and ions

This Box provides an introduction to term symbols for free atoms and ions; for the most part, use of these symbols is confined to this chapter. In Section 1.7, we showed how to assign a set of quantum numbers to a given electron. For many purposes, this level of discussion is adequate. However, for an understanding of term symbols, a more detailed study is required; before studying this background information, readers may wish to review Box 1.4.

Quantum numbers for multi-electron species

Consider worked example 1.7; in the answer, we ignored a complication. In assigning quantum numbers to the four $2p$ electrons, how do we distinguish between the possibilities of placing the last electron in an orbital with $m_l = +1, 0$ or -1 ? This, and related questions, can be answered only by considering the interaction of electrons, primarily by means of the *coupling* of magnetic fields generated by their spin or orbital motion: hence the importance of spin and orbital angular momentum (see Section 1.6).

As we have seen, for any system containing more than one electron, the energy of an electron in a shell of principal quantum number n depends on the value of l and this also determines the orbital angular momentum of the electrons:

$$\text{orbital angular momentum} = \left[\sqrt{l(l+1)} \right] \frac{h}{2\pi}$$

We assume that the energy of a multi-electron species and its orbital angular momentum is determined by a *resultant orbital quantum number*, L , which is obtained directly from the values of l for the individual electrons; since the orbital angular momentum has magnitude and $(2l+1)$ spatial orientations (the number of values of m_l), *vectorial* summation of individual l values is necessary. Since the value of m_l for any electron denotes the component of its orbital angular momentum along the z axis, $m_l(h/2\pi)$, algebraic summation of m_l values for individual electrons gives the resultant orbital magnetic quantum number M_L and the component of the resultant orbital angular momentum along the z axis $M_L(h/2\pi)$. Just as m_l may have the $(2l+1)$ values $l, (l-1) \dots 0 \dots -(l-1), -l$, so M_L may have the $(2L+1)$ values $L, (L-1) \dots 0 \dots -(L-1), -L$, and if, for the multi-electron system, we can find all possible values of M_L , this tells us the value of L . Energy states for which $L = 0, 1, 2, 3, 4 \dots$ are known as *S, P, D, F, G* ... terms respectively, the letters corresponding to *s, p, d, f, g* ... used to denote orbitals for which $l = 0, 1, 2, 3, 4 \dots$ in the one-electron case. The resultant orbital angular momentum is given by:

$$\text{orbital angular momentum for a multi-electron species} = \left[\sqrt{L(L+1)} \right] \frac{h}{2\pi}$$

The resultant spin quantum number, S , from which the resultant spin angular momentum is determined by:

$$\text{spin angular momentum for a multi-electron species} = \left[\sqrt{S(S+1)} \right] \frac{h}{2\pi}$$

M_S is obtained by algebraic summation of the m_s values for individual electrons. One electron with $s = \frac{1}{2}$ obviously has $S = \frac{1}{2}$ with $M_S = +\frac{1}{2}$ or $-\frac{1}{2}$; M_S for the multi-electron system is analogous to m_s for the one-electron species. Two electrons lead to $S = 0$ ($m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ giving $M_S = 0$) or $S = 1$ ($m_s = +\frac{1}{2}$ and $+\frac{1}{2}$, or $+\frac{1}{2}$ and $-\frac{1}{2}$, or $-\frac{1}{2}$ and $-\frac{1}{2}$ giving $M_S = 1, 0$ or -1). In general, for any value of S , there are $(2S+1)$ values of M_S : $S, (S-1) \dots 0 \dots -(S-1), -S$.

The quantity $(2S+1)$ is the *multiplicity* of the term where S is the total spin quantum number. Terms for which $(2S+1) = 1, 2, 3, 4 \dots$ (corresponding to $S = 0, \frac{1}{2}, 1, \frac{3}{2} \dots$) are called *singlets, doublets, triplets, quartets* ...

The use of S for the resultant spin quantum number, a term for which $L = 0$, and screening constants is unfortunate, but is firmly established and in practice rarely causes confusion.

Finally, we have the resultant inner quantum number, J , also called the total angular momentum quantum number since the total angular momentum is given by:

$$\text{total angular momentum for a multi-electron species} = \left[\sqrt{J(J+1)} \right] \frac{h}{2\pi}$$

where J is compounded vectorially from L and S , i.e. algebraically from M_L and M_S . Quantum number J can take values $(L+S), (L+S-1) \dots |L-S|$, the last symbol denoting the modulus of the quantity (i.e. only the magnitude, and not the sign is involved). Like j (see Box 1.4) for a single electron, J for the multi-electron system must be positive or zero. There are thus $(2S+1)$ possible values of J for $S < L$, and $(2L+1)$ possible values for $L < S$.

This method of obtaining J from L and S is based on *LS* (or *Russell-Saunders*) *coupling*. Although it is the only form of coupling of orbital and spin angular momentum that we shall consider in this book, it is not valid for all elements (especially those with high atomic numbers). In an alternative method of coupling, l and s for all the individual electrons are first combined to give j , and the individual j values are combined in a *j-j coupling* scheme.

Term symbols

If we know $(2S+1)$, L and J for an energy state, we can write the full *term symbol*. This is done by writing the symbol of the value of L (i.e. *S, P, D* ...) with the value of $(2S+1)$ as a left-superscript and the value of J as a right-subscript. Thus, the electronic ground state of carbon is 3P_0 ('triplet P zero') denoting $L = 1$, $(2S+1) = 3$ (i.e. $S = 1$) and $J = 0$. Different values of J denote different

levels within the term, i.e. $(2S+1)L_{J_1}, (2S+1)L_{J_2}, \dots$, the levels having different energies. Inorganic chemists often omit the value of J and refer to a $(2S+1)L$ term; we shall usually follow this practice in this book.

Now we look in detail at the electronic ground states of atoms with $Z = 1$ to 10.

Hydrogen ($Z = 1$)

A hydrogen atom has an electronic configuration of $1s^1$; for the electron, $l = 0$ so L must be 0 and, therefore, we have an S term. The total spin quantum number $S = \frac{1}{2}$ so $(2S+1) = 2$ (a doublet term). The only possible value of J is $\frac{1}{2}$, and so the term symbol for the hydrogen atom is $^2S_{1/2}$.

Helium ($Z = 2$)

For helium ($1s^2$), both electrons have $l = 0$, so $L = 0$. Two electrons both with $n = 1$ and $l = 0$ must have $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$, so $S = 0$ and $(2S+1) = 1$ (a singlet term). The only value of J is 0, and so the term symbol is 1S_0 . Thus, the ns^2 configuration, having $L = 0$, $S = 0$, and $J = 0$ will contribute nothing to the term symbol in lithium and later atoms. The same conclusion can be drawn for any np^6 configuration and the reader is left to confirm this statement.

Lithium ($Z = 3$) and beryllium ($Z = 4$)

Atomic lithium has the electronic configuration $1s^2 2s^1$, and its term symbol is the same as that for hydrogen, $^2S_{1/2}$. Similarly, the term symbol for beryllium ($1s^2 2s^2$) is the same as that for helium, 1S_0 .

Boron ($Z = 5$)

For boron ($1s^2 2s^2 2p^1$) we need only consider the p electron for reasons outlined above. For this, $l = 1$ so $L = 1$ (a P term); $S = \frac{1}{2}$ and so $(2S+1) = 2$ (a doublet term). J can take values $(L+S), (L+S-1) \dots |L-S|$, and so $J = \frac{3}{2}$ or $\frac{1}{2}$. The term symbol for boron may be $^2P_{3/2}$ or $^2P_{1/2}$.

Carbon ($Z = 6$)

For carbon ($1s^2 2s^2 2p^2$), only the p electrons need be considered, and each has $l = 1$. Values of m_l may be $+1, 0$ or -1 , and the algebraic sum of m_l for the individual electrons gives values of $L = 2, 1$ or 0 (D, P or S terms respectively). The two electrons may be spin-paired or have parallel spins and so $S = 0$ or 1 , giving $(2S+1) = 1$ (singlet term) or 3 (triplet term). It might seem that J could be $3, 2, 1$ or 0 , but this is not so. If, for example, the two electrons each have $n = 2, l = 1$ and $m_l = 1$ (giving $L = 2$), they cannot both have $m_s = +\frac{1}{2}$ as this would violate Pauli's principle. The only allowed combinations of m_l and m_s (and corresponding values of M_L and M_S) for two p electrons with the same value of n are shown in the table; such combinations are called *microstates*.

Table: Microstates for two electrons in an np level: values of m_l and m_s (represented as paired or unpaired electrons) and resultant values of M_L, M_S and M_J .

$m_l = +1$	$m_l = 0$	$m_l = -1$	M_L	M_S	M_J
$\uparrow\downarrow$			2	0	2
	$\uparrow\downarrow$		0	0	0
		$\uparrow\downarrow$	-2	0	-2
\uparrow	\uparrow		1	1	2
\uparrow		\uparrow	0	1	1
	\uparrow	\uparrow	-1	1	0
\downarrow	\downarrow		1	-1	0
\downarrow		\downarrow	0	-1	-1
	\downarrow	\downarrow	-1	-1	-2
\uparrow	\downarrow		1	0	1
\downarrow	\uparrow		1	0	1
\uparrow		\downarrow	0	0	0
\downarrow		\uparrow	0	0	0
	\uparrow	\downarrow	-1	0	-1
	\downarrow	\uparrow	-1	0	-1

Inspection of the table reveals the following:

- the 15 microstates can be grouped into three sets, with the proviso that no set can contain a repetition;
- there is a set of 5 microstates with $M_L = 2, 1, 0, -1, -2$ and $M_S = 0$ (and thus $M_J = 2, 1, 0, -1, -2$) corresponding to $L = 1$ and a D term; moreover, since $S = 0$ (singlet) and $J = 2$, the term symbol is 1D_2 ;
- there is a set of 9 microstates with $M_L = 1, 0, -1$ and $M_S = 1, 0, -1$ which can be assigned the term 3P (because $L = 1$ and $S = 1$);
- further examination of this last set of microstates reveals that it can be subdivided into a set of 5 with $J = 2$ (term symbol 3P_2), a set of 3 with $J = 1$ (3P_1), and a single entry with $J = 0$ (3P_0);
- one entry in the table remains unaccounted for and has $M_L = 0, M_S = 0$ and $M_J = 0$, corresponding to the term 1S_0 .

We have, of course, no means of telling which entry with $M_L = 0$ and $M_S = 0$ should be assigned to which term (or similarly, how entries with $M_L = 1$ and $M_S = 0$, or $M_L = -1$ and $M_S = 0$ should be assigned). Indeed, it is *not* meaningful to do so.

Of the five terms that we have denoted for carbon ($^1D_2, ^3P_2, ^3P_1, ^3P_0$ and 1S_0), the one with the lowest energy is 3P_0 and this is the electronic ground state. The others are excited states; notice that *Hund's rules do not always apply to excited states*.

Nitrogen to neon ($Z = 7-10$)

A similar treatment for the nitrogen atom shows that the $2p^3$ configuration gives rise to $^4S, ^2P$ and 2D terms. For the $2p^4$ configuration (oxygen), we introduce a useful simplification by considering it as $2p^6$ plus two positrons which annihilate two of the electrons. Since positrons differ from electrons only in charge, the terms arising from the np^4 and np^2 configurations are the same. Similarly, np^5 is equivalent to np^1 . This

positron or *positive hole* concept is very useful and can be extended to nd configurations.

Relative energies of terms and levels

In regard to relative energies of terms, we state all of Hund's rules in a formal way. It is found from analysis of spectroscopic data that, provided that Russell–Saunders coupling holds:

- the term having the highest spin multiplicity (highest value of S) is the most stable (lowest energy);
- if two or more terms have the same value of S , the term having the higher value of L is the more stable;
- for all terms having the same values of S and L , the level with the lowest value of J is the most stable if the sub-shell is less than half-filled, and the level with the highest value of J is most stable if the sub-shell is more than half-filled (if the sub-shell is half-filled and S has the highest possible

value, $L = 0$ and $J = S$).

Thus for the terms corresponding to the electronic configuration np^2 (1D_2 , 3P_2 , 3P_1 , 3P_0 and 1S_0 , see above, that of lowest energy is 3P and the level of lowest energy is 3P_0 .

Further reading

For a detailed, but readable, account of state symbols which includes j - j coupling, see: M. Gerloch (1986) *Orbitals, Terms and States*, Wiley, Chichester.

A good introduction to term symbols is included in Chapter 13 of: P.W. Atkins (1998) *Physical Chemistry*, 6th edn, Oxford University Press, Oxford.

A related topic not covered in this book is term symbols for diatomic molecules; an extremely good summary is: M.L. Campbell (1996) *Journal of Chemical Education*, vol. 73, p. 749.

d^{10} configuration by replacing one electron by a positive hole; thus, whereas the d^1 configuration contains one electron, d^9 contains one 'hole' (see Box 20.5). For a d^9 ion in an octahedral field, the splitting diagram is an inversion of that for the octahedral d^1 ion. This relationship is shown in Figure 20.17 (an *Orgel diagram*) where the right-hand side describes the octahedral d^1 case and the left-hand side, the octahedral d^9 ion.

Just as there is a relationship between the d^1 and d^9 configurations, there is a similar relationship between the d^4 and d^6 configurations. Further, we can relate the four configurations in an octahedral field as follows. In the weak-field limit, a d^5 ion is high-spin and spherically symmetric, and in this latter regard, d^0 , d^5 and d^{10} configurations are analogous. Addition

of one electron to the high-spin d^5 ion to give a d^6 configuration mimics going from a d^0 to d^1 configuration; likewise, going from d^5 to d^4 by adding a positive hole mimics going from d^{10} to d^9 . The result is that the Orgel diagram for octahedral d^1 and d^6 ions are the same, as are the diagrams for octahedral d^4 and d^9 (Figure 20.17).

Figure 20.17 also shows that the diagram for a d^1 or d^9 ion is inverted by going from an octahedral to tetrahedral field. Because the Orgel diagram uses a single representation for octahedral and tetrahedral fields, it is not possible to indicate that $\Delta_{\text{tet}} = \frac{4}{9}\Delta_{\text{oct}}$. Tetrahedral d^4 and d^6 ions can also be represented on the same Orgel diagram.

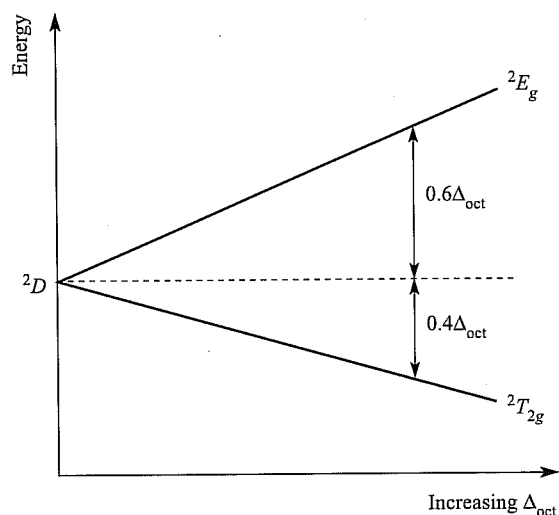


Fig. 20.16 Energy level diagram for a d^1 ion in an octahedral field.

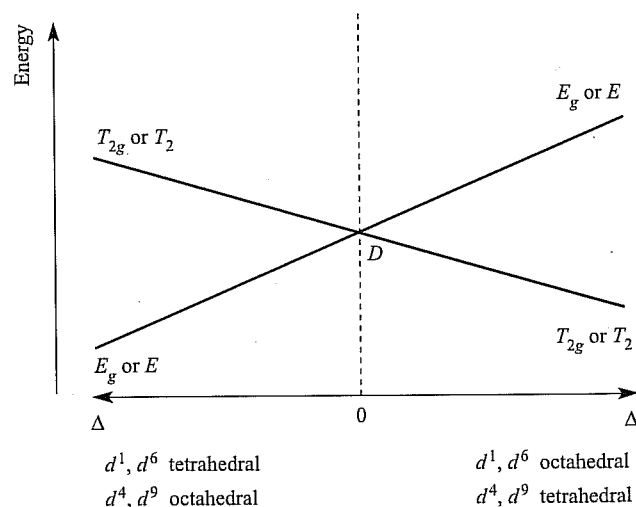


Fig. 20.17 Orgel diagram for d^1 , d^4 (high-spin), d^6 (high-spin) and d^9 ions in octahedral (for which T_{2g} and E_g labels are relevant) and tetrahedral (E and T_2 labels) fields. In contrast to Figure 20.16, multiplicities are not stated because they depend on the d^n configuration.