

Dr. Ajay Kumar Das
Associate Professor
Department of Chemistry
MLT College, Saharsa
ajaykumardas518@gmail.com
9431863881

REVIEW OF ATOMIC TERM SYMBOLS

I. The Meaning of an Atomic Term Symbol

Because the operators \hat{L}^2 , \hat{S}^2 , $\hat{J}^2 \equiv (\hat{L} + \hat{S})^2$, and \hat{J}_z all commute with the atomic Hamiltonian, \hat{H} , and with each other in the limit of negligible spin-orbit coupling, it is possible to classify the eigenfunctions of this Hamiltonian according to the L , S , J , and M_J quantum numbers which define the eigenvalues of these operators, respectively. In common parlance these quantum numbers are called the "good" quantum numbers because the eigenfunctions of the Hamiltonian, \hat{H} , are also eigenfunctions of these operators. Thus, these operators represent quantities which for a given energy level are precisely known with no uncertainty whatsoever. (Again, this is valid only in the limit of small spin-orbit coupling). The resulting eigenvalues can then be used to classify the eigenfunction in question. If we neglect M_J , we can summarize these good quantum numbers for an atomic eigenfunction in the general form of $^{(2S+1)}L_J$. This representation of the atomic eigenfunction really has two parts. The first is the $^{(2S+1)}L$ portion which defines the *term* for the atomic eigenfunction and is known as the *term symbol*. The value of J , appended as a right subscript, defines the *level*. Further specifying the M_J quantum number would define the *state* for the atomic eigenfunction. In principle, then, it should be straightforward to classify an atomic eigenfunction with $S=1$, $L=2$, and $J=1$ by an atomic term symbol written as 32_1 . By a long tradition stretching back to the time when atomic spectroscopy was ignorant of the full quantum nature of the atom, however, this is not the way atomic term symbols are written. Instead, the numerical value of L is replaced with a unique capital letter according to the code shown in the following table.

Value of L	-----	0	1	2	3	4	5
Term Symbol Code	-----	S	P	D	F	G	H

Using this code, the same eigenfunction would be classified with the atomic term symbol 3D_1 , which should be read as "triplet d one."

There is another operator of relevance to atomic term symbols that commutes with the atomic Hamiltonian (even with spin-orbit coupling considered). This is the operator for the inversion of the atom-fixed coordinates of all electrons through the center of mass of the atom, which is the nucleus for all practical purposes. This operator is denoted \hat{i} , and when it is allowed to act on an atomic eigenfunction the result is either +1 or -1. If the result is +1, the eigenfunction is designated as "g" (gerade or even); whereas, if the result is -1 the eigenfunction is designated "u" (ungerade or odd). Unlike orbital angular momentum, spin, and total angular momentum, we do not give the eigenvalue of \hat{i} the symbol i . Instead, we call this eigenvalue the *parity* of an atomic eigenfunction. The parity of an atomic eigenfunction is designated in an atomic term symbol as a right subscript "g" or "u". If both J and parity are to be designated, the value of J is typically listed first, followed by a comma and then the parity. There is an alternate notation that does not use the "g" and "u" labels but instead denotes ungerade terms with a right superscript "o" and leaves the gerade terms unmodified. This is the notation I will most frequently use.

Two essential concepts necessary for a full understanding of atomic term symbols are (1) that the angular momenta operators \hat{L} , \hat{S} , and \hat{J} are vectors and (2) that the quantum numbers L , S , and J designate the length of these vectors, respectively. Because L , S , and J designate the length of vectors, the value of J can be found from L and S only by using vector addition on L and S . The resultant allowed values for J , given L and S , are specified by $|L - S| \leq J \leq L + S$. In the absence of spin-orbit coupling all of the various J levels deriving from a given atomic term (a given set of values for L and S) will be degenerate. It is only the existence of spin-orbit coupling that leads to a splitting of the atomic *term* into its J *levels*. If spin-orbit coupling is sufficiently strong, however, it is no longer appropriate to consider L and S as good quantum numbers. The \hat{L}^2 and \hat{S}^2 operators no longer commute with the full Hamiltonian for the atomic system which must now contain a significant spin-orbit term. This is because the spin-orbit interaction can mix states differing by one unit in L and S . In practice this does not occur to a significant degree until one reaches heavier elements. In such cases the only operators which still commute with the Hamiltonian including spin-orbit interaction are \hat{J}^2 and inversion, \hat{i} , so the only remaining good quantum numbers are J and

parity. As a result the electronic states of some of the heavier elements are just denoted by $J_{g/u}$ or by J and a superscript "o" for ungerade states.

II. Derivation of Atomic Term Symbols from Electronic Configurations

A. The combination of term symbols assigned for the occupied subshells

The various atomic term symbols which derive from a given electronic configuration may be obtained by breaking the electronic configuration up into its component subshells, assigning term symbols to each, and then combining the term symbols using vector addition. For example, an excited configuration of carbon is the $1s^2 2s^2 2p^1 3d^1$ configuration. By examining the individual subshells we see that the atom may be broken up into a $1s^2$ subshell, a $2s^2$ subshell, a $2p^1$ subshell, and a $3d^1$ subshell. Now that the configuration has been broken up into its component subshells, we must assign term symbols to each. In this case the $1s^2$ subshell is a closed subshell so it has no net spin ($S=0$, $2S+1=1$) or orbital angular momentum ($L=0$). The term symbol for this subshell configuration is therefore 1S . Likewise, the $2s^2$ subshell also gives a 1S term symbol. The $2p^1$ subshell has a single unpaired electron which means that it possess non-zero spin ($S=1/2$, $2S+1=2$), and because the electron is in a p orbital it possess one unit of orbital angular momentum ($L=1$). The p orbital wavefunction changes sign when all the coordinates are inverted through the nucleus which means that the wavefunction is odd, or ungerade. All of this information about the $2p^1$ subshell can be summarized by the term symbol $^2P^o$. By a similar analysis the $3d^1$ subshell gives the term symbol 2D ($S=1/2$, $L=2$). We can now combine all of these term symbols for the four different subshells (1S , 1S , $^2P^o$, 2D) by doing three things.

First, we take the vector sum of all the values of S to obtain all the possible resultant values of S . The vector sum of $(0+0+1/2+1/2)$ is simply $|1/2 - 1/2| \leq S \leq 1/2 + 1/2$ which means that the resultant value of S can range from 0 to 1 in steps of one. This means that S can only be 0 or 1, $S=0$ or 1. Note that we do not need to consider the $S = 0$ subshells because they will leave the total S unaltered. In a similar fashion we next need to find the vector sum of the L values for each subshell. The vector sum of $(0+0+1+2)$ is

$|1 - 2| \leq L \leq 1 + 2$ which means that L can range from 1 to 3 in steps of 1. In other words, $L = 1, 2, \text{ or } 3$. Finally, we need to find the combined parity by multiplying the parities of the individual subshells. The following rules for multiplying parities should be remembered:

$$g \times g = g \quad g \times u = u \quad u \times g = u \quad u \times u = g.$$

In our example, we need to multiply $g \times g \times u \times g$. The multiplication is associative so we can straight away write down that the result is u . All the terms will be odd in parity.

At this point we have all the information necessary to write down the term symbols that result from the atomic configuration $1s^2 2s^2 2p^1 3d^1$ of carbon. Before doing so it is important to keep in mind that the p and d electrons are independent in the sense that nothing restricts the orientation of their spins relative to each other. In other words, it is perfectly possible for both electrons to be spin up because no Pauli principle applies to them. Because this is the case, each of the possible spins determined above (0 and 1) can combine with each of the possible orbital angular momenta (1, 2, and 3) to give the possible term symbols for this configuration. And, of course, all the terms will be odd in parity. The terms that result from the configuration $1s^2 2s^2 2p^1 3d^1$ are thus $^1P^\circ$, $^1D^\circ$, $^1F^\circ$, $^3P^\circ$, $^3D^\circ$, and $^3F^\circ$.

I have presented this in this way so that you can see how to combine subshells and generate term symbols for more complicated configurations. For example, many of the excited states of palladium derive from the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^8 5s^1 5p^1$ configuration. Because the lowest energy term of the $4d^8$ configuration is 3F (something you will be able to determine for yourself after reading this entire review), you can deduce that the lowest energy terms of this configuration in palladium derive from a coupling of the partially filled $4d^8$, 3F subshell with the $5s^1$ (2S) and the $5p^1$ ($^2P^\circ$) subshells of the atom.

Another reason for presenting this in this way is that it makes it absolutely clear why we don't need to consider the closed shells of a configuration. These always have $S=0$ and $L=0$ and gerade (even) parity. As such, they contribute nothing to the total S , L , or parity of the overall atom and may be ignored.

B. Partially filled subshells

When one is dealing with partially filled subshells as in the $1s^2 2s^2 2p^2$ ground configuration of the carbon atom or the $4d^8$ subshell of palladium, one cannot simply consider all possible angular momentum couplings of the two $2p$ electrons (or the eight $4d$ electrons). This is because the electrons are in the same subshell and the Pauli principle will prevent some of the angular momentum couplings which might be possible if the electrons were in different subshells. For example, if one were to use the procedure outlined above to derive the possible terms for the ground configuration of the carbon atom one would obtain six possible terms: 1S , 1P , 1D , 3S , 3P , and 3D . This is just not correct, however, because Pauli will forbid some of these terms. These would be the correct set of terms for a configuration in which the two p electrons occupied different subshells such as in the $1s^2 2s^2 2p^1 3p^1$ configuration. The remainder of this section is dedicated to illustrating how the Pauli Principle restricts the allowed term symbols deriving from the configuration in which the two p electrons occupy the same subshell.

Let's first consider all possible arrangements of the $2p^2$ electrons in the three $2p$ orbitals which have $m_l = +1, 0,$ and -1 . Because the first electron can be placed in any of the three orbitals, either spin up or spin down, there are 6 places it can go. The Pauli Principle says the second electron can occupy one of the remaining 5 spin-orbitals, but it absolutely cannot go into the same orbital with the same spin as the first electron. Thus one might expect there to be 6 possible assignments for electron one and 5 for electron two, yielding 30 different possible arrangements of the electrons in the $2p^2$ configuration, but this is incorrect. It is immaterial in which order we assign electron one and electron two to the available orbitals because the electrons are, in fact, indistinguishable. To be precise, we should not be calling them electron *one* and electron *two*. We should refer to them as electron and electron, but this makes it hopelessly difficult to keep track of what we are doing. We therefore must correct our result of 30 possible arrangements by dividing this number by $2!$, to get 15 different electronic arrangements for the $2p^2$ configuration. To convince you this is true, only one example need be given. Consider assigning electron one to the orbital with $m_l = +1$ spin up

and electron two to the orbital with $m_l = 0$ spin down. Because the electrons are indistinguishable, this is exactly the same assignment as electron one in $m_l = 0$ spin down and electron two in $m_l = +1$ spin up. They should *not* be counted as separate arrangements. This is the reason for the division by $2!$.

The following table summarizes all the possible arrangements of electrons in the $2p^2$ configuration in the $2p$ orbitals. The spin of the electrons in each arrangement is indicated by arrows that point either up or down for spin up and spin down. Here, M_L represents the algebraic sum of the value of m_l for each electron while M_S is the algebraic sum of the value of m_s for each electron.

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

By examining this table and noting the highest value of M_L and the highest value of M_S that occurs with this value of M_L (in this case, $M_L = 2$ and $M_S = 0$) we can deduce that the ground configuration of carbon must generate a term with L and S equal to these values of M_L and M_S . Since M_L and M_S are really projections of L and S along some fixed laboratory axis, they can be no larger than the length of their corresponding vector. Remember, L and S are vector lengths. We are deducing that because no greater value of M_L exists, there must be a term with $L=2$. Thus, our $2p^2$ configuration does generate an $L = 2, S = 0$ (1D) term. Moreover, a 1D term generates pairs of (M_L, M_S) values corresponding to $(2,0)$, $(1,0)$, $(0,0)$, $(-1,0)$, and $(-2,0)$. These values result because a vector with length $L = 2$ can have a projection along a laboratory fixed axis of 2, 1, 0, -1, and -2. All such arrangements of

electrons in these orbitals thus constitute the 1D term and must be deleted from further consideration. Accordingly, arbitrarily chosen entries in the table which possess the above listed (M_L, M_S) pairs may be assigned to the 1D term to give the new table listed below:

$m_t = +1$	$\uparrow\downarrow$			\uparrow	\uparrow	\downarrow	\downarrow	\uparrow	\uparrow	\downarrow	\downarrow				
$m_t = 0$		$\uparrow\downarrow$		\uparrow	\downarrow	\uparrow	\downarrow					\uparrow	\uparrow	\downarrow	\downarrow
$m_t = -1$			$\uparrow\downarrow$					\uparrow	\downarrow	\uparrow	\downarrow	\uparrow	\downarrow	\uparrow	\downarrow
M_L	2	0	-2	1	1	1	1	0	0	0	0	-1	-1	-1	-1
M_S	0	0	0	1	0	0	-1	1	0	0	-1	1	0	0	-1
Term	1D	1D	1D		1D								1D		

Next, we need to examine the various remaining entries in the table to locate the largest M_L and the largest M_S that occurs with it. In this case, these are $M_L = 1$ and $M_S = 1$. This implies the existence of an $L = 1, S = 1$ (3P) term. A 3P term generates $(M_L, M_S) = (1,1), (1,0), (1,-1), (0,1), (0,0), (0,-1), (-1,1), (-1,0),$ and $(-1,-1)$. Again, arbitrary entries in the table corresponding to these values may be assigned as 3P to give another revision in the table:

$m_t = +1$	$\uparrow\downarrow$			\uparrow	\uparrow	\downarrow	\downarrow	\uparrow	\uparrow	\downarrow	\downarrow				
$m_t = 0$		$\uparrow\downarrow$		\uparrow	\downarrow	\uparrow	\downarrow					\uparrow	\uparrow	\downarrow	\downarrow
$m_t = -1$			$\uparrow\downarrow$					\uparrow	\downarrow	\uparrow	\downarrow	\uparrow	\downarrow	\uparrow	\downarrow
M_L	2	0	-2	1	1	1	1	0	0	0	0	-1	-1	-1	-1
M_S	0	0	0	1	0	0	-1	1	0	0	-1	1	0	0	-1
Term	1D	1D	1D	3P	1D	3P	3P	3P	3P		3P	3P	1D	3P	3P

Finally we note that there is one unassigned state left in the table, corresponding to $M_L = 0$ and $M_S = 0$. This must be due to a 1S term, which gives only this one (M_L, M_S) combination. It is designated as the 1S term in the final revision of the table:

$m_l = +1$	$\uparrow\downarrow$			\uparrow	\uparrow	\downarrow	\downarrow	\uparrow	\uparrow	\downarrow	\downarrow				
$m_l = 0$		$\uparrow\downarrow$		\uparrow	\downarrow	\uparrow	\downarrow					\uparrow	\uparrow	\downarrow	\downarrow
$m_l = -1$			$\uparrow\downarrow$					\uparrow	\downarrow	\uparrow	\downarrow	\uparrow	\downarrow	\uparrow	\downarrow
M_L	2	0	-2	1	1	1	1	0	0	0	0	-1	-1	-1	-1
M_S	0	0	0	1	0	0	-1	1	0	0	-1	1	0	0	-1
Term	1D	1D	1D	3P	1D	3P	3P	3P	3P	3P	1S	3P	3P	1D	3P

Note that these designations of the entries in the table as 1D , 1S , or 3P does not mean that the particular orbital occupations indicated by the arrows correspond to these term symbols. All that one can really state definitely about any particular orbital occupation indicated by the arrows are what the resulting values of M_L and M_S are. Thus, for example, the first entry in the table corresponding to $(M_L, M_S) = (2, 0)$ must correspond to a 1D term, since none of the other terms gives $M_L = 2$. On the other hand, there are three entries in the table with $(M_L, M_S) = (0, 0)$, and one of these arises from 1D , one from 1S , and one from 3P . There is no way (at this point) to tell which is which. In fact, the $M_L = 0$, $M_S = 0$ state arising from the 1D term is a linear combination of these three orbital occupations, the $M_L = 0$, $M_S = 0$ state arising from the 1S term is a different linear combination of these three orbital occupations, and the $M_L = 0$, $M_S = 0$ state arising from the 3P term is yet another linear combination of the same three orbital occupations.

The net result of all this is that the $2p^2$ configuration gives only the 1S , 3P , and 1D terms, while the $2p^13p^1$ configuration gives 1S , 1P , 1D , 3S , 3P , and 3D terms. The fact that the two p electrons are in the same subshell in the $2p^2$ configuration causes some of the terms

which occur in the $2p^13p^1$ configuration to be forbidden due to the Pauli exclusion principle. Thus, the procedure for determining the terms deriving from a partially filled subshell are as follows:

1. Tabulate all the possible arrangements of electrons in the orbitals in question in a manner consistent with the Pauli principle.
2. Find the value of M_L and M_S for each arrangement.
3. Find the largest value of M_L and the largest M_S that goes with it.
4. Allow $L = M_L$ and $S = M_S$ and assign this L,S pair to the appropriate term.
5. Find all other M_L, M_S pairs that can arise from the previously determined L,S pair (term) and arbitrarily assign table entries with these same M_L, M_S pairs to the same term until all pairs for this term have been assigned.
6. Return to step 3 and continue repeating until all entries have been assigned.

If one were to carry out this procedure for any possible configuration of p and d electrons one would arrive at the following list of terms.

<u>Configuration</u>	<u>Terms</u>
p^2, p^4	$^1S, ^1D, ^3P$
p^3	$^2P^o, ^2D^o, ^4S^o$
d^2, d^8	$^1S, ^1D, ^1G, ^3P, ^3F$
d^3, d^7	$^2P, ^2D$ (2 terms), $^2F, ^2G, ^2H, ^4P, ^4F$
d^4, d^6	1S (2 terms), 1D (2 terms), $^1F, ^1G$ (2 terms), $^1I, ^3P$ (2 terms), $^3D, ^3F$ (2 terms), $^3G, ^3H, ^5D$
d^5	$^2S, ^2P, ^2D$ (3 terms), 2F (2 terms), 2G (2 terms), $^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$

It is useful to note that if one does not remember this table or have it available, the terms for configurations such as d^8 can be derived easily by considering only the holes in the d shell. The terms that arise are exactly the same.

Finally, one may note that the parity of the terms arising from a partially filled subshell is easily determined by counting the number of electrons in orbitals of odd parity (i.e., p, f, h

orbitals). If this number is odd, then the parity of the resulting terms is odd or ungerade (as in the p^3 configuration listed above). If it is even, the parity of the resulting terms is even or gerade (as in the p^2 configuration considered above).

III. Counting States

It is absolutely imperative that the reader keep in mind that in all of this manipulation (prestidigitation to some) the total number of atomic *states* has remained the same, conserved. Another way to say this is that a given atomic configuration has a distinct number of (J, M_J) pairs that never changes no matter how we classify them. Since the determination of the terms that arise from a given configuration can often become a tedious process it is prone to errors. It would be beneficial to have a means of quickly checking to make sure that the results are at least consistent, i. e., that the number of states is always conserved. In particular, when initially writing down all the possible electron arrangements in a set of orbitals as in the table in section II B, it would be nice to know before beginning this process how many are expected so as to avoid missing any. The following sections have as their goal to give the reader the necessary tool to check for this consistency: the ability to count states.

A. Counting of states for configurations

To count up the number of states deriving from a given configuration, one should multiply the number of states arising from each subshell. In this regard closed subshells contribute only one state because there is only one possible arrangement of electrons within the subshell. Again, we see that closed subshells can be ignored. For partially occupied subshells the general procedure is shown by example in what follows.

Let us consider the $2p^3$ subshell. The first electron can be placed in any one of the 6 possible spin-orbitals. The second electron only has five places it can be placed while the third and final electron can only be placed in one of four remaining spin-orbitals. This results in $6 \times 5 \times 4 = 120$ possible arrangements for these three electrons. This over counts the number of states, however, because the three electrons are indistinguishable. Using the same set of

three spin-orbitals originally assigned to the three electrons, there are $3!$ ways of labeling them that are all identical because the electrons are identical. Thus the above result of 120 must be divided by $3!$ to account for this. The number of states arising from the $2p^3$ configuration is thus $(6 \times 5 \times 4) / 3! = 20$.

This general procedure can be used to count the number of possible ways of arranging the electrons in any partially filled subshell. For example, a $4f^2$ subshell will give rise to $(14 \times 13) / 2! = 91$ states.

That takes care of determining the total number of states arising from a given subshell. To obtain the total number of states for a complete configuration, simply multiply the number of states arising from each partially filled subshell. Thus, the $[...]4d^85s^15p^1$ configuration of palladium that we considered earlier contains $[(10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3) / 8!] \times 2 \times 6 = 540$ states.

B. Counting of states for terms

A term is specified by $^{(2S+1)}L$. It corresponds to values of M_S ranging from $-S$ to S which gives $2S+1$ different values of M_S (which is why the value of $2S+1$ is called the multiplicity or spin multiplicity of a term). It also gives rise to values of M_L ranging from $-L$ to L , again, $2L+1$ altogether. Thus, the number of states deriving from a given term is simply $(2S+1) \times (2L+1)$. When the possible terms arising from a given configuration are determined, the number of states arising from them had better match the number of states calculated from the configuration. The number of states hasn't changed, only their classification.

C. Counting of states for levels

A level is specified by $^{(2S+1)}L_J$. Now, the various possible values of M_L and M_S states can no longer be specified because L and S have been coupled to give a state of definite J . In this case the number of states deriving from the level is simply specified by the number of possible values of M_J . Since M_J can range from $-J$ to J , the number of states deriving from a given level is $2J + 1$.

D. Conservation of the number of states

In the $2p^2$ configuration considered in section II B, it was found that there were 15 distinct entries in the table, corresponding to the 15 distinct states that arise from this configuration. However, this configuration also yielded the terms 1S , 3P , and 1D . These terms should together also give 15 states. This can be tested using the $(2S + 1) \times (2L + 1)$ rule.

$$\begin{array}{ll}
 ^1S \text{ gives } 1 \times 1 = 1 \text{ state} & \\
 ^3P \text{ gives } 3 \times 3 = 9 \text{ states} & \\
 ^1D \text{ gives } 1 \times 5 = 5 \text{ states} & \\
 \text{Altogether:} & 15 \text{ states, as expected}
 \end{array}$$

When considering the possible J values, the 1S state has $S=0$, $L=0$, so J must be 0. The 3P state has $S=1$, $L=1$, so J must fall in the range $|1 - 1| \leq J \leq 1 + 1$, giving $J = 0, 1$, or 2. For the 1D state $S=0$ and $L=2$ so $J=2$ is the only value that can result. For each level the number of states that arises is $2J + 1$. We therefore obtain:

$$\begin{array}{ll}
 ^1S_0 & 2J+1 = 1 \text{ state only (as found for the } ^1S \text{ term above)} \\
 ^1D_2 & 2J+1 = 5 \text{ states (as found for } ^1D \text{ term above)} \\
 ^3P_2 & 2J+1 = 5 \text{ states} \\
 ^3P_1 & 2J+1 = 3 \text{ states} \\
 ^3P_0 & 2J+1 = 1 \text{ state}
 \end{array}$$

The new number of states coming from the 3P term is then $5 + 3 + 1 = 9$, just as found when using the $(2L+1) \times (2S+1)$ rule on the 3P term. In addition, the total number of states generated here based on the $2J+1$ rule is 15, just as it was for the terms, and just as it was for the configuration. If the states determined in these three ways do not agree, a mistake has been made somewhere along the line.

IV. Energy ordering of terms and levels

We now come to quite a different problem. In the absence of any laboratory electric or magnetic field, all the states in a given level are degenerate. If there were no spin-orbit coupling, all the levels of a given term would be degenerate. If we stretch our imaginations

even further and explore what would happen in the absence of electron-electron repulsion we would find that all terms arising from a given configuration would be degenerate as well. Only the configuration would determine the energy. As we turn on electron-electron repulsions the terms in a configuration split out to different energies. The question becomes, how do they split? Which is lowest in energy? Moreover, when spin-orbit coupling is turned on the levels in a given term from a given configuration again split out to different energy. How do these split? Though these splittings could be calculated by *ab initio* means, it would be found that a pattern develops if one does such a calculation for a large number of configurations. This pattern can be summarized by a set of rules that were first set forth by Felix Hund. Because it is easier to carry around a few general rules than a computer, these rules, Hund's Rules, are reproduced below:

- (i) For terms deriving from a given configuration, the term of highest S will lie lowest in energy.
- (ii) For more than one term deriving from a given configuration, all having the highest possible value of S, the term having the highest L (and S) will lie lowest in energy.
- (iii) For terms having a spin-orbit splitting, the states will be ordered with the lowest J values lying lowest in energy if the subshell responsible for the splitting is less than half-full; the states will be ordered with the highest J value lying lowest in energy if the subshell responsible for the splitting is more than half-full.

It should be noted that although we would like to know in what order the terms from a given configuration lie, Hund's rules do not tell us. The first two rules only allow us to make a prediction about which term will be the lowest in energy. They simply state that we should search for the largest value of S and then, within that subset of terms, search for the highest value of L. That is then the lowest energy term. These rules make no prediction about the ordering of the remaining terms whatsoever.

So, for the $2p^2$ configuration we originally considered in section II B, we can now predict that the 3P term will be lowest in energy and that the levels will split out in increasing energy in the order 3P_0 , 3P_1 , 3P_2 . We can say absolutely nothing about the ordering of the 1D and 1S terms arising from this configuration except that they will lie somewhere above the 3P term.