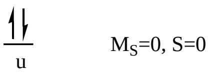
Determination of atomic term symbols of “equivalent electrons” using spin arrangement diagrams

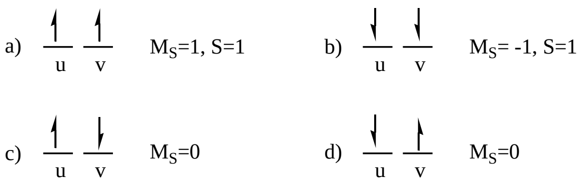
The diagrams below show one electron in orbital u with α spin (left), and with β spin (right)

If there are 2 electrons in the same orbital, their spin orientations (i.e their m_s values) must be opposite due to Pauli principle; we say that the 2 electrons are spin-paired. This case is shown below.



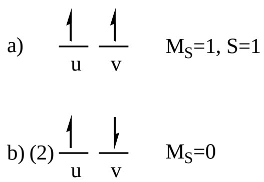
The total M_S value is obtained by adding m_s values of individual electrons: M_S=1/2+(-1/2)=0. Thus when an orbital is doubly occupied, the only allowed value of S is 0 (singlet).

When 2 electrons are in two separate orbitals u and v, we depict the possible spin arrangements as shown below.



In case (a), M_S=1; therefore S has to be 1, and if S=1, then M_S must be 1, 0, and -1. Case (b) shows the M_S=-1 spin arrangement ; there must also be an M_S=0 belonging to this S=1 triplet state. Cases (c) and (d) depicts two different spin arrangements with M_S=0; one of these should belong to S=1, leaving the other to a lower S value, namely S=0. In conclusion, when 2 electrons are in 2 different orbitals, there are two possible values for the total spin quantum number: S=1 and S=0 are both allowed.

A note about avoiding too many drawings: drawing of case (b) above is not necessary because we know that if M_S=1, there must also be M_S=-1 spin configuration; further, we will indicate the two cases (c) and (d) by using just one of them and indicating how many spin arrangements there are by an integer in parantheses.

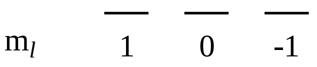


Instead of drawing 4 diagrams, just 2 diagrams are sufficient for the purpose here.

In the following we will not draw spin arrangements for negative M_S values; in cases involving electrons in different orbitals with opposite spins (i.e. unpaired α spins, and unpaired β spins both present), we will indicate the number of different spin arrangements by putting an integer within a parantheses before the diagram as exemplified above.

Term symbols for p^2 configuration

There are 3 p orbitals: p_1, p_0, and p_{-1}; these space orbitals are represented by the diagram below.

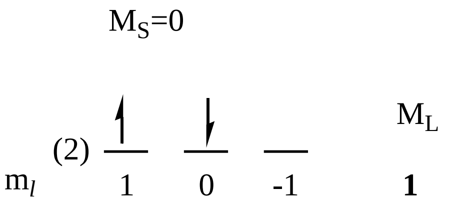


The two electrons are placed in this diagram to give maximum M_S value.

The two spins must be paralel, and in different orbitals; in placing the spins into the orbitals we made sure to obtain maximum M_L, which is obtained by adding m_l values of the electrons (i.e. 1+0=1). Since only 1 diagram can be drawn with M_S=1, M_L=1, we conclude that S must be 1, and also L must be 1. We should remember that when S=1, M_S=1,0,-1 components must all exist; same remark is true for L=1 and its components M_L=1,0,-1. The diagram above shows only the case with M_S=1, M_L=1; diagrams with other (M_S,M_L) combinations will appear below.

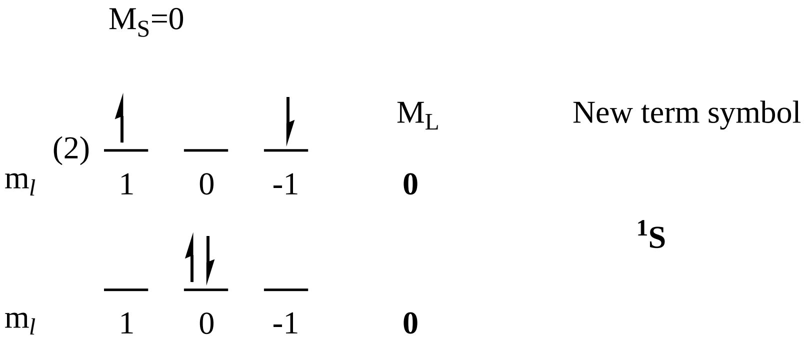
Now we consider M_S=0 spin arrangement; the two spins must have opposite directions. The diagram with highest M_L=2 for M_S=0 is given below.

There is only 1 diagram with M_L=2 and M_S=0; we conclude that L must be 2, and S=0, giving the ^{1}D term. Next we draw diagrams with M_L=1 for the M_S=0 case.



This diagram contains 1 unpaired α spin, and 1 unpaired β spin. The “2” in paranthesis indicates that there are 2 different spin arrangements. We expect 1 state with M_L=1 from the L=2, ^{1}D term; and another from the L=1, ^{3}P term with M_S=0; thus the total number of states expected for (M_L=1, M_S=0) is 2, and the above diagram shows only 2 spin arrangements. We conclude that no new term is present.

Now we consider the M_L=0 case with M_S=0; the spin diagrams are shown below.



There are 3 spin arrangements for M_L=0 and M_S=0; one of them must arise from ^{3}P term, another from ^{1}D; the third one signals the presence of a new term. Since M_S=0, S must be 0; similarly, since M_L=0, L must also be 0, giving the ^{1}S term.

It is not necessary to consider spin arrangements with negative values of M_S or M_L; they can be drawn, but they do not give additional term symbols.

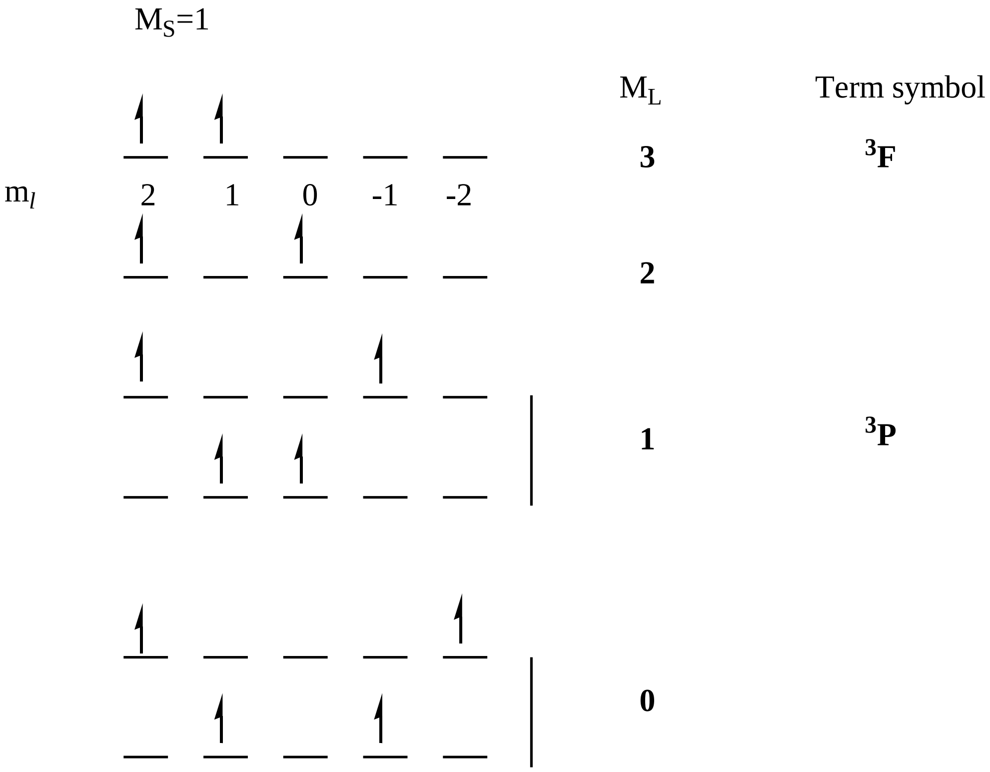
Our final result is that the term symbols for the p^2 configuration are: ^{1}D, ^{3}P, and ^{1}S. The number of states for a given term is (2S+1)(2L+1). Thus ^{1}D represents (1)(5)=5 states, ^{3}P has (3)(3)=9, and ^{1}S has (1)(1)=1. The total number of states from all terms is 5+9+1=15; this number is the total number of Pauli allowed states arising from the p^2 electron configuration. There is an independent check for this total number: in general, if $n_{max}=2(2l+1)$ is the maximum occupation number of a subshell l, the total number of Pauli allowed states from a configuration l^n is given by:

$$\binom{n_{max}}{n} = \frac{(n_{max})!}{(n_{max}-n)!\,n!}$$

For the p^2 configuration, n=2, n_{max}=6, and the above expression gives 15; it is the same total, as obtained by adding number of states arising from ^{1}D, ^{3}P, and ^{1}S terms; thus there are no additional term symbols. According to Hund rule, the term with the lowest energy is ^{3}P.

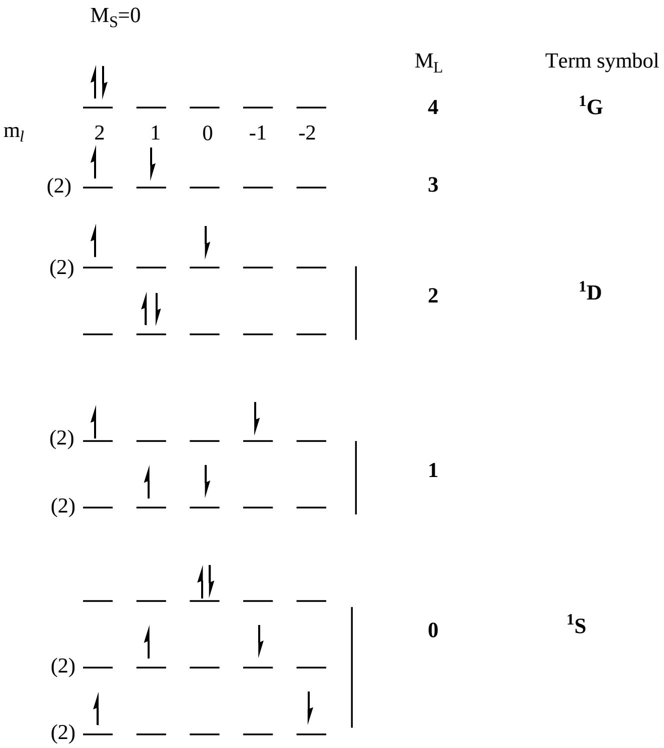
Term symbols for d^2 configuration

The total number of states from the d^2 configuration must be 10!/(8!2!)=45. We always start with the highest M_S value; since, as in the previous example, there are 2 electrons, the highest M_S=1, and the spin diagrams below show the spin arrangements for M_L=3,2,1, and 0.



There is only 1 diagram with M_L=3 and M_S=1, therefore L=3 and S=1, giving ^{3}F term. There is only 1 diagram with M_L=2, this must belong to ^{3}F term; i.e. no new triplet term. There are 2 diagrams with M_L=1: one of them must belong to ^{3}F term, and the other must arise from a new term with L=1, thus giving ^{3}P. There are 2 diagrams for M_L=0; one of them must belong to ^{3}F, and the other to ^{3}P; thus no new term is possible.

Next, we construct spin diagrams for M_S=0; i.e. the two electrons will have anti-parallel spins; they are shown below for M_L=4,3,2,1,0.



There is only 1 spin diagram with M_L=4 and M_S=0; consequently L must be 4, and S must be 0, giving the singlet ^{1}G term.

There are 2 diagrams with M_L=3; one of these must belong to ^{1}G, and the other comes from M_S=0, M_L=3 of ^{3}F term; therefore there is no new term.

There are 3 spin diagrams for M_L=2. Two of them correspond to M_L=2 components of ^{1}G and ^{3}F terms; presence of a 3rd spin diagram indicates that there must be a new term with L=2 and S=0; thus ^{1}D term.

There are 4 diagrams with M_L=1; these correspond to M_L=1, M_S=0 components of ^{3}F, ^{3}P, ^{1}G, and ^{1}D terms; no new term is present.

Finally, for M_L=0, there are 5 spin diagrams: 4 of them correspond to the M_L=0 components of the 4 terms already found; the fifth one indicates that there is new term with L=0 and S=0; thus ^{1}S term.

Let us now verify our results. There must be a total of 45 states, and we should obtain the same number by adding the states contributed by each term: ^{3}F has 21, ^{3}P has 9, ^{1}G has 9, ^{1}D has 5, and ^{1}S has 1 state: the sum: 21+9+9+5+1=45. We have found all of the possible term symbols.

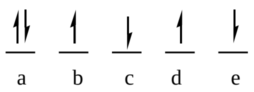
The term with the lowest energy is ^{3}F, according to Hund rule (there are 2 triplet terms here, Hund rule states that the one with larger L value is lower in energy).

This procedure exemplified by the p^2 and d^2 configurations can also be applied to p^3 or d^3, d^4 and d^5 configurations (remember that term symbols of l^n are identical to those of $l^{(n_{max}-n)}$ configuration). We start with the highest possible M_S value and prepare spin digrams for M_L="highest value" down to M_L=0. When a diagram contains unpaired α spins together with unpaired β spins, then there will be a number of equivalent diagrams. Let n_α be the number of <u>unpaired</u> α spins; similarly let n_β be the number of <u>unpaired</u> β spins, in a diagram with a given M_L; the number of equivalent diagrams that can be drawn is

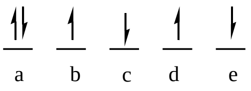
$$n = \frac{(n_\alpha + n_\beta)!}{n_\alpha!\, n_\beta!}$$

We draw only 1 of these n diagrams, and indicate how many, by putting this number (n) before the diagram. Please note that n_α and n_β has no contribution from doubly occupied orbitals.

Example: Consider the following spin diagram with 6 electrons in 5 orbitals.

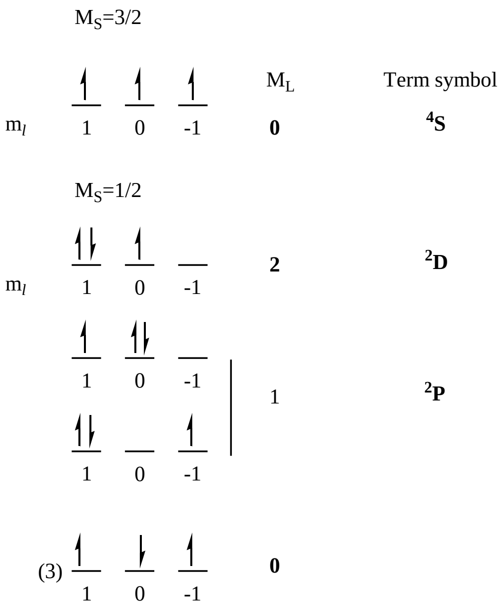


Here, n_α=2, n_β=2; and n=4!/(2!2!)=6. Orbital "a" is doubly occupied; it has no contribution. The 6 spin arrangements is represented by a single diagram

(6) 

We repeat the above procedure by taking the next smaller M_S value, until we cover all nonnegative M_S values. After obtaining the total set of term symbols, the total number of states should be checked as done above.

As a final example let us consider the term symbols arising from p^3 configuration. The total number of Pauli allowed states must be 6!/(3!3!)=20. The spin diagrams are shown below.



The complete set of term symbols is: ^{4}S (4 states), ^{2}D (10 states), and ^{2}P (6 states); the total number of states is 4+10+6=20, and agrees with 6!/(3!3!)=20.

The term with the lowest energy is ^{4}S.