A New Method of Deducing Atomic Spectroscopic Terms

The Method of Number Arrangement

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At present there are three methods for deducing atomic spectroscopic terms of equivalent configurations. They are: the method of progressive extinction (*1–3*), the method of permutation of groups (*4, 5*), and the method of quick computation (*6, 7*). All are complicated and tedious. For example, the f^5 configuration has 26,334 microstates, and people can hardly get the spectroscopic terms by manual calculation. Though an IBM-PC/XT microcomputer can be used to compute the spectroscopic terms, it takes much time, for example, the g^8 configuration takes 96 h. We report a new method that solves the problem of finding the atomic spectroscopic terms of equivalent configuration of multielectrons and can be performed by manual calculation. Up to now, the spectroscopic terms given in the literature are only those for the s^X, p^x, d^x, f^x (*8*) and g^x (*9*) configurations. By use of a computer and the method reported herein, we can determine the spectroscopic terms of h^x, i^x, j^x, k^x, and l^x configurations. The spectroscopic terms of even higher configuration may be calculated if the computer possesses high quality. It takes between 1 and 10 min to deduce all spectroscopic terms for the listed electronic configurations.

Deducing Process

(1) Factor equivalent electron configurations into α and β spin states. For example, the f^5 configuration can be factored into (e_α^5), $(e_\alpha^4)(e_\beta^1)$, and $(e_\alpha^3)(e_\beta^2)$. Do this until the number of *electrons of the two kinds of spin states is equal or the* difference between them is one. The total spin magnet quantum number may be calculated as

$$M_S = \sum_i m_{s_i} \tag{1}$$

For each factored spin-state pair, we only take the values of $M_S \geq 0$.

(2) Compute the M_L values, semimicrostates, and the number of semimicrostates of each α (or β) spin state.

Semimicrostates are different from common microstates. In microstates each orbital may contain electrons of α, β spin states, but for semimicrostates only one electron of α (or β) spin state may be placed in each orbital. The M_L value for a semimicrostate equals the sum of the m_l values of the electrons in the occupied orbitals. Thus,

$$M_L = \sum_i m_{l_i} \tag{2}$$

For example, the $(e_\alpha^3)(e_\beta^2)$ spin-state pair of the f^5 configuration possesses two kinds of spin states and total spin magnet quantum number is $M_S = 3\,{}^1\!/_2 + 2 \times (-{}^1\!/_2) = {}^1\!/_2$. For the three electrons of the e_α^3 semimicrostates of the f^5 configuration, the m_l values line up from the maximum to minimum as 3, 2, 1; hence, the total orbital magnet quantum number is $M_L = 3 + 2 + 1 = 6$. There is only one semimicrostate for the e_α^3 spin state with $M_L = 6$, and it can be represented by using the m_l values 3, 2, 1 of the three electrons. We set 3, 2, 1 as the three digits 321, and this serves to designate the single semimicrostate. To find the number of semimicrostates of $M_L = 5$, subtract 1 from the right most digit of 321, thus leaving 320. Continue the subtraction process since there are no repeat

Table 1. M_L Value of e^i Spin State, the Semimicrostate, and the Semimicrostate Number of 1^N Configuration

Electronic configuration	Type of spin state	M_L value of semimicrostate	Semimicrostate Designation	Number of semimicrostates with that M_L value
p^N	e^1	1	1	1
		0	0	1
d^N	e^1	2	2	1
		1	1	1
		0	0	1
	e^2	3	21	1
		2	20	1
		1	2-1 10	2
		0	2-2 1-1	2
f^N	e^1	3	3	1
		2	2	1
		1	1	1
		0	0	1
	e^2	5	32	1
		4	31	1
		3	30 21	2
		2	3-1 20	2
		1	3-2 2-1 10	3
		0	3-3 2-2 1-1	3
	e^3	6	321	1
		5	320	1
		4	32-1 310	2
		3	32-2 31-1 210	3
		2	32-3 31-2 30-1 21-1	4
		1	31-3 30-2 21-2 20-1	4
		0	30-3 21-3 3-1-2 20-2 10-1	5

digits; thus subtract 1 from the middle digit of 321 to give 311, and finally 221 by subtracting 1 from the left most digit of 321. Since the two semimicrostates 311 and 221 have repeated digits, cancel them; thus, only the 320 semimicrostate is left for $M_L = 5$. Cancel identical semimicrostates whenever they appear. Follow the above method until the m_l of each orbital type is at its minimum value (−3 for f electrons). Repeat the process when the M_L value for each semimicrostate is positive or zero, $M_L = 0$. This produces the results seen in the bottom section of Table 1 for the e_α^3 semimicrostate of the f^N electronic configuration.

According to complementary principle of electrons and holes, the number of semimicrostates produced by the e^i and $e[(21 + 1) - i]$ spin states of the 1^N configuration are the same. For the p^N configuration, the number of semimicrostates produced by the e^i spin state of the p^N configuration is equal to that of e^{3-i} spin state.

(3) M_L^α is used to represent the M_L value of the α spin state; M_L^β that of the β spin state. Here $M_L^\alpha, M_L^\beta \geq 0$. The notation used in the following equation is to set α as the M_L^α value and to set $f(\alpha)$ as the number of M_L^α values. Similarly, set the M_L^β value as β and the number of M_L^β values as $g(\beta)$. A M_L value is designated as i, and the number of M_L values is $h(i)$. Thus we have the following equation.

$$h(i) = \sum_{\alpha+\beta=i} f(\alpha)\cdot g(\beta) + \sum_{\alpha-\beta=i} f(\alpha)\cdot g(\beta) + \sum_{\beta-\alpha=i} f(\alpha)\cdot g(\beta) \qquad (3)$$

$\alpha,\beta \geq 0$ for the first item, $\alpha,\beta > 0$ for the second and third items in the eq 3, and $i = 0, 1, 2, 3, 4, \ldots$.

The M_L value and its corresponding number of α and β spin states are calculated by use of the eq 3, and the M_L and M_S values are used to generate a M_L–M_S matrix (see Table 9), and then the total orbital angular-momentum quantum number L values and its corresponding number are obtained by the M_L values, and finally the atomic spectroscopic terms and its corresponding number are found out by use of the L values and its corresponding number, e.g. $M_L \leq L$.

$$M_L = 5\ (3),\ L = 5\ (3)$$

$$\begin{array}{lcccccc} L = & 0, & 1, & 2, & 3, & 4, & 5 \\ & \mathrm{S} & \mathrm{P} & \mathrm{D} & \mathrm{F} & \mathrm{G} & \mathrm{H} \end{array}$$

Thus we get the atomic spectroscopic term H and its corresponding number 3, i.e., H (3).

Examples

Deduce the spectroscopic terms of the f^5 configuration. Three spin-state pairs arise, and each is analyzed as shown below.

(1) $M_S = 5/2$ set, (e_α^5). (See Table 2, and note that this table is simply generated from the e_α^2 only for the f^N configuration in Table 1 by use of the electron hole correspondence.)
(2) $M_S = 3/2$ set, $(e_\alpha^4)(e_\beta^1)$. (See Tables 3, 4, and 5, and again realize that the e_α^4 is equivalent to the e_α^3 only in Table 1.)
(3) $M_S = 1/2$ set, $(e_\alpha^3)(e_\beta^2)$. (See Tables 6, 7, and 8.)

Now we arrange the number pairs of M_L–M_S found at the bottom of Tables 2, 5, and 8 to form the matrix for the atomic spectroscopic terms. (See Table 9.)

Each number on the left side of the parentheses is the microstate number, and the number in the parentheses is the number of the spectroscopic terms for each line in Table 9. The first microstate number of each line is the number of the spectroscopic terms with the corresponding M_L and M_S values. The calculation is carried out from the leftmost line to right line, and then up to down. Starting the calculation with the second microstate number of each line, every microstate number is reduced by its above neighbor microstate number as well as the numbers in the parentheses with the same M_L value to the immediate left. For example, $M_L = 5$, the number (7) of the spectroscopic terms in 35 (7) on the rightmost line comes from 35 − 24 − (3) − (1) (with same M_L value). The numbers obtained from the calculation (the numbers in the parentheses in Table 9) are the numbers of

Table 2. The M_L^α Value of the e_α^5 Spin State with M_L^α Value Number

e_α^5	α	5	4	3	2	1	0
		1	1	2	2	3	3

Table 3. The M_L^α Value of the e_α^4 Spin State with the M_L^α Value Number

e_α^4	α	6	5	4	3	2	1	0
	f (α)	1	1	2	3	4	4	5

Table 4. The M_L^β Value of the e_β^1 Spin State with the M_L^β Value Number

e_β^1	β	3	2	1	0
	g (β)	1	1	1	1

Table 5. The M_L Value of (e_α^4)(e_β^1) Spin States with the M_L Value Number

i	9	8	7	6	5	4	3	2	1	0
$\sum_{\alpha+\beta=i}^{\alpha,\beta\geq 0}$ f(α)·g(β)	1	2	4	7	10	13	16	13	9	5
$\sum_{\alpha-\beta=i}^{\alpha,\beta>0}$ f(α)·g(β)					1	2	4	6	9	11
$\sum_{\beta-\alpha=i}^{\alpha,\beta>0}$ f(α)·g(β)								4	8	11
h (i)	1	2	4	7	11	15	20	23	26	27

Table 6. The M_L^α Value of the e_α^3 Spin State with the M_L^α Value Number

e_α^3	α	6	5	4	3	2	1	0
	f (α)	1	1	2	3	4	4	5

Table 7. The M_L^β Value of the e_β^2 Spin State with the M_L^β Value Number

e_β^2	β	5	4	3	2	1	0
	g (β)	1	1	2	2	3	3

Table 8. The M_L Value of (e_α^3)($e_\beta{}^2$) Spin States with the M_L Value Number

i	11	10	9	8	7	6	5	4	3	2	1	0
$\sum_{\alpha+\beta=i}^{\alpha,\beta\geq 0}$ f(α)·g(β)	1	2	5	9	16	24	32	36	39	34	27	15
$\sum_{\alpha-\beta=i}^{\alpha,\beta>0}$ f(α)·g(β)							3	5	10	16	24	29
$\sum_{\beta-\alpha=i}^{\alpha,\beta>0}$ f(α)·g(β)								4	8	15	21	29
h (i)	1	2	5	9	16	24	35	45	57	65	72	73

Table 9. M_L–M_S Matrix

	M_S		
M_L	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
11			1 (1)
10			2 (1)
9		1 (1)	5 (2)
8		2 (1)	9 (3)
7		4 (2)	16 (5)
6		7 (3)	24 (5)
5	1 (1)	11 (3)	35 (7)
4	1 (0)	15 (4)	45 (6)
3	2 (1)	20 (4)	57 (7)
2	2 (0)	23 (3)	65 (5)
1	3 (1)	26 (2)	72 (4)
0	3 (0)	27 (1)	73 (0)

the spectroscopic terms with the corresponding M_L value (i.e., L value), M_S value (i.e., S value). Thus, the numbers of the spectroscopic terms of the f^5 configuration represented by the matrix in Table 9 are shown below.

^{6}(H, F, P)
^{4}(L, K, J (2), I (3), H (3), G (4), F (4), D (3), P (2), S)
^{2}(N, M, L (2), K (3), J (5), I (5), H (7), G (6), F (7), D (5), P (4))

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