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New Approaches
Нови подходи

USE OF VECTORS AND FACTORIALS FOR CALCULATION OF MICROSTATES FROM P², D², F² CONFIGURATIONS AND DESCRIPTION OF THE P² ELECTRON CONFIGURATION

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Abstract. The aim of this research was to compute the number of microstates for p^2 configuration $n=6$ and $x=2$, for d^2 configuration $n=10$ and $x=2$ and f^2 configuration $n=14$ and $x=2$ using vectors and the math function factorial as well as to describe in detail the microstates for p^2 configuration $n=6$ and $x=2$. The following results were obtained: for p^2 configuration $n=6$ and $x=2$, $N=15$ microstates; for d^2 configuration $n=10$ and $x=2$, microstates; for f^2 configuration $n=14$ and $x=2$, $N=91$ microstates. It was established that the 15 microstates of the p^2 configuration. It was found that the 15 microstates of the p^2 electron configuration belonged to three terms as followed: 5 microstates corresponding to the ^{1}D term; 9 microstates to the ^{3}P term and 1 microstate to the ^{1}S term.

Keywords: vector, factorial, microstate

Introduction

Linear algebra and analytical geometry theory and methods are increasingly applied in chemistry. The states of multi-electron atoms or ions in chemistry are described and classified by two schemes (Russell-Saunders (L-S) and j-j coupling schemes). Both use vectors and factorials.

Vectors

Definitions

A *vector* is a geometric object that has both magnitude (length) and direction.

The *tail* of the vector is the end opposite the arrow. It represents where the vector is moving from.

The *head* of the vector is the end with the arrow. It represents where the vector is moving to.

The *zero vector* is denoted $\vec{o}$. It has zero length and all the properties of zero.

Two vectors are *equal* is they have both the same magnitude and the same direction.

Two vectors are *parallel* if they have the same $(\uparrow\uparrow \text{ or } \uparrow\downarrow)$ or opposite $(\uparrow\downarrow)$ directions. That is, if the angles of the vectors are the same or 180^0 different.

Two vectors are *perpendicular* if the difference of the angles of the vectors is 90^0 or 270^0 [1,2] (Gantert, 2016; Shriver & Atkins, 2002).

Magnitude of a vector

The magnitude of a vector $\overrightarrow{AB}$ is the distance between the initial point $A(x_1, y_1)$ and the end point $B(x_2, y_2)$. In symbols the magnitude of $\overrightarrow{AB}$ is written as $|\overrightarrow{AB}|$. If the coordinates of the initial point and the end point of a vector is given, the *distance formula* can be used to find its magnitude:

$$|\vec{\mathbf{v}}| = |\overrightarrow{AB}| = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2} \ .$$

Let us remark that $|\overrightarrow{AB}| = |\overrightarrow{BA}|$. The directions of the two vectors are opposite, but their magnitudes are the same[1,2] (Gantert, 2016; Shiver & Atkins, 2002).

Adding and subtracting of vectors

To add or subtract two vectors, add or subtract the corresponding components.

Let $\vec{\mathbf{u}} = \langle u_1, u_2 \rangle$ and $\vec{\mathbf{v}} = \langle v_1, v_2 \rangle$ be two vectors. Then, the sum of $\vec{\mathbf{u}}$ and $\vec{\mathbf{v}}$ is the vector

$$\vec{\mathbf{u}} + \vec{\mathbf{v}} = \langle u_1, u_2 \rangle + \langle v_1, v_2 \rangle = \langle u_1 + v_1, u_2 + v_2 \rangle .$$

The difference of $\vec{\mathbf{u}}$ and $\vec{\mathbf{v}}$ is

$$\vec{\mathbf{u}} - \vec{\mathbf{v}} = \vec{\mathbf{u}} + (-\vec{\mathbf{v}}) = \langle u_1 - v_1, u_2 - v_2 \rangle .$$

The sum of two or more vectors is called the resultant. The resultant of two vectors can be found using either the *parallelogram method* or the *triangle method*.

Factorial

In mathematics, the *factorial* of a non-negative integer n, denoted by $n!$, is the product of all positive integers less than or equal to n,

$$n! = 1.2 \ldots (n-2).(n-1),$$
$$0! = 1! = 1.$$

The aim of this research was to calculate the number of microstates for for p^2 configuration $n = 6$ and $x = 2$, for d^2 configuration $n = 10$ and $x = 2$ and f^2 configuration $n = 14$ and $x = 2$ using vectors and the math function factorial as well as to describe in detail the microstates for p^2 configuration $n = 6$ and $x = 2$.

Methodology

It is acknowledged that the movement of an electron in an atom could be represented by the orbital angular momentum. Similarly, the intrinsic motion of the electron is given by the spin angular momentum. Both angular momenta should be presented by vectors which have length and direction. Vectors will be identified by letters, their projections with m (for a single electron) or M (for more than 1 electron), and lengths will be represented by $|m|$ and $| \quad |$, respectively. For an electron with quantum numbers l and s, and orbital and spin angular momenta $\vec{l}$ and $\vec{s}$, the total angular momentum describing both motions is a sum of vectors: $\vec{j} = \vec{l} + \vec{s}$ (Puri et al., 2002; Meena et al., 2011a; 2011b; 2012; Kumar et al., 2012). Both vectors are in precession (rotation of an vector around an axis with only vectors' initial point lying on the axis; the vector and the axis are under a specific angle). Due to this motion, both vectors described a cone each. The addition of $\vec{l}$ and $\vec{s}$ could not be random. The angle between them remains constant in the course of precession. This results from the strict spatial orientation of both vectors. They could be oriented in a way such as their vector sum has strictly defined values of $\vec{j}$ projections. Also, the differences between these projections *(h)* should be integers[3] (Meena et al., 2013; 2014; Aggarwal & Keenan, 2014; Peters et al., 2014; Polinski et al., 2014; Thakral et al., 2014; Van den Heuvel et al., 2015).

The above mentioned is illustrated in Fig. 1 for an electron on p-AO.

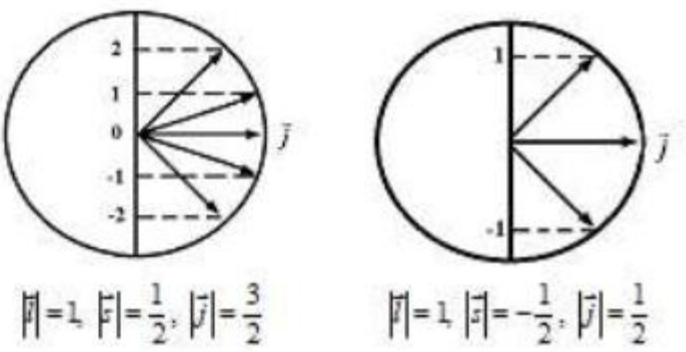

Fig. 1. Addition of vectors of orbital and spin angular momenta for $|\vec{l}| = 1$ and $|\vec{s}| = 1/2$. Both circles represent the space quantization of the total angular momentum $\vec{j}$. The lengths of vectors are shown below the circles.

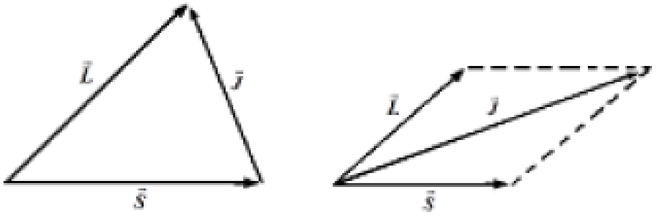

Fig. 2. Addition of vectors of orbital angular momentum $\vec{l}$ and spin angular momentum $\vec{s}$ for $\left|\vec{l}\right| = 1$ and $\left|\vec{s}\right| = 1$.

The total angular momentum $\vec{j}$ or $\vec{J}$ for one or more electrons, respectively is quantized in space in the same way, as shown on both figures.

Russell-Saunders coupling scheme: LS scheme

In the Russell-Saunders scheme, the spin and orbital angular momenta are always summed independently:

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \ldots + \vec{l}_N = \sum_{i=1}^{N} \vec{l}_i, \quad \vec{S} = \vec{s}_1 + \vec{s}_2 + \ldots + \vec{s}_N = \sum_{i=1}^{N} \vec{s}_i \ .$$

Then the resulting two vectors $\vec{L}$ and $\vec{S}$ are combined to obtain the total angular momentum $\vec{J}$: $\vec{J} = \vec{L} + \vec{S}$.

j-j coupling scheme

The combination of angular momenta of a multi-electron atom according to the j-j coupling scheme is done by combining each individual orbital to respective spin momentum $\vec{j}_i = \vec{l}_i + \vec{s}_i$ and thereafter, the total angular momentum is obtained as the sum of individual total angular momenta:

$$\vec{J} = \vec{j}_1 + \vec{j}_2 + \ldots + \vec{j}_N = \sum_{i=1}^{N} \vec{j}_i \ .$$

This order of combining is derived from the nature of the j-j scheme – each electron determines its own momentum, and then follow the combination of total individual angular momenta of all electrons.

The spin multiplicity is denoted with 2S + 1. It is added as a superscript to the left of the letter expressing the sum of orbital momenta (electron state). For example, the electron state derived from the electronic configuration $1s^1$ is:

$$s = 1/2 \quad l = 0 \quad 2s + 1 = 2 \quad {}^2S \ .$$

The symbol ^{2}S (read as doublet es) is an electron term derived from the electronic configuration 1 s^1 and including two microstates

$$\mathrm{m}_s = 1/2 \qquad \mathrm{m}_l = 0;$$
$$\mathrm{m}_s = -1/2 \qquad \mathrm{m}_l = 0.$$

The six microstates of the electronic configuration $2p^1$ are:

$$\mathrm{m}_s = +1/2 \qquad \mathrm{m}_l = 1, 0, -1;$$
$$\mathrm{m}_s = -1/2 \qquad \mathrm{m}_l = 1, 0, -1.$$

They could be grouped into:

$$s = 1/2 \qquad l = 1 \qquad 2s+1 = 2 \qquad \text{term.}\ {}^2P.$$

The symbol ^{2}P (read as doublet pe), and ^{2}S (read as doublet es) are called electron terms. Therefore, electron terms are a group of microstates (or combinations between them) with the same energy.

The Russell-Saunders scheme could be illustrated with several examples: (a) *closed shell* — the general rule for this shell type that it always has S = 0 and L = 0 or term ^{1}S; (b) *open shell* — only one of atomic orbitals making up a given electronic configuration without the maximum number of electrons is enough to have an open shell.

The total number of microstates for any configuration can be counted using by following expression (Dougles et al., 1994).

Number of ways of filling electrons N:

$$N = \frac{2(2l+1)!}{x!\left(2(2l+1)! - x!\right)} \quad \text{or} \quad \frac{n!}{x!\left(n! - x!\right)}$$

$n = 2(2l+1)$ or double of the total number of orbital's (for s-AO = 2, p-AO = 6, d-AO = 10, f-AO = 14); x = total number of electrons in sub shell.

Results and discussion

So, for p^2 configuration $n = 6$ and $x = 2$:

$$N = \frac{6!}{2!\left(6! - 2!\right)}, \quad N = \frac{6.5.4.3.2.1}{4.3.2.1.2.1}, \quad N = 15 \text{ microstates.}$$

For d^2 configuration $n = 10$ and $x = 2$:

$$N = \frac{10!}{2!\left(10! - 2!\right)}, \quad N = \frac{10.9.8.7.6.5.4.3.2.1}{8.7.6.5.4.3.2.1.2.1}, \quad N = 45 \text{ microstates.}$$

For f^2 configuration $n = 14$ and $x = 2$:

$$N = \frac{14!}{2!\left(14! - 2!\right)}, \quad N = \frac{14.13.12.11.10.9.8.7.6.5.4.3.2.1}{12.11.10.9.8.7.6.5.4.3.2.1.2.1}, \quad N = 91 \text{ microstates.}$$

In Table 1 we present 15 microstates obtained for p^2 configuration $n=6$ and $x=2$ (M$_L$ and M$_S$ denote the projections of respective $\vec{L}$ and $\vec{S}$ vectors).

Table 1. Microstates of the electronic configuration p^2

	Ms		
ML	1	0	-1
2		$\left(\overset{+}{1},\overset{-}{1}\right)$	
1	$\left(\overset{+}{1},\overset{+}{0}\right)$	$\left(\overset{+}{1},\overset{-}{0}\right),\left(\overset{-}{1},\overset{+}{0}\right)$	$\left(\overset{-}{1},\overset{-}{0}\right)$
0	$\left(\overset{+}{1},\overset{+}{-1}\right)$	$\left(\overset{+}{1},\overset{-}{-1}\right),\left(\overset{+}{0},\overset{-}{0}\right),\left(\overset{-}{1},\overset{+}{-1}\right)$	$\left(\overset{-}{1},\overset{-}{-1}\right)$
-1	$\left(\overset{+}{0},\overset{+}{-1}\right)$	$\left(\overset{+}{0},\overset{-}{-1}\right),\left(\overset{-}{0},\overset{+}{-1}\right)$	$\left(\overset{-}{0},\overset{-}{-1}\right)$
-2		$\left(\overset{+}{-1},\overset{-}{-1}\right)$	

Let us now take a look on Table 1 from another aspect. If we begin with the microstate with highest $\mathrm{M_L}$ value – this is $\left(\overset{+}{1},\overset{-}{1}\right)$, after addition of the two vectors, each with length $\sqrt{2}$ and projection on the selected axis 1, we obtain a vector with length of $\sqrt{6}$ and projection on the same axis 2 (in $h/2\pi$ units). In other words, the microstate $\left(\overset{+}{1},\overset{-}{1}\right)$ has to be a function of this vector. Once obtained however, this vector is quantized in the space and apart the projection +2, it could be also oriented in a way such as to have projections equal to +1, 0, -1, -2. Also, the orientation of the spins of both electron should be always opposite. It is important to understand that one of respective combinations in the column with Ms = 0 belongs to the vector derived from $\left(\overset{+}{1},\overset{-}{1}\right)$. This vector is denoted with the letter D. The spin multiplicity is $2\mathrm{S}+1=1$, or there is one term ^{1}D (singlet de), which includes 5 microstates or combinations, all of which (without exceptions) are arranged vertically in the middle column of Table 1.

As these combinations are unknown to us, we will randomly remove one microstate from each row of the second column as belonging to the term ^1D. The result is illustrated in the new Table 2.

Table 2. Microstates of p^2 after removing ^1D

	Ms		
ML	1	0	-1
2			
1	$\begin{pmatrix}\overset{+}{1},\overset{+}{0}\end{pmatrix}$	$\begin{pmatrix}\overset{+}{1},\overset{-}{0}\end{pmatrix}$	$\begin{pmatrix}\overset{-}{1},\overset{-}{0}\end{pmatrix}$
0	$\begin{pmatrix}\overset{+}{1},-\overset{+}{1}\end{pmatrix}$	$\begin{pmatrix}\overset{+}{0},\overset{-}{0}\end{pmatrix},\begin{pmatrix}\overset{-}{1},-\overset{+}{1}\end{pmatrix}$	$\begin{pmatrix}\overset{-}{1},-\overset{-}{1}\end{pmatrix}$
-1	$\begin{pmatrix}\overset{+}{0},-\overset{+}{1}\end{pmatrix}$	$\begin{pmatrix}\overset{-}{\grave{u}}\ \overset{+}{-}\end{pmatrix}$	$\begin{pmatrix}\overset{-}{0},-\overset{-}{1}\end{pmatrix}$
-2			

With the new table, we proceed in the same way as with Table 1 – choosing the microstate with highest value for $M_{L.}$ These are $\begin{pmatrix}\overset{+}{1},\overset{+}{0}\end{pmatrix},\begin{pmatrix}\overset{+}{1},\overset{-}{0}\end{pmatrix},\begin{pmatrix}\overset{-}{1},\overset{-}{0}\end{pmatrix}$. From them, we retain the microstate with maximum value for M_S, i.e. $\begin{pmatrix}\overset{+}{1},\overset{+}{0}\end{pmatrix}$. It corresponds to $M_L = 1$ and $M_S = 1$ or it is derived from vectors $\vec{L}$ and $\vec{S}$ each with a length of $\sqrt{2}$, whose projections could be 1, 0, -1. These two vectors determine the existence of nine microstates with different energy, differing in projections on a random axis. These nine microstates constitute the electron term ^3P. If these microstates (or their combination in the middle column) are removed from Table 2, only one combination of microstates is left, which is not mentioned so far and whose energy in different from the energy of ^1D and ^3P terms. It is

$$3^{-1/2}\left[\begin{pmatrix}\overset{+}{0},\overset{-}{0}\end{pmatrix}-\begin{pmatrix}\overset{+}{1},-\overset{-}{1}\end{pmatrix}-\begin{pmatrix}-\overset{+}{1},\overset{-}{1}\end{pmatrix}\right]$$

and due to the fact that it has $M_L = 0$ and $M_S = 0$, it forms the term ^1S.

Conclusions

Ultimately, the description of the 15 microstates derived from the electronic configuration P^2 led to the following result. These microstates fell into three energy terms as follows: (A) five microstates included in the electron term ^1D; (B) nine microstates included in the electron term ^3P; (C) one microstate included in the electron term ^1S.

NOTES

1. http://hotmath.com
2. http://mathguy.us/Handbooks/GeometryHandbook.pdf
3. http://www.chem.helsinki.fi/~sundholm/winterschool/lecture_notes_2014/Slageren-helsinki14.pdf

REFERENCES

Aggarwal, K.M. & Keenan, F.P. (2014). Energy levels, radiative rates and electron impact excitation rates for transitions in Fe XIV. *Mon. Not. R. Astron. Soc., 445*, 201 – 2027.

Gantert, A.X. (2016). *Amsco's geometry*. New York: Amsco School Publications.

Dougles, B.E., McDaniel, D.H. & Alexander, J.J. (1994). *Concepts of model of inorganic chemistry*. New York: John Wiley & Sons.

Kumar, N., Meena, K.S., Meena, P.K. & Jain, P. K. (2012). Calculation of atomic spectroscopic terms for nonequivalent electrons of f^2d^1 configuration and assigning the term symbols. *Asian J. Chem.*, *24*, 5677 – 5679.

Meena, P.L., Jain, P.K., Kumar, K. & Meena, S. (2011a). Study on the atomic term symbols for f^3 (M+3 free ion) configuration. *Int. J. Chem, 9*, 1364 – 1372.

Meena, P. L., Jain, P.K., Kumar, N. Meena, K.S. & Goyal, R. (2011b). Study on the atomic term symbols for f^4 (M+3 free ion) configuration*, J. Chem. Biol. & Phys. Sci., 1*, 188 – 203.

Meena, P.L., Jain, P.K., Kumar, N. & Meena, K.S. (2012). A comparative study of the atomic term symbols of f^3 and f^{11} configuration. *Acta Chimica & Pharmatica Indica*, *2*(1), 32 – 45.

Meena, P.L., Kumar, N., Meena, K.S. & Jain, P.K. (2013). Calculation of atomic spectroscopic terms for f^2 and f^{12} orbital configuration, assigning the term symbols and a comparative Study. *Bulg. Chem. Comm., 45*, 338 – 393.

Meena, P.L., Kumar, N., Meena, M.K. & Meena, A.S. (2014). Comparative studies on Russell-Saunders atomic term symbols (terms) for equivalent electrons of nf^4 and nf^{10} configurations. *Bulg. Chem. Comm., 46*, 141 – 149.

Peters, L., Di Marco, I., Thunström, P., Katsnelson, M.I., Kirilyuk, A. & Eriksson, O. (2014). Treatment of 4f states of the rare earths: the case study of TbN. *Phys. Rev. B, 89*, art. no. 205109.

Polinski, M.J., Garner III, E., Maurice, R., Planas, N., Stritzinger, J.T., Parker, T.G., Cross, J.N., Green, T.D., Alekseev, E.V., Van Cleve, S.M., Depmeier, W., Gagliarti, L., Shatruk. M., Knappenberger, K.L., Liu, G., Skanthakumar, S., Soderholm, L., Dixon, D.A., & Albrecht-Schnitt, T.E. (2014). Unusual structure, bonding and properties in a californium borate. *Nature Chem., 6,* 387 – 392.

Puri, B.R., Sharma, L.R. & Pathania, M.S. (2008). *Principle of physical chemistry.* New Delhi: Vishal Publishing.

Shriver, D.F. & Atkins, P.W. (2002). *Inorganic chemistry*. New York: Oxford University Press.

Thakral, P., Kapoor, V. & Bakhshi, A.K. (2014). *In silico* architecturing of novel hetero – atomic bicyclic copolymers using particle swarm optimization algorithm. *Indian J. Chem., 53 A,* 9 – 16.

Van den Heuvel, W., Calvello, S. & Soncini, A. (2015). Configuration-averaged open shell ab initio method for crystal field levels and magnetic properties of lanthanide (III) complexes. *arXiv*:1509.00974v1.

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