



# New Numerical Approach to Calculate Microstates of Equivalent and Non-Equivalent Electrons

Misha Shafi<sup>1</sup>, Saba Javaid<sup>2,3\*</sup>, Roohi Zafar<sup>2</sup>, Ahmed Ali Rajput<sup>1</sup>,  
Muhammad Mustaqeem Zahid<sup>1</sup>, and Muhammad Daniyal<sup>1</sup>

<sup>1</sup>Department of Physics, University of Karachi, Karachi, Pakistan

<sup>2</sup>Department of Physics, NED University of Engineering & Technology, Karachi, Pakistan

<sup>3</sup>Department of Physics, Federal Urdu University of Arts, Science & Technology,  
Karachi, Pakistan

**Abstract:** A term symbol is used to describe atomic microstate states, which give the multiplicity and total angular momentum of the atomic state. Russel Sauder coupling scheme is used to generate terms of equivalent and non-equivalent electronic configurations. For equivalent electrons, the terms are calculated using Pauli's principle, and the number of terms is limited and is calculated by the combination rule. The total possible electrons and total available electrons are used in the combination formula. In case of non-equivalent electrons, the number of terms are found by the permutation rule. The number of terms for equivalent electrons is less than the terms for non-equivalent electrons. The number of possible microstates for  $p^2$  and  $d^5$  configurations are 15 and 252 respectively. While the number of final microstates for  $1p2p$  and  $3d4d$  configurations are 36 and 100. In the proposed study, a Python programme was developed that generates the microstate according to filled and half-filled subshell electronic configurations for equivalent, non-equivalent, and combinations of both. Examples of microstates for non-equivalent electrons of configuration  $1s2s$ ,  $sp$ ,  $sd$ ,  $ss$ ,  $2p3p$ ,  $pd$ ,  $pf$ ,  $3d4d$ ,  $df$ ,  $4f5f$  and for equivalent electrons of configuration  $s^u$ ,  $p^v$ ,  $d^x$ , and  $f^y$  are presented.

**Keywords:** Microstates, Term Symbols, Equivalent and Non-Equivalent Electrons, Pauli Exclusion Principle, L-S Coupling.

## 1. INTRODUCTION

Atomic microstates are identified by a spectral term that specifies their multiplicity and overall angular momentum. Term symbols provide information on the spectral and magnetic properties of various elements [1]. These term values are helpful to identify coefficients of fractional parentage of wavefunctions of elements having complex structures like Praseodymium, Tantalum etc. Henry Russell and Frederick Saunders introduced the Russell-Saunders (which is abbreviated as R-S) scheme for the first time in 1923. Initially, it was used to electrons in half-filled orbits of atoms with lower atomic numbers since the spin-orbit coupling is less effective than the electrostatic effect [2]. However, spin-orbit coupling due to higher nuclear charge seems to be more important for those

elements that have a higher atomic number. The R-S technique is still useful for rare Earth elements and heavier transition elements. The complex spectra of structures containing valence electrons in distinct sub shells were successfully interpreted by using a vector model for terms that were established before the quantum mechanical approach [3]. The three vectors,  $\vec{S}$ ,  $\vec{L}$  and  $\vec{J}$  are produced as a result of the R-S coupling, which is the basis for the present nomenclature for the specific energy level  $(2S+1) L_J$ , where  $2S+1$  is the multiplicity or spin multiplicity of a term, the orbital angular momentum vectors of the valence electrons are vectorially added together to form  $L$  and spin angular momentum vectors of valence electrons are vectorially summed to generate  $S$ , and vectorial sum of  $L$  and  $S$  is  $J$ . A given term produces the number of microstates which are simply  $(2S + 1) \times$

( $2L + 1$ ) and by applying Hund's rule, ground state term and the order of stability can be determined. A state of definite  $J$  can be achieved when  $L$  and  $S$  coupled together and  $J$ 's allowed values range from  $|L + S|$  to  $|L - S|$  [4, 5].

$$\mathbf{L} = \sum_i \mathbf{l}_i \quad (1)$$

$$\mathbf{S} = \sum_i \mathbf{s}_i \quad (2)$$

Each term split into ( $2\mathbf{J} + 1$ ) terms with energy difference proportional to the applied field intensity (Zeeman Effect) and a quantum number  $\mathbf{M}_J$  that can have the values  $\mathbf{J}, \mathbf{J}-1, \mathbf{J}-2, \dots, -\mathbf{J}$  is used to define states. As a result,  $\mathbf{J}$  can take  $2\mathbf{S} + 1$  values when  $\mathbf{L} \geq \mathbf{S}$  but  $2\mathbf{L} + 1$  values when  $\mathbf{L} < \mathbf{S}$  and  $\mathbf{J}$  can only take one value when  $\mathbf{L} = \mathbf{0}$ . The valence electrons' energy levels may be defined if the possible  $L$ ,  $S$  and  $J$  values are known [6]. Energy associated with the state of an atom taking part in a transition is described by an R-S spectral term, and energy levels in an atom with many electrons are briefly described by term symbols.

When an ion or atom is placed into a lattice, electronic repulsion splits the degenerate state into two or more states. Equivalent electrons are ones whose  $l$  and  $n$  values are the same such as  $\mathbf{np}^2, \mathbf{nd}^6, \mathbf{nf}^4$ , or  $\mathbf{nf}^6$  configuration [7]. As a result, identical terms are produced for  $\mathbf{nf}^4$  and  $\mathbf{nf}^{10}$  configurations. The number of microstates for the sub shell increases when the number of electrons in orbital of the incomplete sub shell increases, but the non-equivalent electronic system produces a number of microstates that is much greater than that of the similar equivalent electronic system [8-13]. In 2019, Javaid *et al.* [14] evaluated 187 spectral terms with 457  $J$  values and 106 wavefunctions for  $4f2\ 5d2$  configuration of Praseodymium II by using Russell – Saunders technique. Zafar *et al.* [15] determined 46 orthonormal wave functions for  $4f^3\ 6s^2$  ground state configuration of Praseodymium I using spectral terms in 2020.

The main purpose of our study is to develop a machine algorithm using the Python language to evaluate term symbols of equivalent and non-equivalent electronic configurations. This program provides a user input interface for saving datasets into the program directory. It asks either to enter '0' for equivalent electron configuration or to hit '1' for non-equivalent electron configuration.

## 2. METHODOLOGY

In this article, the term symbols and the microstates

of filled and half-filled subshell electronic configurations are calculated. Microstates are the numerous ways in which electrons can be arranged in a set of orbitals, each of which has a unique energy. The total number of microstates ( $W$ ) of a system is the total number of definite arrangements for "e" number of electrons to be placed in "n" number of possible orbital positions. The number of microstates for equivalent electrons can be calculated by using a simple expression:

$$W = \frac{n!}{e!(n-e)!} \dots \dots \dots (3)$$

where  $e$  denotes the number of electrons, and  $n$  is the total available orbitals [16].

Spectral Term corresponds to energy states and provides knowledge of angular momenta. For the non-equivalent electrons, there are more available microstates than for the equivalent electrons. Some of the available microstates for non-equivalent electrons are forbidden for equivalent electrons because of Pauli's principle [17, 18]. In Russell Saunders Coupling Scheme, term symbols are provided by  $(2S+1)LJ$ , where  $S$  shows the total spin angular momentum,  $L$  denotes the orbital angular momentum and  $J$  symbolizes the total angular momentum [19-21].  $L$  can have the following values in a term symbol: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, ..., and the English capital letters "S, P, D, F, G, H, I, K, K" are used to represent each value of  $L$ .  $2S+1$  denotes the spin multiplicity of the spectral terms like singlet, doublet, triplet and so on. The Russell-Saunders technique makes the assumption that spin-orbit coupling  $<$  orbit-orbit coupling  $<$  spin-spin coupling [22, 23].

A computer algorithm was designed that generates terms of equivalent electrons and non equivalent electrons of any configuration. A user inputs either '0 and 1' for generation of microstates of equivalent and non-equivalent electrons. An algorithm flowchart has been given in Figure 1. It further requires orbital numbers (e.g., 0, 1, 2, 3 for  $s, p, d, f$  respectively) as input. These inputs must be given for the task's completion, or it may lead to the failure of the program. Permitted terms for the configuration of  $s^u, p^v, d^x, \text{ and } f^y$  where  $u=1 \text{ and } 2, v = 1 \text{ to } 5, x = 1 \text{ to } 9 \text{ and } y=1 \text{ to } 13$  are found by considering these equivalent configuration. The configurations  $1s2s, sp, sd, ss, 2p3p, pd, pf, 3d4d, df, 4f5f$  have non-equivalent electrons. Term symbols for these non equivalent electronic system are generated by calculating total orbital angular momentum and total spin angular momentum. For non equivalent electrons, Pauli's Exclusion Principle is not taken into account [24, 25].

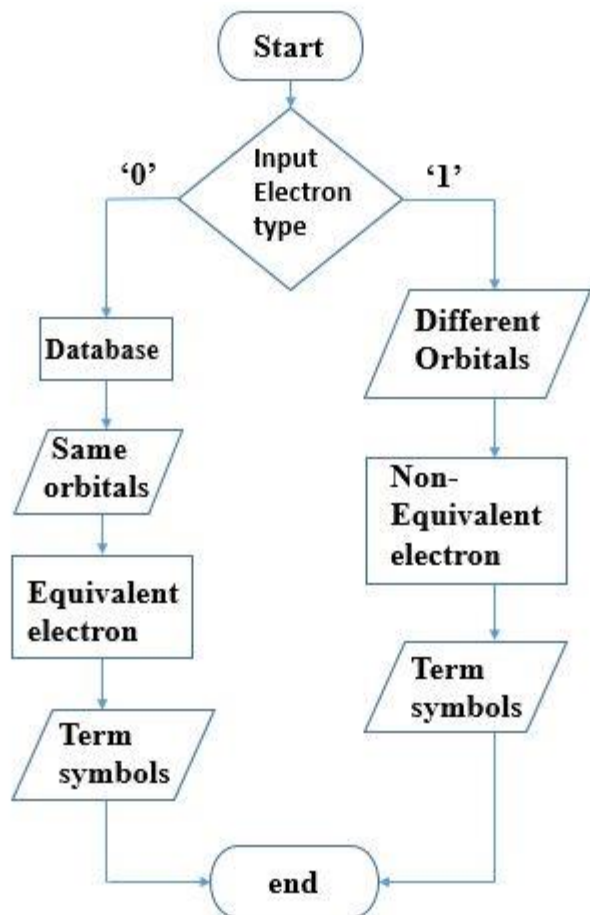


Fig. 1. Algorithm flowchart

### 3. RESULTS AND DISCUSSION

The filling of electrons in a shell depends on the nature of electrons, the electrons having same principal quantum number and same orbital quantum number face the limitations in filling the energy level slots, As they have to follow the Pauli’s principle, no two electrons having same four set of quantum number can occupy the same energy level. Hence the number of microstates in case of equivalent electrons are less than that are available for non-equivalent electrons.

We used the theory of the coupling of orbital and spin angular momenta. Using a Python programme, we evaluated the term symbols for both equivalent and non-equivalent electrons. These configurations  $s^u, p^v, d^x,$  and  $f^y$  have equivalent electrons (where  $u=1$  and  $2, v = 1$  to  $5, x = 1$  to  $9$  and  $y = 1$  to  $13$ ) and the microstates for these configurations are calculated by our program and are given in Table 1. Moreover, the configurations  $1s2s, sp, sd, ss, 2p3p, pd, pf, 3d4d, df, 4f5f$  have non-equivalent electrons, the microstates for these configurations are found by using combination rule for two non-equivalent orbitals. Table 2. shows the some of the microstates for two non-equivalent orbitals.

For example  $l_1 = 1, l_2 = 1$  then  $L = 2, 1, 0$  using  $L = |l_1 + l_2|, \dots, |l_1 - l_2|$  so the states  $D, P,$  and  $S$  will be generated. To find the multiplicity, we find the

Table 1. Term symbols for equivalent electrons

Orbitals	No. of Electrons	Total No. of Microstates	Final No. of Microstates	Term Symbols
S	1	2	(0, 0.5)	<sup>2</sup> S
	2	1	(0, 0.0)	<sup>1</sup> S
P	1	6	(1, 0.5)	<sup>2</sup> P
	2	15	(2, 0.0), (1, 1.0), (0, 0.0)	<sup>1</sup> D, <sup>3</sup> P, <sup>1</sup> S
	3	20	(2, 0.5), (1, 0.5), (0, 1.5)	<sup>2</sup> D, <sup>2</sup> P, <sup>4</sup> S
D	1	10	(2, 0.5)]	<sup>2</sup> D
	2	45	(4, 0.0), (3, 1.0), (2, 0.0), (1, 1.0), (0, 0.0)	<sup>1</sup> G, <sup>3</sup> F, <sup>1</sup> D, <sup>3</sup> P, <sup>1</sup> S
	3	120	(5, 0.5), (4, 0.5), (3, 1.5), (3, 0.5), (2, 0.5), (2, 0.5), (1, 1.5), (1, 0.5)	<sup>2</sup> H, <sup>2</sup> G, <sup>4</sup> F, <sup>2</sup> F, <sup>2</sup> D, <sup>2</sup> D, <sup>4</sup> P, <sup>2</sup> P
F	1	14	(3, 0.5)	<sup>2</sup> F
	2	91	(6, 0.0), (5, 1.0), (4, 0.0), (3, 1.0), (2, 0.0), (1, 1.0), (0, 0.0)	<sup>1</sup> I, <sup>3</sup> H, <sup>1</sup> G, <sup>3</sup> F, <sup>1</sup> D, <sup>3</sup> P, <sup>1</sup> S
	3	364	(8, 0.5), (7, 0.5), (6, 1.5), (6, 0.5), (5, 0.5), (5, 0.5), (4, 1.5), (4, 0.5), (4, 0.5), (3, 1.5), (3, 0.5), (3, 0.5), (2, 1.5), (2, 0.5), (2, 0.5), (1, 0.5), (0, 1.5)	<sup>2</sup> L, <sup>2</sup> K, <sup>4</sup> I, <sup>2</sup> I, <sup>2</sup> H, <sup>2</sup> H, <sup>4</sup> G, <sup>2</sup> G, <sup>2</sup> G, <sup>4</sup> F, <sup>2</sup> F, <sup>2</sup> F, <sup>4</sup> D, <sup>2</sup> D, <sup>2</sup> D, <sup>2</sup> P, <sup>4</sup> S

**Table 2. Term symbols for non-equivalent electrons**

1st Orbital	1st Orbital Number	2nd Orbital	2nd Orbital Number	Total Orbital Quantum Number	Total Spin Quantum Number	Multiplicity	Final Microstates
s	0	s	0	[0]	[0. 1.]	[1, 3]	['1S', '3S']
s	0	p	1	[1]	[0. 1.]	[1, 3]	['1P', '3P']
s	0	d	2	[2]	[0. 1.]	[1, 3]	['1D', '3D']
s	0	f	3	[3]	[0. 1.]	[1, 3]	['1F', '3F']
p	1	p	1	[0 1 2]	[0. 1.]	[1, 3]	['1S', '1P', '1D', '3S', '3P', '3D']
p	1	d	2	[1 2 3]	[0. 1.]	[1, 3]	['1P', '1D', '1F', '3P', '3D', '3F']
p	1	f	3	[2 3 4]	[0. 1.]	[1, 3]	['1D', '1F', '1G', '3D', '3F', '3G']
d	2	d	2	[0 1 2 3 4]	[0. 1.]	[1, 3]	['1S', '1P', '1D', '1F', '1G', '3S', '3P', '3D', '3F', '3G']

total spin generated by two electrons each having spin half. The total spin will be 1 and 0, that would lead to a multiplicity of 3 and 1. Therefore, the terms generated by two non-equivalent p-electrons are  $^3D$ ,  $^3P$ ,  $^3S$ ,  $^1D$ ,  $^1P$ , and  $^1S$ . The GitHub program repository can be accessed at <https://github.com/AhmedAliRajput/Term-Symbol-Calculation.git>.

#### 4. CONCLUSIONS

A computer program is developed in Python to generate term values of various electronic configurations of atoms and ions. Russell Saunder coupling scheme is implemented for equivalent, non-equivalent, and combinations of both electrons in open and close shells of atoms and ions. It is very complicated to calculate terms using pen and paper, even for three equivalent electrons in a  $d$  shell. With the help of this program the task can be completed in a few seconds. This term calculator is useful for students working in the field of spectroscopy or quantum chemistry. For example, if students require to determine the microstates of  $np^2$  configuration that is the case of equivalent electrons, generates 3 microstates that accommodates 18 electrons, whereas for  $np(n+1)p$  configuration of non-equivalent electrons, program will generate 6 microstates that accommodate 36 electrons. If microstates for higher orbitals is to determine, it would cost a lot of time, therefore, this programs

would be handy tool to deal with such lengthy calculations. The code can be downloaded from <https://github.com/AhmedAliRajput/Term-Symbol-Calculation.git>.

#### 5. CONFLICT OF INTEREST

The authors declare no conflict of interest.

#### 6. ACKNOWLEDGEMENTS

We would like to express our sincere gratitude to our research supervisor Professor Dr. Zaheer Uddin, Department of Physics, University of Karachi, Pakistan for his invaluable guidance throughout this research work.

#### 7. REFERENCES

1. P.L. Meena, P.K. Jain, N. Kumar, and K.S. Meena. A comparative study of the atomic term symbols of  $f^3$  and  $f^1$  configuration. *Acta Chimica and Pharmaceutica Indica* 2(1): 32-45 (2012).
2. P.L. Meena, N. Kumar, A.S. Meena, and K.S. Meena. Comparative studies on Russell-Saunders atomic term symbols (terms) for equivalent electrons of  $nf^4$  and  $nf^0$  configurations. *Bulgarian Chemical Communications* 46: 141-149 (2014).
3. P. Armentrout. Chemistry of excited electronic states. *Science* 251(4990): 175-179 (1991).
4. E.S.J. Gauerke, and M.L. Campbell. A simple, systematic method for determining j levels for jj

- coupling. *Journal of Chemical Education* 71(6): 457 (1994).
5. J.A. Olson. Atomic term symbols via partitioning techniques. *International Journal of Quantum Chemistry* 111(12): 2844-2850 (2011).
  6. W. Demtröder. Atoms, molecules and photons. *Springer Heidelberg Dordrecht London New York* (2010).
  7. A.K Bose, and A. Bose. Combinatorial computation of atomic terms for equivalent electrons. *Computer Physics Communications* 13(4): 241-246 (1977).
  8. R.F. Curl Jr, and J.E. Kilpatrick. Atomic term symbols by group theory. *American Journal of Physics* 28(4): 357-365 (1960).
  9. N. Karayianis. Atomic terms for equivalent electrons. *Journal of Mathematical Physics* 6(8): 1204-1209 (1965).
  10. E. Tuttle. Terms obtained from configurations of equivalent electrons. *American Journal of Physics* 35(1): 26-29 (1967).
  11. B. Judd. Atomic shell theory recast. *Physical Review* 162(1): 28 (1967).
  12. Y. Liu, Y. Liu, and B. Liu. A New Method for Obtaining Russell- Saunders Terms. *Journal of Chemical Education* 88(3): 295-298 (2011).
  13. C.J. Foot. Atomic physics. *Oxford University Press, Oxford, USA* (2004).
  14. S. Javaid, R. Zafar, and Z. Uddin. Theoretical analysis of  $4f^2 5d^2$  configuration of singly ionized praseodymium. *Journal of Physics Communications* 3(9): 095012 (2019).
  15. R. Zafar, S. Javaid, and Z. Uddin. Wavefunctions for ground state  $4f^3 6s^2$  configuration of praseodymium to calculate energy of fine levels and other spectroscopic quantities. *Journal of Physics Communications* 4(3): 035003 (2020).
  16. P.L. Meena. Terms for Non-equivalent Electrons in  $d^x p^y s^z$  Configurations. *Journal of Science Education* 19: 52 (2018).
  17. H.A. Murthy, and V.M. Rao. A Study on Atomic Spectroscopic Term Symbols for Non-equivalent Electrons of  $(n-1) d s p$  Configuration Using Russell-Saunders Coupling Scheme. *International Journal of Engineering & Research* 7: 27-33 (2017).
  18. M. Suhail, and I. Ali. A magic trick for determination of ground state term of s, p & d-orbital electrons. *Chemistry International* 6(4): 218-223 (2020).
  19. P.L. Meena, P.K. Jain., N. Kumar, K.S. Meena, R. Goyal. Study on the Atomic Term Symbols for  $f^1$  ( $M^{+3}$  free ion) Configuration. *Journal of Chemical Biological and Physical Science* 1(2): 188-203 (2011).
  20. J.A. Odutola. Review of Term Symbols Computation from Multi-Electron Systems for Chemistry Students. *Contemporary Chemistry* (2019).
  21. E. Kiremire. A numerical algorithm technique for deriving Russell-Saunders (RS) terms. *Journal of Chemical Education* 64(11): 951 (1987).
  22. L. Guofan, and M. Ellzey. Finding the terms of configurations of equivalent electrons by partitioning total spins. *Journal of Chemical Education* 64(9): 771 (1987).
  23. Y. Ge. On Teaching Molecular Term Symbols: From the Atomic Term Symbols in a Two-Dimensional World to the Molecular Term Symbols in a Three-Dimensional World. *Journal of Chemical Education* 95(9): 1682-1683 (2018).
  24. M. Ivanova, and L. Dospatliev. Use of Vectors and Factorials for Calculation of Microstates from  $p^2$ ,  $d^2$ ,  $f^2$  Configurations and Description of the  $p^2$  Electron Configuration. *Journal of Chemistry. Natural Sciences in Education*, 26(3): 677-685 (2016).
  25. R.B. Jha, W. Rehman, S. Kumar, and S. Lamba. Assigning Atomic Term Symbols for d-block Elements-A. *International Conference on Chemistry Frontiers & Challenges* 2:(3) (2013).