❖ Magnetic Properties of Free Ions

The resultant magnetic behavior of free ions; whether we talk about transition metals or lanthanides; arises as a result of spin-spin, orbital-orbital and spin-orbital interactions. Now stating more precisely, after considering the effect of spin-spin coupling and orbital-orbital coupling, the further degeneracy removal of the free ion terms is carried out by spin-orbital interaction (L-S coupling) that mainly leads to three different cases depending upon its relative magnitude with thermal energy. The determination of magnetic moment or magnetic susceptibility in these three situations is discussed below.

➢ *Magnitude of L-S Coupling in Ground State is Much Greater Than Thermal Energy*

If the *J* states after spin-orbital interaction are very far from each other energetically, the thermal energy (*kT*) would not be adequate to populate all *J*-levels of ^{2S+1}L state. This, in turn, would result in a Boltzmann distribution in which almost all of the population density is lying in the ground state ($^{2S+1}L_J$). Consequently, the effective magnetic moment will be given by equation (43) as:

$$\mu_{\text{eff}} = g\sqrt{J(J+1)}\ \text{B.M.} \tag{43}$$

Where *g* is the Lande splitting factor or gyromagnetic ratio whose value can be found as follows:

$$g = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \tag{44}$$

In case the resultant orbital angular momentum quantum number is zero i.e. $L = 0$, The value of $J = S$ and equation (43) will become:

$$\mu_{\text{eff}} = g\sqrt{S(S+1)}\ \text{B.M.} \tag{45}$$

Now because the value of the gyromagnetic ratio or Lande splitting factor for free-electron is 2, equation (45) takes the following form.

$$\mu_{\text{eff}} = 2\sqrt{S(S+1)}\ \text{B.M.} \tag{46}$$

Owing to the relationship between resultant spin quantum number and number of unpaired electrons ($S = n/2$), equation (46) can also be written in the form given below.

$$\mu_{\text{eff}} = \sqrt{n(n+2)}\ \text{B.M.} \tag{47}$$

Where *S* is the resultant spin quantum number and *n* is the number of unpaired electrons. The equation (45 – 47) is also called as spin only formula as they do not include any contribution from the orbital motion.

This type of magnetic behavior is generally shown by lanthanide ions. A comparison of theoretically calculated magnetic moments of various lanthanide ions with their experimental observed values is presented in the following table.

Table 3. The comparison of theoretically calculated and experimental magnetic moments (B.M.) of trivalent lanthanide ions.

Metal ion	Electronic configuration	Ground state term symbol	Gyromagnetic ratio	$\mu_{\mathrm{eff}} = g[J(J+1)]^{1/2}$	μ_{eff} (experimental)
La^{3+}	f^0	$^1S_0$	–	0	0
Ce^{3+}	f^1	$^2F_{5/2}$	6/7	2.54	2.3 – 2.5
Pr^{3+}	f^2	$^3H_4$	4/5	3.58	3.4 – 3.6
Nd^{3+}	f^3	$^4I_{9/2}$	8/11	3.62	3.5 – 3.6
Pm^{3+}	f^4	$^5I_4$	3/5	2.68	2.7 – 2.8
Sm^{3+}	f^5	$^6H_{5/2}$	2/7	0.84	1.5 – 1.6
Eu^{3+}	f^6	$^7F_0$	–	0	3.4 – 3.6
Gd^{3+}	f^7	$^8S_{7/2}$	2	7.94	7.8 – 8.0
Tb^{3+}	f^8	$^7F_6$	3/2	9.72	9.4 – 9.6
Dy^{3+}	f^9	$^6H_{15/2}$	4/3	10.63	10.4 – 10.5
Ho^{3+}	f^{10}	$^5I_8$	5/4	10.60	10.3 – 10.5
Er^{3+}	f^{11}	$^4I_{15/2}$	6/5	9.57	9.4 – 9.6
Tm^{3+}	f^{12}	$^3H_6$	7/6	7.63	7.1 – 7.4
Yb^{3+}	f^{13}	$^2F_{7/2}$	8/7	4.50	4.4 – 4.9
Lu^{3+}	f^{14}	$^1S_0$	–	0	0

The results clearly indicate that the experimental values of μ_{eff} for most of the lanthanide ions are pretty much comparable to their theoretical counterparts. However, the magnetic moment for Eu^{3+} and Sm^{3+} calculated using equation (43) are zero, suggesting them as diamagnetic which is quite strange as they are actually having a considerable amount of paramagnetism. This is obviously due to the fact that the energy difference between their ground state term and the first excited state is comparable to thermal energy i.e. $\Delta E \approx kT$. Therefore, even at room temperature, a part of the total population of Sm^{3+} and Eu^{3+} ions would be present in their excited states, which in turn are obviously having a different value of total angular momentum quantum number (J-value) and gyromagnetic ratio (g-value).

➢ *Magnitude of L-S Coupling in Ground State is Comparable to Thermal Energy*

If the separation between *J* states after spin-orbital interaction is comparable to the thermal energy (*kT*) available, the resultant value of the magnetic moment is governed by a complex function of temperature. In this scenario, the total magnetic susceptibility will be having contributions from first-order Zeeman effects of involved states according to their Boltzmann weights, as well as from second-order Zeeman effects from neighboring levels. Mathematically, the magnetic susceptibility will be given as follows:

$$\chi_{\mathrm{M}} = \frac{N}{3kT}\sum g^2\beta^2 J(J+1)(2J+1)e^{-\Delta E/kT}\sum (2J+1)e^{-\Delta E/kT} \qquad (48)$$

It can clearly be seen from equation (48) that the magnitude of magnetic susceptibility does not depend directly on the reciprocal of temperature, and thus does not follow Curie-Weiss law. The theoretical calculation for Sm^{3+} ion, according to equation (48), yielded a magnetic moment of 1.38 B.M.; which pretty much comparable to the experimental one. Similarly, satisfactory results are also obtained for trivalent europium ions.

➢ *Magnitude of L-S Coupling in Ground State is Much Less Than Thermal Energy*

If the energy separation between *J* states (generated after *L*-*S* coupling) is much less than the thermal energy (*kT*) available, all of the *J*-levels of ${}^{2S+1}L$ ground state. This situation is pretty much analogs to the case when spin and orbital motion are completely decoupled from each other. In other words, *L*-*S* interaction would not be effective in distinguishing different metal ions on the basis of total motion. Therefore, the effective magnetic moment will be given by the following relation:

$$\mu_{\mathrm{eff}} = \sqrt{4S(S+1) + L(L+1)}\ \mathrm{B.M.} \qquad (49)$$

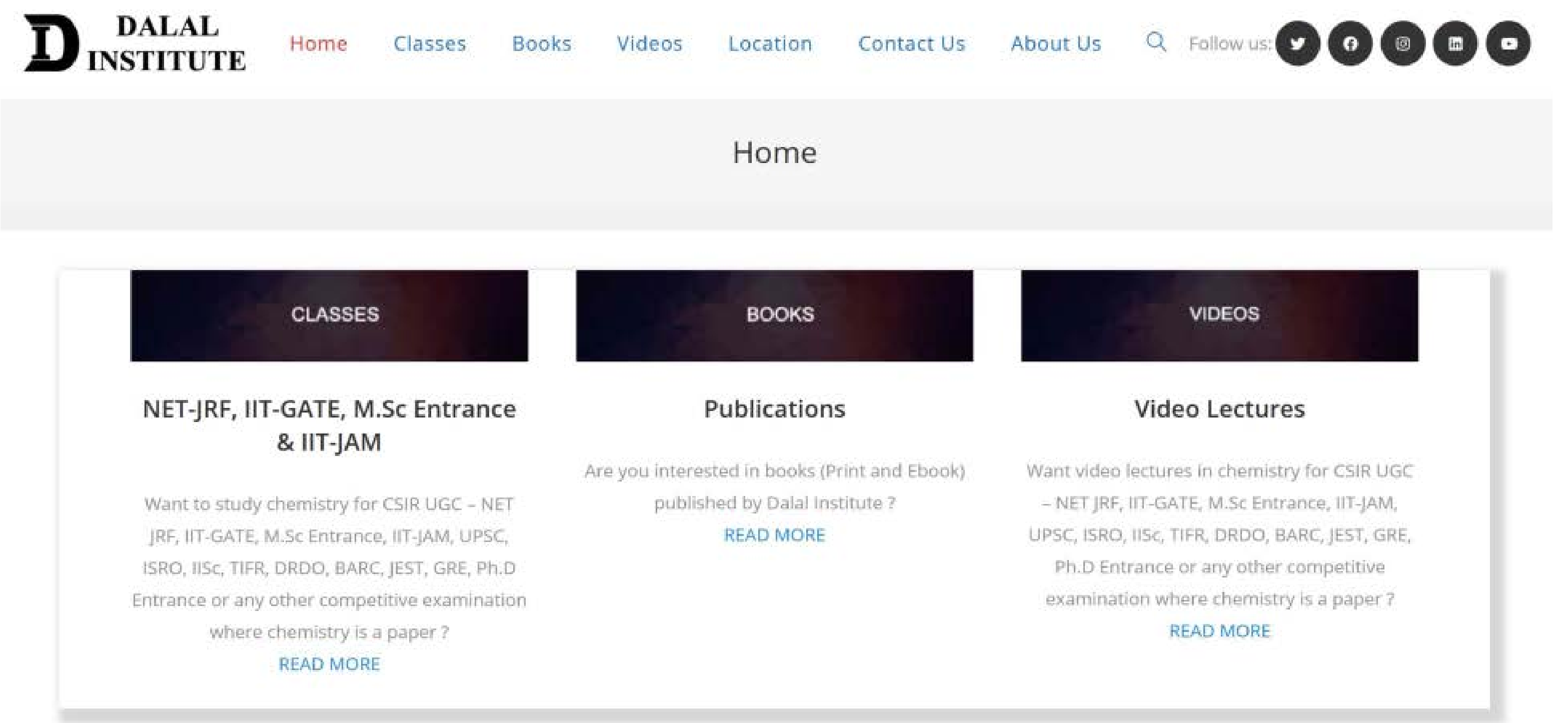
Hence, the relationship shown in the equation (49) does not consider any quenching of orbital magnetic moment at all. In this case, the resultant orbital angular momentum quantum number is zero i.e. $L = 0$, the L will be completely eliminated from equation (49) and we will get:

$$\mu_{\mathrm{eff}} = \sqrt{4S(S+1)}\ \mathrm{B.M.} \qquad (50)$$

Owing to the relationship between spin multiplicity and the number of unpaired electrons ($S = n/2$), equation (50) can also be written in the form given below.

$$\mu_{\mathrm{eff}} = \sqrt{n(n+2)}\ \mathrm{B.M.} \qquad (51)$$

Where *S* is the spin multiplicity and *n* is the number of unpaired electrons. The equations (50, 51) are also called as spin only formulas as they do not include any contribution from orbital motion. Now it is worthy to note that no free transition metal exists with very small *J*-separation relative to thermal energy; however, had they shown such behavior, we would have used the equation (49) to calculate their magnetic moment. In that case, a comparative analysis of the results from equation (49) and equation (51) could be used to estimate the contribution exclusively from the orbital motion.



Home

CLASSES

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM

Want to study chemistry for CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

READ MORE

BOOKS

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute ?

READ MORE

VIDEOS

Video Lectures

Want video lectures in chemistry for CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

READ MORE

Home: https://www.dalalinstitute.com/
Classes: https://www.dalalinstitute.com/classes/
Books: https://www.dalalinstitute.com/books/
Videos: https://www.dalalinstitute.com/videos/
Location: https://www.dalalinstitute.com/location/
Contact Us: https://www.dalalinstitute.com/contact-us/
About Us: https://www.dalalinstitute.com/about-us/

Postgraduate Level Classes
(NET-JRF & IIT-GATE)
Admission
Regular Program
Distance Learning
Test Series
Result

Undergraduate Level Classes
(M.Sc Entrance & IIT-JAM)
Admission
Regular Program
Distance Learning
Test Series
Result

A Textbook of Inorganic Chemistry – Volume 1

"A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal" is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.
READ MORE

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

Sign Up

International
Edition

A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

MANDEEP DALAL

First Edition

DALAL INSTITUTE

Table of Contents

Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

ISBN: 978-81-938720-0-0
9 788193 872000
MRP: Rs 800.00

DALAL INSTITUTE
Main Market, Sector 14, Rohtak, Haryana 124001, India
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com