I.G.N.O.U. *Based*

NEERAJ®

C.H.E.-10

SPECTROSCOPY

By: *Uttam*

Question Bank Cum Chapterwise Reference Book
Including **Many Solved Question Papers**

NEERAJ
PUBLICATIONS
(Publishers of Educational Books)
(An ISO 9001 : 2008 Certified Company)

Sales Office:
1507, 1st Floor, Nai Sarak, Delhi - 6
Ph.: 011-23260329, 45704411,
23244362, 23285501
E-mail: info@neerajignoubooks.com
Website: www.neerajignoubooks.com

MRP ₹ 200/-

Published by:

NEERAJ PUBLICATIONS

Sales Office : **1507, 1st Floor, Nai Sarak, Delhi-110 006**
E-mail: **info@neerajignoubooks.com**
Website: **www.neerajignoubooks.com**

Reprint Edition with Updation of Sample Question Paper Only

Typesetting by: *Competent Computers*

Printed at: *Novelty Printer*

Notes:

1. *For the best & upto-date study & results, please prefer the recommended textbooks/study material only.*
2. *This book is just a Guide Book/Reference Book published by NEERAJ PUBLICATIONS based on the suggested syllabus by a particular Board /University.*
3. *The information and data etc. given in this Book are from the best of the data arranged by the Author, but for the complete and upto-date information and data etc. see the Govt. of India Publications/textbooks recommended by the Board/University.*
4. *Publisher is not responsible for any omission or error though every care has been taken while preparing, printing, composing and proof reading of the Book. As all the Composing, Printing, Publishing and Proof Reading etc. are done by Human only and chances of Human Error could not be denied. If any reader is not satisfied, then he is requested not to buy this book.*
5. *In case of any dispute whatsoever the maximum anybody can claim against NEERAJ PUBLICATIONS is just for the price of the Book.*
6. *If anyone finds any mistake or error in this Book, he is requested to inform the Publisher, so that the same could be rectified and he would be provided the rectified Book free of cost.*
7. *The number of questions in NEERAJ study materials are indicative of general scope and design of the question paper.*
8. *Question Paper and their answers given in this Book provide you just the approximate pattern of the actual paper and is prepared based on the memory only. However, the actual Question Paper might somewhat vary in its contents, distribution of marks and their level of difficulty.*
9. *Any type of ONLINE Sale/Resale of "NEERAJ BOOKS/NEERAJ IGNOU BOOKS" published by "NEERAJ PUBLICATIONS" on Websites, Web Portals, Online Shopping Sites, like Amazon, Flipkart, Ebay, Snapdeal, etc. is strictly not permitted without prior written permission from NEERAJ PUBLICATIONS. Any such online sale activity by an Individual, Company, Dealer, Bookseller, Book Trader or Distributor will be termed as ILLEGAL SALE of NEERAJ IGNOU BOOKS/NEERAJ BOOKS and will invite legal action against the offenders.*
10. *Subject to Delhi Jurisdiction only.*

NEERAJ PUBLICATIONS
(Publishers of Educational Books)
(An ISO 9001 : 2008 Certified Company)
1507, 1st Floor, NAI SARAK, DELHI - 110006
Ph. 011-23260329, 45704411, 23244362, 23285501
E-mail: **info@neerajignoubooks.com** *Website:* **www.neerajignoubooks.com**

CONTENTS

SPECTROSCOPY

Question Bank – (Previous Year Solved Question Papers)

Question Paper—June, 2019 (Solved)	**1-3**
Question Paper—June, 2018 (Solved)	**1-3**
Question Paper—June, 2017 (Solved)	**1-4**
Question Paper—June, 2016 (Solved)	**1-4**
Question Paper—June, 2015 (Solved)	**1-4**
Question Paper—June, 2014 (Solved)	**1-5**
Question Paper—June, 2013 (Solved)	**1-5**
Question Paper—June, 2012 (Solved)	**1-4**

S.No. ***Chapterwise Reference Book*** ***Page***

BASIC CONCEPTS AND ROTATIONAL SPECTRA

1. Spectra of Atoms **1**

2. Symmetry of Molecules **10**

3. Rotational Spectra **18**

IR AND RAMAN SPECTRA

4. Vibrational Spectra of Diatomic Molecules **26**

5. Infrared Spectra of Polyatomic Molecule **36**

6. Raman Spectroscopy **47**

ELECTRONIC SPECTRA AND INSTRUMENTATION

7. Electronic Spectra-I **57**

S.No. *Chapter* *Page*

8. Electronic Spectra-II **66**

9. Optical Spectroscopy: Instrumentation and Sampling **73**

RESONANCE SPECTROSCOPY AND MASS SPECTROMETRY

10. Nuclear Magnetic Resonance Spectroscopy **81**

11. Electron Spin Resonance Spectroscopy **90**

12. Mass Spectrometry **97**

13. Exercises in Problem Solving Using IR, UV, NMR and Mass Spectral Techniques **104**

■■

Sample Preview
of the
Solved
Sample Question
Papers

Published by:

NEERAJ
PUBLICATIONS
www.neerajbooks.com

QUESTION PAPER

(June – 2019)

(Solved)

SPECTROSCOPY

Time : 2 Hours] *[Maximum Marks : 50*

Note : *(i) Answer any five questions.*

(ii) Use of log tables and non-programmable calculators is allowed.

β_e, = 9.274 × 10^{-24} JT^{-1} h = 6.626 × 10^{-34} Js ; c = 2.998 × 10^8 ms^{-1}; e = 1.6 × 10^{-19}C

Q. 1. *(a)* Derive the term symbol for the possible spectroscopic states of carbon.

Ans. Ref.: See Chapter-1, Page No. 6, 'Spectroscopic States of Carbon'.

***(b)* The staggered conformation of ethane has S_6 improper axis of symmetry. Illustrate the operations involved.**

Ans. Ref.: See Chapter-2, Page No. 16, Q. No. 7.

***(c)* Calculate the energy (in Joules) associated with a radiation of wavelength, λ = 460nm.**

Ans. Ref.: See Chapter-1, Page No. 8, Q. No. 1.

Also Add:

$$\in = h\nu = \frac{hc}{\lambda}$$

$$h = 6.626 \times 10^{-34}\ \text{J}s$$

$$c = 2.998 \times 10^{8}\ \text{ms}^{-1}$$

$$\lambda = 460\ \text{nm}$$

$$\in = \frac{6.626 \times 10^{-34}\ \text{J}s \times 2.998 \times 10^{8}\ \text{ms}^{-1}}{460 \times 10^{-9}\ \text{m}}$$

$$= \frac{19.864 \times 10^{-26}}{460 \times 10^{-9}\ \text{m}}$$

$$= 0.0431 \times 10^{-17}$$

$$= 4.31 \times 10^{-19}\ \text{J}.$$

Q. 2 *(a)* The rotational constants of ^{12}C ^{16}O and ^{13}C ^{16}O are 1.92118 cm^{-1} and 1.83669 cm^{-1}, respectively. Given that the atomic masses of ^{12}C and $^{16}0$ are, respectively 12 and 15.9994 find the atomic mass of ^{13}C.

Ans. Ref.: See Chapter-3, Page No. 21-22, 'Applications of Study of Rotational Spectra *(ii)*'.

***(b)* Give reasons for the following :**

***(i)* The >C=0 group frequency in acyl chlorides is higher than that in alkyl esters.**

***(ii)* The >C=0 group frequency in methyl acetate is less than that in phenyl acetate.**

Ans. Ref.: See Chapter-5, Page No. 45, Q. No. 5.

***(c)* Predict the shape of PCI_3 using VSEPR theory. Draw its structure.**

Ans. Ref.: See Chapter-2, Page No. 15, Q. No. 1.

Q. 3. *(a)* HCI molecule shows an IR absorption at 2890 cm^{-1}. Determine its force constant and maximum displacement for v = 3. Given that the atomic masses of H and C*l* are 1 × 10^{-3} kg and 35.5 × 10^{-3} kg, respectively.

Ans. The value of force constant can be calculated by:

$$k = 4\,\pi v^2 \mu$$

Given that,

$$\mu = 1.627 \times 10^{-27}\ \text{kg}$$

$$v = 2890\ \text{cm}^{-1}$$

$$= 4 \times 3.14 \times 3.14 \times 2890 \times 2890 \times 1.627$$

$$= 535\ \text{kg}\,s^{-2}$$

$$= 535\ \text{Nm}^{-1}$$

The value of maximum displacement can be calculated by:

$$\Delta r = \Delta r_0 \cos 2\pi\ v_{\text{osc}}$$

Maximum displacement for $r_{-3} = 2.86 \times 10^{-9}$.

***(b)* The two peaks at 2349 and 667 cm^{-1} in the IR spectrum of CO_2 are found to be absent in Raman spectrum while the peak at 1340 cm^{-1} is Raman active only. Explain by assigning the peaks to respective modes of vibration.**

Ans. Ref.: See Chapter-5, Page No. 38, 'IR Spectrum of CO_2 molecule'.

***(c)* What are Stokes and anti-Stokes lines ? Why is the intensity of Stokes lines generally greater than that of anti-stokes lines?**

Ans. A stokes line is the radiation of particular wavelengths present in the spectra associated with fluorescence and the Raman scattering. Stokes lines are of longer wavelength than that of the exciting radiation responsible for the fluorescence or Raman effect.

Anti-stokes lines are found in fluorescence and in Raman spectra when the atoms or molecules of the material are already in an excited state. In this case the radiated line energy is the sum of the pre-excitation energy and the energy absorbed from the exciting radiation. Thus, anti-stokes lines are always of shorter wavelength than that of the light that produces them.

Also Ref.: See Chapter-6, Page No. 56, Q. No. 3.

Q. 4. *(a)* Name the sources used for the following spectrophotometric techniques :

***(i)* Microwave**
***(ii)* Infrared**
***(iii)* Raman**
***(iv)* Ultraviolet**

Ans. Ref.: See Chapter-9, Page No. 73-74, 'Spectroscopic Components (Sources)'.

***(b)* State Franck-Condon principle.**

Ans. Ref.: See Chapter-7, Page No. 59, 'Franck-Condon Principle and Intensities of Electronic Spectra'.

***(c)* The absorbance of an aqueous solution of a substance X at 600nm is found to be 0.45. Calculate the molar absorption coefficient if its concentration is 1×10^{-4} M. What will be the transmittance of 7.5×10^{-5} M solution of this substance? Path length, l = 1cm.**

Ans. According to Beer's Law

$$A = \in bc$$

Where $\in$ is the molar absorptivity in 2/m of cm, b is the path length of the cuvetic and c is the concentration in mol/L which is 1×10^{-4}.

Therefore,

$$\text{Molar Absorptivity } \in = \frac{A}{bc}$$

$$= \frac{0.45}{1\times1\times10^{-4}\,\text{M}}$$

$$= 0.45 \times 10^{4}\ \text{L/mol. cm.}$$

***(d)* $KMnO_4$ and $K_2Cr_2O_7$ are intensely coloured though there is no possibility of d-d transition in them. Explain.**

Ans. Ref.: See Chapter-8, Page No. 72, Q. No. 3.

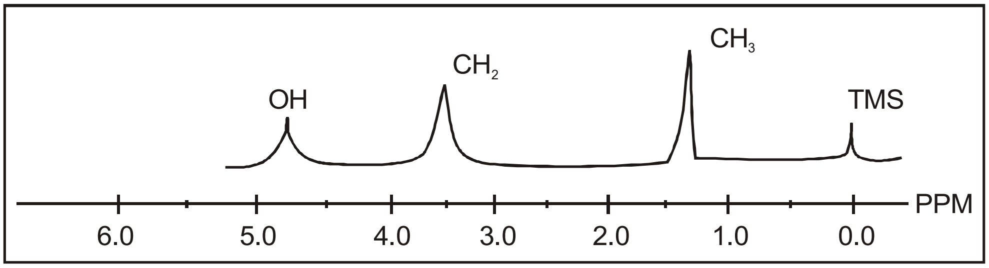
Q. 5. *(a)* Name the reference standard used in NMR spectroscopy. Give reasons for its choice.

Ans. Tetramethylsilane (TMS) is the organosilicon compound with the formula $Si(CH_3)_4$. It is the simplest tetraorganosilane. Like all silanes, the TMS framework is tetrahedral and it is a building block in organometallic chemistry.

TMS (tetramethylsilane) is the accepted internal standard for calibrating chemical shift for ^{1}H, ^{13}C and ^{29}Si.NMR spectroscopy in organic solvents where TMS is soluble. In water, where it is not soluble, sodium salts of DSS, *z*, 2-dimethyl- *z*-silapentane 5-sulfonate, are used instead. Because of its high votality, TMS can easily be evaporated which is convenient for recovery of samples analysed by NMR spectroscopy.

***(b)* Draw and explain the ^{1}H-NMR spectrum of CH_3CH_2OH.**

Ans.



SPECTROSCOPY

BASIC CONCEPTS AND ROTATIONAL SPECTRA

1

Spectra of Atoms

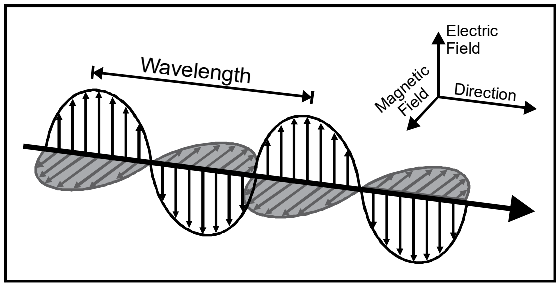
INTRODUCTION

With the starting of the first chapter of the "Spectroscopy Course", we are pre-assuming that you are already familiar with "Atoms and Molecules". We are also sure of the fact that there is enough time gap in-between, it will be advisable that a refreshment of the concepts dealt within the "Atoms and Molecules" course. This chapter will describe the concept of the spectra of Atoms. Let's start with the explanation of electromagnetic radiation and its associated concepts.

CHAPTER AT A GLANCE

THE ELECTROMAGNETIC RADIATION

Electromagnetic radiation (EM radiation or EMR) is a form of energy emitted and absorbed by charged particles which exhibits wave-like behaviour as it travels through space. EMR has both electric and magnetic field components, which stand in a fixed ratio of intensity to each other, and which oscillate in phase perpendicular to each other and perpendicular to the direction of energy and wave propagation.



Some parameters will be repeated often during this chapter forthcoming chapters too viz. wavelength, frequency, wave number, the relation between wavelength and frequency for electromagnetic radiation is:

$$\lambda = \frac{c}{v}$$

In the SI system of units the wavelength λ is measured in metres (*m*) and since wavelengths are usually very small one often uses the nano metre (*nm*) which is 10^{-9} m.

The frequency *v* in the SI system is measured in reciprocal seconds s^{-1} which is called a Hertz and represented by Hz. Often in Chemistry one will use the reciprocal of the wavelength in centimetres as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by $\overline{v}$ and is defined by

$$\overline{v} = \frac{1}{\lambda} = \frac{v}{c}$$

There is an inverse relationship between the energy of a photon (E) and the wavelength of the light (λ) given by the equation:

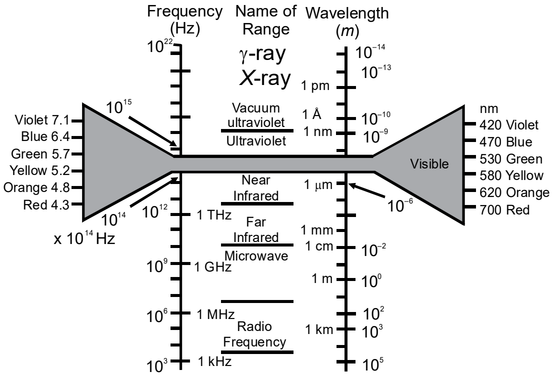
$$E = \frac{hc}{\lambda}$$

Where *h* is Planck's constant and *c* is the speed of light. The value of these and other commonly used constants is given in the constants page.

$h = 6.626 \times 10^{-34}$ joules

$c = 2.998 \times 10^{8}$ m/s

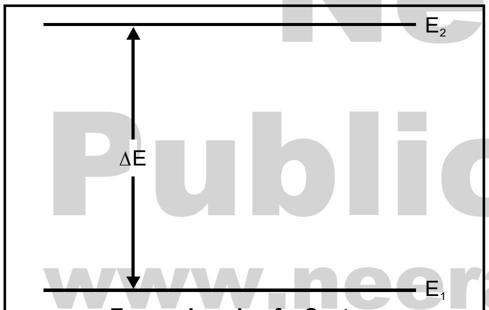
Electromagnetic Spectrum: As shown in this figure range of electromagnetic radiation.



Range of Electromagnetic Radiation

INTERACTION OF RADIATION WITH MATTER

When the energy is absorbed then lower energy state (E_1) get transfer to higher energy state (E_2). In higher energy state the (E_2) lose energy then state is transferred to lower energy state (E_1).



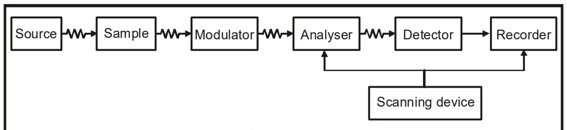
Energy Levels of a System

Energy difference (E) between these two states:

$$\Delta E = E_2 - E_1 = hv$$

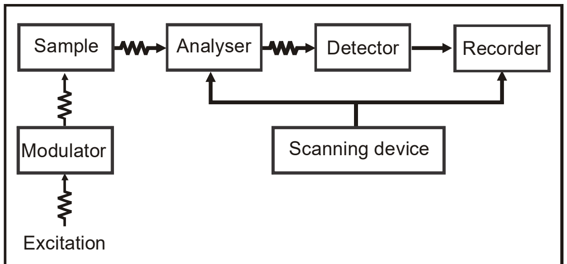
hv = energy absorbed or emitted

We determine the absorbed or emitted energy using by some instrument, these instruments are known as absorption or emission spectrophotometer. These instruments measure frequencies of radiation that are absorbed or emitted from any irradiated sample. We can represent the absorbed or emitted spectrophotometer by block diagrams:



Absorption Spectrophotometer

Absorption spectroscopy refers to spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample.



Emission Spectrophotometer

Emission spectrophotometer uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration. Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized, and atomized by a flame, discharge, or plasma.

THE ATOMIC SPECTRUM OF HYDROGEN

The energy of the n^{th} electron is:

$$E_n = \frac{-Z^2e^4m}{8\varepsilon_0^2h^2n^2}$$

Where,

Z = atomic number

e = charge the electron

m = mass of the electron

$\varepsilon_0 = 8.854 \times 10^{-12}\ C^2\ N^{-1}\ m^{-2}$

h = plank's constant

n = number the orbit

then the energy difference:

$$\begin{aligned}\Delta E &= E_2 - E_1 \\ &= \frac{-Z^2e^4m}{8\varepsilon_0^2h^2n_2^2} - \frac{-Z^2e^4m}{8\varepsilon_0^2h^2n_1^2} \\ &= \frac{Z^2e^4m}{8\varepsilon_0^2h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\end{aligned}$$

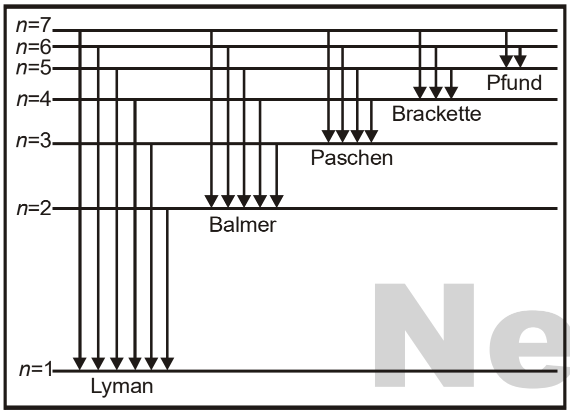
$$\bar{v} = \frac{\Delta E}{hc} = \frac{Z^2e^4m}{8\varepsilon_0^2h^2c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where,

$$R_H = \frac{Z^2e^4m}{8\varepsilon_0^2h^3c} \qquad (R_H = \text{Rydberg Constant})$$

$$\bar{v} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

When a high potential is applied to hydrogen gas at low pressure in a discharge tube, it starts emitting a bright light. It is separated into several radiations and forms a spectrum upon passing through a prism or grating. The spectrum consists of separate lines corresponding to different wavelengths. This is called Hydrogen atomic spectrum.The spectral lines are formed due to electronic transitions from one energy level to another. These lines are divided into five series according to the range of wavelengths:



The wave numbers of spectral lines in each series can be calculated using Rydberg's equation as follows:

$$\frac{1}{\lambda} = R_H Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where

n_1 and n_2 are the principal quantum numbers of orbits corresponding to the electronic transition.

R_H = Rydberg's constant = 1,09,677 cm^{-1}

Z = atomic number

Note: Every element has its own characteristic line spectrum. There is regularity in the line spectrum of each element. These spectra can be considered as the finger prints of elements. Hydrogen has the simplest line spectrum among all the elements. The line spectra become complex with increase in atomic number of the element.

FINE STRUCTURE OF HYDROGEN ATOM SPECTRUM

When the spectral lines of the hydrogen spectrum are examined at very high resolution, they are found to be closely-spaced doublets. This splitting is called fine structure and was one of the first experimental evidences for electron spin.The small splitting of the spectral line is attributed to an interaction between the electron spin S and the orbital angular momentum L. It is called the spin-orbit interaction.

The magnitude of these momentums orbital angular momentum | 1 | and Spin angular momentum | s | is given by the following equations:

$$| 1 | = \sqrt{l\,(\,l+1)}\,.\,\frac{h}{2\pi}$$

$$| s | = \sqrt{s\,(\,s+1)}\,.\,\frac{h}{2\pi}$$

Where, | 1 | is angular momentum these values from 0 to $n - 1$

S = spin quantum number

$$\frac{h}{2\pi} = 1.055 \times 10^{-34}\text{ Js} = \hbar$$

$$| 1 | = \sqrt{l\,(l+1)}\text{ in units of }\hbar = \sqrt{l\,(l+1)}\,\hbar$$

$$| s | = \sqrt{s\,(s+1)}\text{ in units of }\hbar = \sqrt{s\,(s+1)}\,\hbar$$

Total angular momentum of the electron:

$$J = \vec{l} + \vec{s}$$

Vector Nature of Orbital Angular Momentum

The orbital angular momentum for an atomic electron can be visualized in terms of a vector model where the angular momentum vector is seen as precessing about a direction in space. While the angular momentum vector has the magnitude shown, only a maximum of l units can be measured along a given direction, where l is the orbital quantum number.

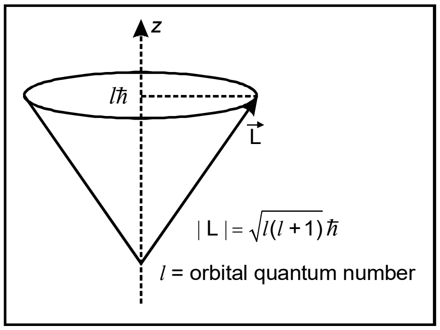
Since there is a magnetic moment associated with the orbital angular momentum, the precession can be compared to the precession of a classical magnetic moment caused by the torque exerted by a magnetic field. This precession is called Larmor precession and has a characteristic frequency called the Larmor frequency.

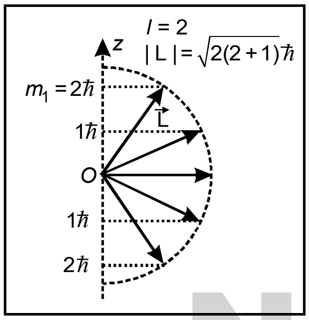
While called a "vector", it is a special kind of vector because it's projection along a direction in space is quantized to values one unit of angular momentum apart. The diagram shows that the possible values for the "magnetic quantum number" m_l for $l = 2$ can take the values

$$m_l = -2, -1, 0, 1, 2$$

or, in general

$$m_l = -l, -l+1, ..., l-1, l\,.$$





Vector Nature of Spin Angular Momentum

In vector nature of spin angular momentum, the total angular momentum is given by:

$$j = \vec{l} + \vec{s}$$

$$|\, j\,| = \sqrt{j(j+1)}\hbar = \sqrt{j(j+1)} \text{ in units of } \hbar$$

Where j can take values:

$$\left|(l+s\right|,\ \left|(l+s-1\right|, \ldots\ldots.,\ \left|(l-s)\right|$$

Term Symbols

Term symbol specifies a certain electronic state of an atom (usually a multi-electron one), by briefing the quantum numbers for the angular momenta of that atom. The form of an atomic term symbol implies Russell-Saunders coupling. Transitions between two different atomic states may be represented using their term symbols, to which certain rules apply. In the Russell-Saunders coupling scheme, term symbols are in the form of

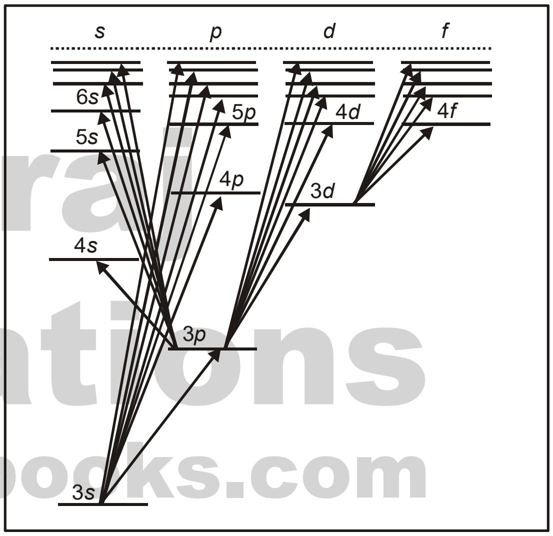
$${}^{2S+1}L_J$$

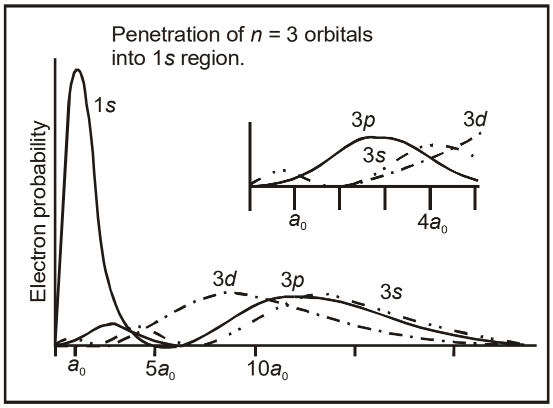
Where S represents the total spin angular momentum, L specifies the total orbital angular momentum, and J refers to the total angular momentum. In a term symbol, L is always an upper-case from the sequence "*s*, *p*, *d*, *f*, *g*, *h*, *i*, *k*...", wherein the first four letters stand for sharp, principal, diffuse and fundamental, and the rest follow in an alphabetical pattern. Note that the letter *j* is omitted.

SPECTRA OF HYDROGEN-LIKE ATOMS

A hydrogen-like ion containing one electron and thus is iso electronic with hydrogen. Except for the hydrogen atom itself (which is neutral), these ions carry the positive charge $e\,(Z-1)$, where Z is the atomic number of the atom.

Hydrogen-like atomic orbitals are eigen functions of the one-electron angular momentum operator L and its z component L_z. The energy eigen values do not depend on the corresponding quantum numbers, but solely on the principal quantum number n. Hence, a hydrogen-like atomic orbital is uniquely identified by the values of: principal quantum number n, angular momentum quantum number l, and magnetic quantum number m.





Sodium Energy Levels

The sodium spectrum is dominated by the bright doublet known as the Sodium D-lines at 588.9950 and