B.Sc. (Sem. - 4) Physics
Course: US04CPHY21

Electromagnetic Theory and Spectroscopy
UNIT-3 Lecture 2

Dr. A. R. Jivani, Physics Department, VPM

Atomic Spectra

Dr. A. R. Jivani, Physics Department, VPM

Outline

- Shortcomings of Bohr theory
- Criticism and limitations of old quantum mechanical models
- The Spinning Electron
- Space Quantization
- Quantum Numbers and their Physical Interpretation

Shortcoming of Bohr Theory

1.13. SHORTCOMINGS OF BOHR THEORY

- The Bohr theory does not give the following information :

- (a) Bohr theory **does not give any idea of the distribution and arrangement of electrons in the atom**.

1.13. SHORTCOMINGS OF BOHR THEORY

- The Bohr theory does not give the following information :

- (b) In this theory we have **two rival theories** viz. classical and quantum.
  - The equilibrium is governed by classical laws, while the emission of radiation is explained by quantum rules.

1.13. SHORTCOMINGS OF BOHR THEORY

- The Bohr theory does not give the following information :

- c) The theory **predicts only the frequency of different spectral lines** but does not give any information about the **intensities of different lines.** Moreover, it is quite inadequate in explaining the **multiplicity and fine structure of spectral lines**.

1.13. SHORTCOMINGS OF BOHR THEORY

- The Bohr theory does not give the following information :

- (d) With the help of Bohr theory it is **difficult to treat dynamical problem of atoms** containing more than one valence electron.

2.7. CRITICISM AND LIMITATIONS OF OLD QUANTUM-MECHANICAL MODELS

2.7. CRITICISM AND LIMITATIONS OF OLD QUANTUM-MECHANICAL MODELS

- Old quantum mechanical models put forth by **Bohr** and **Sommerfeld** succeed in predicting many elementary aspects of atomic spectra of hydrogen and hydrogen-like atoms.
- For example,
  - Explained different series of transitions observed in hydrogen atoms
  - The correct values of excitation and ionisation potentials, etc.
  - But these models were not completely satisfactory.

Drawbacks….

- Both models **could not explain distribution and arrangement of electrons in atoms.**
- Both models could not explain **the variation of intensity of the spectral lines**.

Drawbacks of Bohr and Sommerfeld atomic models:

- In case of **complex atoms**, Bohr’s theory fails to calculate energy of the system and frequencies of radiation emitted.

- Sommerfeld atomic model gave an explanation for splitting of individual spectral lines of H, still it could not predict number of observed fine structure of these lines.

Drawbacks….

- Both models **could not explain the Zeeman and Stark effect.**

2.7. CRITICISM AND LIMITATIONS OF OLD QUANTUM-MECHANICAL MODELS

- Principal limitations of these models are the following :
- (1) The **emission spectrum** from the hydrogen atom exhibits more details, i.e., **large number of lines are revealed** when recorded with high resolving power spectrograph.

2.7. CRITICISM AND LIMITATIONS OF OLD QUANTUM-MECHANICAL MODELS

- (1) By assuming **elliptical orbits** in addition to the **circular** ones and by separately quantizing the angular motion and the radial motion, Sommerfeld contributed substantially to the problem.

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2.7. CRITICISM AND LIMITATIONS OF OLD QUANTUM-MECHANICAL MODELS

- Principal limitations of these models are the following :
- (2) The **quantization of the angular momentum**, mvr = nh, of an individual electron applies only if the electron moves in the **pure central force field**.
- This is not the case when there is more than one electron in the atom because of mutual repulsion between them.

2.7. CRITICISM AND LIMITATIONS OF OLD QUANTUM-MECHANICAL MODELS

- Principal limitations of these models are the following :

- (3) No logical reason for assuming different quantum numbers was given. The quantum.

- (4) The **relative intensities of different transitions** remained unexplained on the basis of these models.

2.7. CRITICISM AND LIMITATIONS OF OLD QUANTUM-MECHANICAL MODELS

- Principal limitations of these models are the following :

- (5) The **spectra of atoms having more than one valence electron** could be accounted for by Bohr and Sommerfeld.
- (6) The **behaviour of the atoms under the influence of electric and magnetic field**s posed a problem to be explained for these models.

Vector Atom Model:

Vector Atom Model:

- To overcome all these objections a new model was proposed known as Vector Atom Model was proposed by
- **Bohr**,
- **Sommerfeld**,
- **Uhelenbeck,**
- **Goudsmith,**
- **Pauli,**
- **Stern and Gerlach.**

Vector Atom Model:

Two main Concepts of Vector Atom Model:

(1) The concepts of quantization of direction

- i.e. spatial quantization

(2) The concept of spinning of electron

Vector Atom Model:

(1) The concept of spinning of electron

- Importance
- To explain multiple character of spectral lines
  - Doublets: yellow sodium line [6 ^{0}A]
  - Triplets Mercury triplet [1400 ^{0}A]
- To explain effect of magnetic fields on the spectral lines

Vector Atom Model:

(2) The concept of spinning of electron

- Uhlenbach and Goudsmit, in the year 1925,put forward their famous hypothesis of electron spin.

Vector Atom Model:

(2) The concept of spinning of electron

- The moving electrons have two types of motion, namely the orbital motion and the spin motion.
- two angular momenta and two magnetic momenta
  - The **total angular momentum** of the electron is the sum of two angular momenta (orbital angular momentum and spin angular momentum)
  - The **total magnetic momenta** is the sum of two parts: the orbital magnetic moment and spin magnetic moment

Vector Atom Model:

(2) The concept of spinning of electron

- The interaction between two **angular momenta** accounts for the multiplicity of the spectral lines

- The interaction between two **magnetic moments** explains the **fine structure of spectral lines**.

Vector Atom Model:-

(2) The concepts of quantization of direction

i.e. spatial quantization

SPACE QUANTISATION

- Till now we have discussed the motion of the electron in elliptical orbits which are two-dimensional and the electron here posesses two degrees of freedom.

- Hence only two quantum numbers are sufficient to define electron orbit or energy state of an atom.

SPACE QUANTISATION

- But, in general, the motion of the electron in an atom is three-dimensional and, therefore, possesses three degrees of freedom.

  Hence, an additional quantum number and corresponding quantum condition are required to describe the true state of affairs.

SPACE QUANTISATION

- The third quantum condition quantizes the orientation of the elliptical orbit in three-dimensional space and does not alter the original Sommerfeld orbits in regard to their size and shape.

SPACE QUANTISATION

- When an electron moves in three-dimensional orbits, the orbits may, according to classical mechanics, possess all orientations with respect to a fixed direction but according to the rule of space quantization, only *certain discrete orientation are allowed.* Thus, we observe the need of a fixed direction in space.

SPACE QUANTISATION

- To obtain the preferred direction, the atom is placed in the uniform magnetic field B and for the sake of simplicity, we assume the direction of B in coincidence with the Z direction, and
- the angle between the field direction and the direction which is perpendicular to the plane of the orbit is θ (according to classical representation the normal to the plane of the orbit represents angular momentum p_{ϕ}).

SPACE QUANTISATION

- Now due to the application of magnetic field, the plane of the orbit processes about B direction that is exactly identical to the precession of a mechanical top in the gravitational field and

SPACE QUANTISATION

- this precession of angular momentum vector Pϕ generates a **cone about B** (the angular momentum Pϕ will now be mentioned as $\mathbf{P}_l$ which is according to the convention adopted in the new quantum theory).

SPACE QUANTISATION

- The rule of space quantization demands that B can take on certain discrete values. The values of angle θ is independent of B the external applied field.

- To reduce this effect, B is reduced to zero while the tendency of the orientation of elliptical orbit with field direction remains.

SPACE QUANTISATION

- The condition by which the quantization of angle θ takes place is derived from the fact that total angular momentum of the electron is constant.

- Thus the introduction of the quantization of the space and quantization of spin of the electron further introduces some new quantum numbers.

Vector Atom Model:-

(1) The concepts of quantization of direction i.e. spatial quantization

- Bohr' Model (r)
  - One degree of freedom
- Sommerfeld Model (r, θ)
  - Two degrees of freedom
- In 3-D, Three degrees of freedom
  - Classically e- can have any θ

Quantum Numbers and their Physical Interpretation

- To describe the **motion of an electron** or **electrons**, the few quantum numbers are, in general, used.

(1) The Principal or Total Quantum Number:

- The principal quantum number of an electron is denoted by the letter n and is identical with that used in Bohr-Sommerfeld theory.
- The quantum number n can take on values 1, 2, 3, 4, .∞ and governs the energy and major axis of the elliptical orbit.
- n = 1, 2 ,3 ...

(1) The Principal or Total Quantum Number:

- Classically, n does represent the ordinal number of the particular orbit occupied by the electron and the orbits having n = 1, 2, 3, 4, etc. are designated as K, L, M, N orbits, respectively.

n	1	2	3	4
Shell	K	L	M	N
Nos of electrons	2	8	18	32
	$1 s^2$	$2 s^2 2 p^6$	$3 s^2 3 p^6 3 d^{10}$	

(1) The Principal or Total Quantum Number:

- In wave mechanics, the concept of definite orbit is discarded; even then it gives the mean distance of an electron from the nucleus locates itself nearer to the nucleus than the electron with principal quantum number two.

- Similarly the latter will, in general, be nearer to the nucleus than will the electron with principal quantum number three, and so on.

(1) The Principal or Total Quantum Number:

- It is also known that the binding energy of an electron decreases as n increases and hence it also confirms the view that large value of principal quantum number n represents the large mean distance from the nucleus.
- It should also be noted here that the letters K, L, M, N, etc. not only represent that an electron lies at a particular mean distance from the orbit but also a group of electrons at that mean distance from the orbit.

(2) An Orbital Quantum Number:

- The orbital quantum number is denoted by the letter *l* and is also known as subsidiary quantum number.

- *l* = 0, 1, 2, 3, … (n -1)

(2) An Orbital Quantum Number:

- The orbital angular momentum p_l for the electron is equal to $\frac{l\,h}{2\,\pi}$ or l denotes the angular momentum in the unit of $\frac{h}{2\,\pi}$.

- $$p_l = l\,\frac{h}{2\,\pi}$$

(2) An Orbital Quantum Number:

- Since *l* can take on integral values, the **magnitude of p_l is also quantized**.

- For a particular value of *l*, all orbits have the same perihelion distance and same quantum defect by penetrating into the core of an atom.
- The orbits having same value of n but different values of *l* have various energy values corresponding to the different values of *l*.

(2) An Orbital Quantum Number:

- The quantum number *l* also governs the **degree with which the electron is attached to the nucleus**-
  - larger is the value of *l* weaker is the bond with which it is maintained with the nucleus.

- Further *l* also indicates the **degree of electronic penetration into the core of the atom**.

(2) An Orbital Quantum Number:

- The **wave mechanics** orbits have no precise meaning; even then the vector *l* is helpful in describing the angular momentum of a particular state.

- The angular momentum according to wave mechanics is given by

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

(2) An Orbital Quantum Number:

l	0	1	2	3
Sub-shell	*s*	*p*	*d*	*f*
	Sharp	Principal	Diffuse	Fundamental
Nos of electrons	2	6	10	14

Nos of electrons = $2(2l+1)$

(2) An Orbital Quantum Number:

- The position of the electron in an atom is represented by an integer number followed by a letter expressing the nature of the series, for example 2s, 3p, etc.

- If there are a number of electrons with same value of n and l, then they are represented, for example, as **$3p^4$**; superscript **4** represents that there are **4** electrons with n value equal to 3 and *l* value equal to one

(2) An Orbital Quantum Number:

- **$4d^5$**
- **n = ______**
- **l = _______**
- Nos of electrons _______

(3) A Spin Quantum Number:

- To explain the fine structure of spectral line the spin of the electron was postulated and to quantise the spin of the electron, it was assumed that the spin of the electron can take a fixed value ½.

- This value ½ for an electron is designated by the small letter s.

(3) A Spin Quantum Number:

- In the beginning, the value ½ for spin was assumed to explain the experimental observed facts and as we shall see it is quite competent in doing so, but later on Dirac's wave mechanical treatment gave it the theoretical justification.

(3) A Spin Quantum Number:

- Physically, the letter, s, denotes the spin angular quantum momentum for an electron in the unit of $\frac{h}{2\pi}$, but wave mechanics assigns for p_s (spin angular momentum) a value

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

(4) A Total Angular Momentum Quantum Number:

- The total angular momentum quantum number j is sometimes also called **inner quantum number.**

- This denotes the total angular momentum of the electron which arises from the orbital revolution and axial spin of the electron.

(4) A Total Angular Momentum Quantum Number:

- Mathematically, this is the vector sum of ***l*** and ***s***,

- i. e. $j = l + s$ or

  $j = l \pm 1/2$ because s = ½ or -1/2.

- The -1/2 value to s is assigned where it is antiparallel to the preferred direction.

(4) A Total Angular Momentum Quantum Number:

- The total angular momentum of the electron is
- $p_j = \frac{h}{2\pi}$, or more correctly
- $p_j = \sqrt{j(j+1)}\frac{h}{2\pi}$.

(4) A Total Angular Momentum Quantum Number:

- Find possible values of j for electron in 2p orbit.
- Here p orbit hence l = 1
- As we know that $j = l + s$ or
- Possible values of j are $j = l \pm 1/2$
- $j = 1 + ½ = 3/2$ and $j = 1 - ½ = 1/2$

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(4) A Total Angular Momentum Quantum Number:

- Find possible values of j for electron in 1s orbit.

(4) A Total Angular Momentum Quantum Number:

- Find possible values of j for electron in 1s orbit.
- Here p orbit hence l = 0

- As we know that $j = l + s$ or
- Possible values of j are $j = l \pm 1/2$
- $j = 0 + ½ = 1/2$ and $j = 0 - ½ = -1/2$
- j can never be negative

Possible value of j is only 1/2

(5) A Magnetic Orbital Angular Momentum Quantum Number:

- In a magnetic field, the vector *l* precessess about the magnetic field direction and forms a cone about the H axis.

- According to rule space quantization, the orientation of *l* with *H* are limited and are determined by the fact that projection of *l* in the field direction is known as **magnetic orbital quantum number** and is designed by letter m_l.

(5) A Magnetic Orbital Angular Momentum Quantum Number:

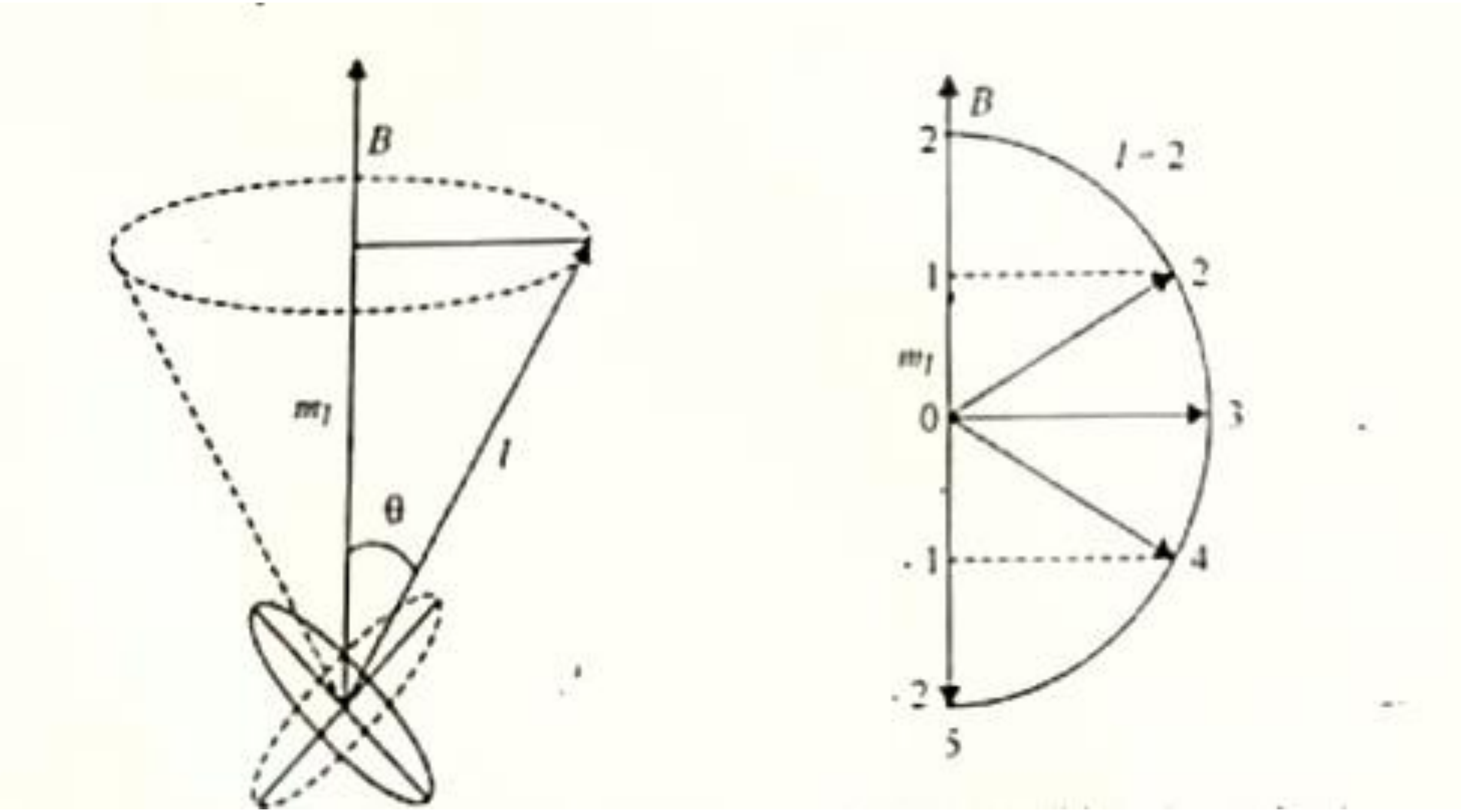
- The maximum positive value of m_l is l and minimum is zero, the possible values are, consequently, given by
- $m_l = l \cos \theta$
- $m_l = l, \; (l-1), (l-2) .. 0, l-1, l-2, l-3..-(l-1), -l$
- There are clearly $(2l + 1)$ possible values of m_l or $(2l + 1)$ possible orientations of l in space.

(5) A Magnetic Orbital Angular Momentum Quantum Number:

- Each **different orientation of angular momentum** vector l is represented by a different value of m_l.

- The negative values of m_l are due to the fact that the component of angular momentum vector may point in the direction opposite to the magnetic field B.

(5) A Magnetic Orbital Angular Momentum Quantum Number:



The orientation of l and possible m_l, values for l = 2.

(5) A Magnetic Orbital Angular Momentum Quantum Number:

Write the possible values of m_l, values for $l = 3$.

(5) A Magnetic Orbital Angular Momentum Quantum Number:

- It should be remembered that in the absence of the magnetic field, the number retains its significance and provides a definite description of the electron but the value of m_l in the absence of magnetic field has no effect on the total energy of the electron.

(6) A Magnetic Spin Quantum Number :

- Just as the vector representing orbital angular momentum precesses in the presence of magnetic field, so does the vector representing the spin angular momentum vector.

- The quantized values of s, along the field directions are ½ and -1/2 and these values of projection of, s, along the field direction are written by a letter, m_s, known as **magnetic spin quantum number**.

(6) A Magnetic Spin Quantum Number :

- The point to be noted is that m_s, cannot take the value zero while m_l can.

(7) Total Magnetic Quantum Number :

- The total magnetic quantum number is designated by the letter m_j and it is the numerical value of the projection of the total angular momentum in the field direction.
- Now since j can have **half integral values**, so m_j, also assumes half integral values.
- The possible values of m_j are written as

$$m_j = -j, (-j + 1), \dots , (j - 1), j$$

excluding zero, of course for single electron.

(7) Total Magnetic Quantum Number :

- It is worthy to note here that in general m_j is used to specify the quantum state of an electron, but when we consider the application of strong magmatic field, m_l and m_s become important and they are mentioned.

Quantum Numbers for complete atom:

Quantum Numbers for complete atom:

- The state of electron, is described in terms of the different values of *l, s and j*.

- The small letters l, s and j depict the state of an electron, while

- the capital letters, L, S and J depict the state of an atom as a whole

Quantum Numbers for complete atom:

- Significance of L:

- **For hydrogen and alkali metals**
- One valence electron system, the values of L, S and J are the same as those of l, s and j, respectively, since the interlocked electrons in closed shells and sub-shells contribute nothing to the total angular momentum.

$$L = l$$

Quantum Numbers for complete atom:

- Significance of L:

For an atom having more than one emission electrons

$$L = \sum l_i .$$

Quantum Numbers for complete atom:

- Significance of L:

  - The minimum possible value for L is zero.
  - If one l_i is larger than the sum of all others, the minimum value is not zero.
  - According to wave mechanics, individual l_i can orient itself in certain discrete directions.
  - The values of L for atom having two emitting electrons with l values as, l_1 and l_2 are written as

$$L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2), \ldots (l_1 - l_2)$$

Quantum Numbers for complete atom:

- Significance of L:
- $L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2), \ldots (l_1 - l_2)$
- Let $l_1 = 2$ and $l_2 = 1$; then
- $L = (2+1), (2+1-1), (2-1),$
- $L = 3, 2, 1.$

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Quantum Numbers for complete atom:

- Significance of L:

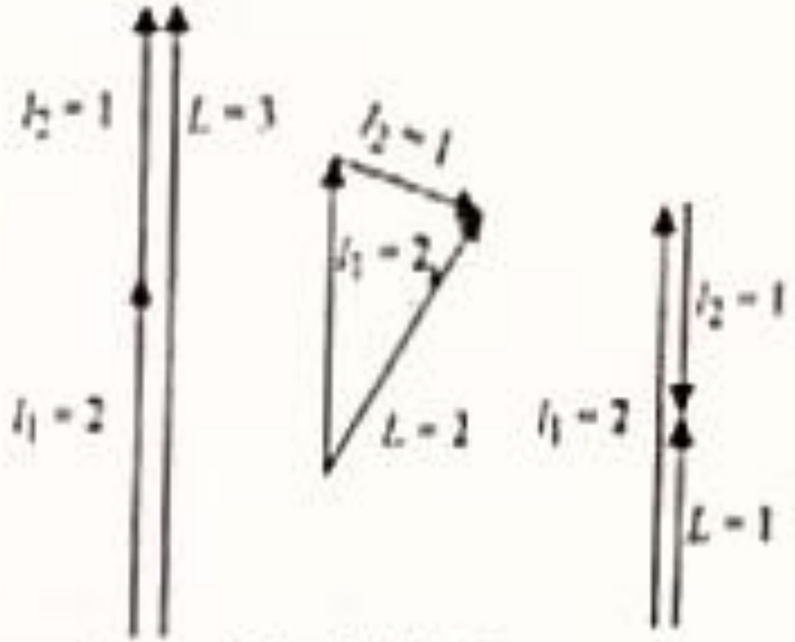


Fig. 3.3. Vector addition of individual angular momentum.

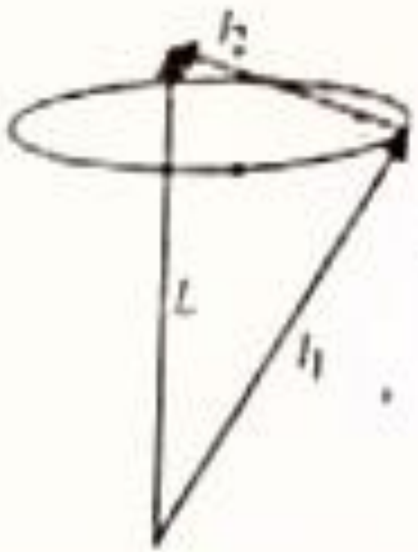


Fig. 3.4. Precession of l_1 and l_2 about L.

Quantum Numbers for complete atom:

- Significance of L:
- $L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2), \ldots (l_1 - l_2)$
- Let $l_1 = 3$ and $l_2 = 1$; then
- L = ?????

Quantum Numbers for complete atom:

- Significance of S:

- It has been postulated that the value of spin for each and every electron is always 1/2.
- This spin may of course be parallel and antiparallel to the preferred direction. The spin of the electron, as we have already discussed, is expressed by a smaller letter, s, for single electron.

$$S = s$$

Quantum Numbers for complete atom:

- Significance of S:

- But when several electrons are present, we ascribe each electron a definite value of spin, s_i (the magnitude of all s_i's is ½ but their directions may be different) and different s_i's like l_i's combine to form a resultant S for the atom.

$$S = \sum s_i$$

Quantum Numbers for complete atom:

- Significance of S:

- The spin angular momentum vector S, like L, can take on certain discrete values. If there are N electrons, the possible S values are written as

$$\frac{N}{2}, \left(\frac{N}{2} - 1\right), \qquad \left(\frac{N}{2} - 2\right), \ldots \frac{1}{2} \; or \; 0$$

Quantum Numbers for complete atom:

- Significance of S:

- For N electrons, the possible S values are written as

$$\frac{N}{2}, \left(\frac{N}{2}-1\right), \quad \left(\frac{N}{2}-2\right), \dots \frac{1}{2} \; or \; 0$$

For N = 1   S = 1/2

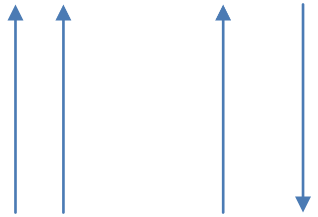
Quantum Numbers for complete atom:

- Significance of S:

- For N electrons, the possible S values are written as

$$\frac{N}{2}, \left(\frac{N}{2}-1\right), \quad \left(\frac{N}{2}-2\right), \ldots \frac{1}{2} \; or \; 0$$

For N = 2   Possible S = 0 , 1



Quantum Numbers for complete atom:

- Significance of S:

- For N electrons, the possible S values are written as

$$\frac{N}{2}, \left(\frac{N}{2} - 1\right), \quad \left(\frac{N}{2} - 2\right), \ldots \frac{1}{2} \; or \; 0$$

For N = 3 Possible values of S = 1/2 , 3/2

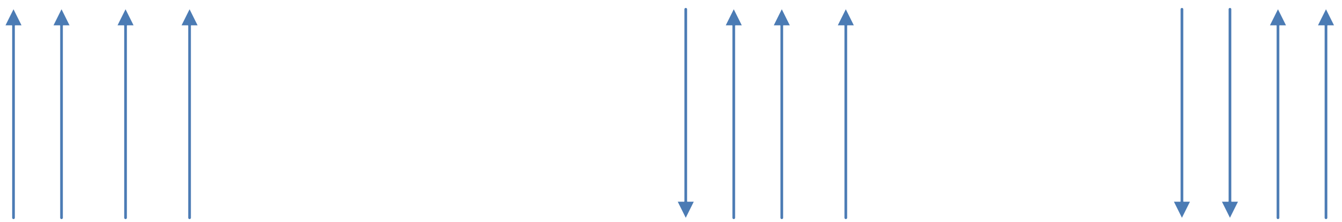
Quantum Numbers for complete atom:

- Significance of S:

- For N electrons, the possible S values are written as

$$\frac{N}{2}, \left(\frac{N}{2}-1\right), \quad \left(\frac{N}{2}-2\right), \dots \frac{1}{2}\ or\ 0$$

For N = 4   Possible values of S = 0, 1, 2



Quantum Numbers for complete atom:

- Significance of S:

- For N electrons, the possible S values are written as

$$\frac{N}{2}, \left(\frac{N}{2} - 1\right), \quad \left(\frac{N}{2} - 2\right), \ldots \frac{1}{2} \; or \; 0$$

For N = 5   Possible values of S = 1/2, 3/2, 5/2

Quantum Numbers for complete atom:

- Significance of S:

- For **odd number of N** electrons, the possible S values are **odd multiple of 1/2**

- For **even number of N** electrons, the possible S values are **even multiple of 1/2**

Quantum Numbers for complete atom:

- Significance of J:

- Just as L and S represent, respectively, total orbital angular momentum and total spin angular momentum for the atom, so does J, i.e., it represents the total angular momentum for the atom as a whole.

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Quantum Numbers for complete atom:

- Significance of J:

- Primarily the letter J was introduced empirically to distinguish different sub-levels with same L value, but now, according to wave mechanics the angular momentum for the atom is essentially the function of J and is written as $\sqrt{J\,(J+1)}\ \frac{h}{2\pi}$ or approximately equal to J in the unit of $\frac{h}{2\pi}$.

Quantum Numbers for complete atom:

- Significance of J:

- Wave mechanically J is the result of interaction of L and S vectors and, as a general rule, it also assumes certain discrete values defined by the following relation:

- $J = | L + S |, | L + S -1|, \ldots | L - S |$

Quantum Numbers for complete atom:

- Significance of J:

- $J = | L + S |, | L + S - 1|, \ldots | L - S |$

- The minimum and maximum values of J for given values of L, and S are obtained directly by subtracting and adding the values of L and S.

Quantum Numbers for complete atom:

- Significance of J:

- $J = | L + S |, | L + S - 1|, \ldots | L - S |$

- The minimum and maximum values of J for given values of L, and S are obtained directly by subtracting and adding the values of L and S.

- As the value of J is always positive and hence magnitude of J is important.

Quantum Numbers for complete atom:

- Significance of J:
- For J values, we can finally say that if the sum and difference of L and S vectors are listed with a difference of unity, we get the values of J.

$$J = | L + S |, | L + S -1|, \ldots | L - S |$$

Quantum Numbers for complete atom:

- Significance of J:
- If L > S, then J assumes (2S + 1) possible values for a given L.
- For example
- If L = 3 and S = 2
- Possible values of J are 5, 4, 3, 2, 1

Quantum Numbers for complete atom:

- Significance of J:
- If L > S, then J assumes (2S + 1) possible values for a given L.
- For example
- If L = 2 and S = 1
- Possible values of J are ?????

Quantum Numbers for complete atom:

- Significance of J:
- If L < S, then J assumes (2L + 1) possible values for a given L.
- For example
- If L = 1 and S = 2
- Possible values of J are 3, 2, 1
- i.e. 3   2 L +1 = 2 (1) +1 = 3

Quantum Numbers for complete atom:

- Significance of J:
- If L < S, then J assumes (2L + 1) possible values for a given L.
- For example
- If L = 2 and S = 3
- Possible values of J are ????
- i.e. 3   2 L +1 = 2 (2) +1 = 5

Quantum Numbers for complete atom:

- Significance of J:

- If L = S, then J = S

- If L = 2 and S = 2

- J = 4

- Thank you..