Orbital Magnetic Dipole Moment: Bohr Magneton

An electron revolving about a nucleus is a minute current loop and has a magnetic field. If thus behaves like a magnetic dipole.

Magnetic dipole moment

\[ |\vec{\mu}_l| = \frac{e\nu a}{2c} \text{emu} \]

Orbital angular momentum, \[ |\vec{I}| \]

\[ |\vec{I}| = mva \]

Gyromagnetic ratio = \[ \frac{|\vec{\mu}_l|}{|\vec{I}|} = \frac{e}{2mc} \]

Bohr Magneton is, \[ \mu_B = \frac{eh}{4\pi m} \]

Larmor Procession

When the atom is placed in an external magnetic field, the electron orbit processes about the field direction as axis. This procession is called the ‘Larmor precession’, and the frequency of this precession is called the ‘Larmor frequency’.

Spectroscopic Terms and their Notations

- The quantized energy states of an atomic electron are described in terms of the quantum numbers \( n, l, s \) and \( j \)
- The electron having orbital quantum number \( l = 0, 1, 2, 3, 4 \ldots \) are named as \( s, p, d, f, g \)
- For example \( n = 2, l = 0 \) is in a \( 2s \) state \( n = 3, l = 1 \) is in a \( 3p \) state.

- By spin orbit interaction, each energy level of a given \( l \) is split into two sub level corresponding to

\[ j = 1 + s = 1 + \frac{1}{2} \]

\[ j = 1 - s = 1 - \frac{1}{2} \]

Important notes

1. The separation increases with increasing atomic number \( Z \)
2. Decreases with increasing values of \( n \)
3. Decreases with increasing \( l \)

Stern – Gerlach Experiment

This experiment shows that the term passing through the field were oriented in space in discrete direction.

The transverse deflection suffered by the atom is given by
\[ z = g_j m_j \frac{\partial B_z}{\partial z} \mu_B q^2 \frac{1}{6kT} \]

where \( \frac{\partial B_z}{\partial z} \) → rate of change of field in the \( z \) direction

This experiment is also an evidence for the existence of electron spin and a value \( \frac{1}{2} \) is assigned to the spin quantum number \( (S = \frac{1}{2}) \)

**Spin – Orbit Interaction**

The spin orbit interaction is an interaction between an electron’s spin magnetic moment and the internal magnetic field of the atom which arises from the orbital motion of the electron through the nuclear electric field.

\[ \Delta T = R \alpha \alpha^2 z^4 / n^3 (l + 1) \]

\( \alpha \rightarrow \) Fine structure constant

**Transition Rules (selection rules)**

These are the rules which do not allow all the transitions from one energy state to another to occur and are given by

\[ \Delta n = \text{Change by any amount} \]

\[ \Delta l = \pm 1 \]

\[ \Delta l = 0 \text{ or } \pm 1 \]

\[ \Delta S = 0 \]

⇒ For weak magnetic field

\[ \Delta m_l = 0 \text{ or } \pm 1 \]

⇒ For strong magnetic field, the coupling between \( l \) and \( s \) is broken up and here

\[ \Delta m_l = +1, \Delta m_s = 0 \]

**Intensity Rules**

Two rules -

1) Qualitative

2) Quantitative

These rules are stated for double spectra but they are valid for all spectral lines in general

**I. Qualitative Rules**

1) The strongest line in a doublet is one which arises due to the transition for which \( j \) and \( l \) change in the same way

- If there are more than one such line, then the line involving the largest \( j \) values is strongest.

  e.g. \( ^2S_{1/2} \rightarrow ^2P_{1/2}, ^2S_{1/2} \leftarrow ^2P_{1/2} \)

  Here second line is stronger because for this \( l \) and \( j \) change by equal amount \((-1)\)

2) The line is faint which arises due to the transition for which \( j \) and \( l \) do not change in the same way

3) The line which arises due to transition for which \( l \) decreases is stronger than the line for which \( l \) increases

4) The line which arises due to transition for which \( l \) increases and \( j \) decreases or vice – versa is not allowed because this violates selection principle

**II. Quantitative Rules**

1) The sum of the intensities of all all lines corresponding to transition from a given level is proportional to the statistical weight (or quantum weight) of that level.

2) The sum of the intensities of all line which end on a common level is proportional to the quantum weight of that level. The quantum weight of a particular level is given by \( (2j + 1) \)

  e.g. The levels \( ^2P_{3/2} \) and \( ^2P_{1/2} \)

  quantum weights – 4 and 2 respectively Intensity in the ratio 2 : 1.

**Quantum Mechanical Relativity Correction**

Besides the energy shifts due to orbit interaction, the relativistic effect is equally important as it produces energy shifts in the hydrogen atom comparable to those produced by spin orbit interaction.

The relativistic term shifts is
\[
\Delta T_r = - \frac{\Delta E_r}{\hbar c}
\]
\[
= \frac{R_\infty a_0^2 \varepsilon^4}{n^5} \left( \frac{1}{l+\frac{1}{2}} - \frac{3}{4n} \right) \text{cm}^{-1}
\]

Hydrogen Fine Structure

Lamb Shift:
- The discrepancy in the separation between the main components of the \(H_\alpha\) line could be explained by assuming the state \(2^2S_{1/2}\) to be about 0.03 cm\(^{-1}\) higher than \(2^2P_{1/2}\) in contradiction to Dirac’s theory which had shown them to have exactly the same energy.
- For hydrogen like atom the states of a particular \(n\) value having term \(s\) with the same \(j\) value but different \(l\) values, such as \(2^2P_{1/2}\) and \(2^2S_{1/2}\), are not degenerate, but are separated. Such a separation is known as ‘Lamb-Shift’

Formulation of Pauli’s Principle

According to Pauli “no two electron in an atom can exist in the same quantum state”. This is known as Pauli’s exclusion principle.

If the particle of the system are Bose particle, the proper wave function is

\[
\psi_{\text{Bose}}(1,2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)]
\]

(symmetric)

- If the particle are Fermi particles, the wave function is

\[
\psi_{\text{Fermi}}(1,2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)]
\]

(antisymmetric)

- If the particles are in the same quantum state, \(a = b\)

then \(\psi_{\text{Bose}}(1,2) \neq 0\)

but \(\psi_{\text{Fermi}}(1,2) = 0\)

Two Bose particles can exist in the same quantum state, two Fermi particles cannot.

Result of the Hartree Theory

1) The electron for the average value of \(r\) (radius of shell) holding for a multi-electron atom would be

\[
\bar{r} = \frac{n^2 a_0}{z_n} \left[ 1 + \frac{1}{2} \left( 1 - \frac{l(l+1)}{n^2} \right) \right]
\]

\[
\approx \frac{n^2 a_0}{z_n}
\]

In multi-electron atoms the radii of the inner shells of small \(n\) are very small. E.g. the radius of the \(n = 1\) shell of argon \((z_n \approx z - 2 \approx 16)\) is very smaller than that of the \(n = 1\) shell of hydrogen by approximately a factor of \(\frac{1}{16}\).

2) For the outermost populated shell of an atom, Hartree calculations show that

\[
z_n \approx n
\]

and so the corresponding radius is

\[
\bar{r} \approx \frac{n^2 a_0}{z_n} \approx \frac{n^2 a_0}{n} = na_0
\]

Thus the radius of the outermost shell of a multielectron atom is roughly \(n\) times the radius of the smallest orbit of hydrogen

3) Like radius, we can approximately express the total energy of an electron in a multi-electron atom by the energy equation of a one-electron atom, where \(z\) is replaced by \(z_n\), i.e.

\[
E \approx \frac{2\pi^2 \mu z_n^2 e^4}{n^2 \hbar^2}
\]

4) For the outermost populated shell of an atom, we have \(z_n \approx z\) and corresponding energy is

\[
E \approx \frac{2\pi^2 \mu e^4}{\hbar^2}
\]

Thus, the total energy of an electron in the outermost shell of any atom is comparable to that of an electron in the ground state of hydrogen atom.
5) The energy equation for a multi-electron atom contains $z^2$ in the numerator and $n^2$ in the denominator.

Meaning: for a given atom the total energy $E$ becomes less negative with increasing $n$.

6) In one electron atom the total energy $E$ depends only on the quantum number $n$, while in a multi-electron atom it depends on $l$ as well as on $n$.

**Lande Interval Rule**

The rule determines the separation of fine structure line in $L-S$ coupling.

The change in energy value may be written as

$$\Delta E = \frac{a}{2} [J(J+1) - L(L+1) - S(S+1)]$$

with $a' = a\hbar^2$

The energy value for two level with fixed value of $L$ and $S$ are

$$E_1 = E_0 + \Delta E = E_0 + \frac{a'}{2} [J(J+1) - L(L+1) - S(S+1)]$$

$$E_{J+1} = E_0 + \frac{a'}{2} [J(J+1)(J+2) - L(L+1)] - S(S+1)$$

The constant $a'$ is assumed same for two levels. This separation is

$$E_{J+1} - E_J = a'(J+1)$$

Therefore, the spacing between consecutive levels of a fine structure multiplet is proportional to $(J+1)$ i.e. larger $J$ value involves.

**Spectroscopic Terms: L – S and j – j Couplings Terminology**

**State** - The ‘State’ of an atom is the condition of motion of all the electron specified by four quantum numbers

**Degenerate** - If several states have the same energy

**Ground state** - The state with lowest energy is the ground state

**Energy level** - A collection of states having the same energy in the absence of external magnetic or electric field constitutes an “energy level”. The level with the lowest energy is the ground level

**Term** - A collection of levels characterized by an orbital angular momentum and multiplicity comprises a ‘spectroscopic term’

E.g: $a^3 D$ term means the weighted average energy of the $D_3, D_2, \text{and } D_1$ levels

**Configuration** - The specification of the quantum numbers $n$ and $l$ for the orbital of all the electron of an atom is called the ‘electron configuration’ of the atom.

E.g. the electron configuration of the $^{6}\text{C}$ atom: $1s^2 2s^2 2p^2$

**Equivalent orbitals** - Orbitals with the same $n$ and $l$ are ‘equivalent’. The electron is equivalent orbitals are called ‘equivalent electrons’

**Statistical weight** - The number of distinct states in a specified collection is the ‘statistical weight’. The statistical weight of a level is $2J + 1$: for term it is $(2S + 1)(2L + 1)$; of a single electron it is $2n^2$

Spectral lines are categorized according to the following nomenclature

**Component** - A transition between two sublevels is called a ‘Component’

**Line** - A transition between two levels is a ‘line’. A line is thus a blend of components

**Multiplet** - A collection of transition between two term is called a multiplet. A multiplet thus consists of a number of lines.

**Resonance line** - Among the lines arising from transition between the ground level and higher levels, the line of lowest frequency is called the ‘resonance line’.
Selection Rules for Multi-electron Atoms in L–S Coupling

In the electric dipole transition in multi-electron atoms, the selection rules are –

1) \( \Delta l = \pm 1 \) (for one electron)

The parity of the configuration must change in an electric dipole transition (odd ↔ even)

For two electron transition we would have

\[ \Delta l_1 = \pm 1; \Delta l_2 = 0, \pm 2 \]

2) There is no restriction on the total quantum number \( n \) of either electron

3) Only transition between even and odd term are allowed for dipole transition

4) For the atom as a whole, the quantum numbers \( L, S \) and \( J \) must change as follows:

\[ \Delta L = 0, \pm 1 \] (In one electron atoms \( \Delta L = 0 \) is not allowed)
\[ \Delta S = 0 \]
\[ \Delta J = 0, \pm 1 \]

\( j – j \) Coupling

a) As a result of the stronger orbit interaction, the orbital and spin angular momentum vectors of each individual electron are strongly coupled together to form a resultant angular momentum vector \( \vec{j} \) of magnitude \( \sqrt{j(j+1) \frac{\hbar}{2\pi}} \), where \( j = 1 - \frac{1}{2} \) and \( l + \frac{1}{2} \), i.e. \( j \) takes half integral value only

b) As a result of the residual electrostatic interaction and spin–spin correlation, the resultant angular momentum vector \( \vec{j} \) of the individual to form the total angular momentum vector \( \vec{J} \) of the atom, of magnitude \( \sqrt{J(J+1) \frac{\hbar}{2\pi}} \), where the quantum number \( j \) has the values.

\[ J = |J_1 + J_2 + \ldots|_{min} |J_1 + J_2 + \ldots|_{min} + 1, \ldots (J_1 + J_2 + \ldots) \]

Selection Rules in \( j – j \) Coupling

1) If two electron jump then
\[ \Delta l_1 = \pm 1, \Delta l_2 = 0 \pm 2 \]

2) \( \Delta j = 0, \pm 1 \) for the jumping electron and \( \Delta j = 0 \) for all the other electron

3) For the atom as a whole
\[ \Delta J = 0, \pm 1 \]

The selection rules \( \Delta S = 0 \) and \( \Delta L = 0, \pm 1 \) no longer hold, since \( L \) and \( S \) are no longer good quantum numbers.

Hence,
\[ \Delta M_j = 0, \pm 1 \]
\[ M_j = 0 \rightarrow M_j = 0 \]

not allowed if \( \Delta J = 0 \)

The Zeeman Effect

- When an atom is placed in an external magnetic field, the spectral lines it emits are split into several polarized components. This effect of magnetic field on the atomic spectral lines is called Zeeman effect.

- A singlet spectral line viewed normal to the field is split into three plane polarized components; a central unshift line with the electric vector vibrating parallel to the field (called \( \pi \) component) and two other lines equally displaced on either side with electric vector perpendicular to the field (called \( \sigma \) components). This is called a “Normal triplet” and effect is “Normal Zeeman effect”.

Under selection rule
\[ \Delta M_L = 0, \pm 1 \] gives rise to Zeeman normal triplet
\[ \Delta M_L = 0 \] corresponds to \( \pi \) components and
\[ \Delta M_L = \pm 1 \] gives \( \sigma \) component
The fine structure components of a multiplet spectral line, however, show a complex Zeeman pattern e.g. $D_1$ and $D_2$ components of sodium yellow doublet give four and six lines respectively in the Zeeman pattern. This is 'anomalous Zeeman effect'.

When the source emitting spectral lines is subjected to weak magnetic field, the spin and orbital angular moments are separately conserved and $L$, $S$ and $J$ are well defined

$$\Delta E'' = \frac{e}{2m_0c}B_zgM_J\hbar$$

The Lande–g–factor is given by

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

And $\mu_B = \frac{eh}{2m_0c}$ (known as Bohar Magneton)

This expression is with the selection rule

$$\Delta M_J = 0, \pm 1$$

Explains anomalous Zeeman effect

$\Delta M_J = 0$ gives $\pi$ components, and $\Delta M_J = \pm 1$ gives $\sigma$ components

**Paschen back Effect**

The strength of the external field is increased, the separation between Zeeman components increase until they become greater than the separations between multiplet fine structure components. The anomalous Zeeman pattern then changes over to like a normal Zeeman pattern. This phenomenon is known as ‘Paschen back effect’.

In a strong field, the selection rules for transitions are

$$\Delta M_L = 0$$

(Components polarized parallel to the field)

$$\Delta M_L = \pm 1$$

(Components polarized perpendicular to the field)

$$\Delta M_S = +1$$

**Stark Effect**

- The splitting of spectral lines in an electric field is known as ‘stark effect’.
- The number of stark lines and the total width of the pattern increase with $n$
- The $\pi$ – components show greater shifts than the $\sigma$ component
- **First order stark effect** – The hydrogen lines with the lower energy states ($H_\alpha, H_\beta$) show only a symmetrical splitting proportional to the field strength about their field free position.
- **Second order Stark effect** – For the line involving the higher state ($H_\gamma, H_\delta$), the Stark components show unidirectional displacements proportional to the square of the field strength
- The Stark Shift for the ground state ($n = 1$) is zero.
- For a non degenerate state, such as the ground state ($n = 1, l = 0, n_l = 0$) of hydrogen atom which has even parity, there is no first order Stark effect.

Only degenerate terms can have a first order Stark effect.
Nuclear Spin and Hyperfine Splitting

- Bismuth exits as a single isotope, but shows six hyperfine components in its line at wavelength 4722 Å

The nuclear angular momentum is

$$|I| = \sqrt{1(I + 1)} \frac{h}{2\pi}$$

$I \rightarrow$ Nuclear spin quantum number

Nuclear magnetic moment

$$\mu_1 = g_1\sqrt{I(I + 1)}\mu_N$$

$$\mu_N = \frac{e\hbar}{4\pi m_p c}$$

- We have only to count the number of hyperfine components for any Zeeman line in a strong magnetic field, and this number is $2I + 1$. Hence I is directly determined. Back and Goudsmit found that in a strong magnetic field each of the Zeeman components of Bi consists of 10 hyperfine components due to nuclear spin. Hence they concluded that for $B_i, I = \frac{9}{2}$

X – Rays

- X rays are produced when high speed electron strike a metal of high atomic number

X rays spectrum of two spectra

1) Continuous spectrum – It is due to continuous deacceleration of the electron as it passes through the field of the nucleus. Its short wavelength limit is given by –

$$\lambda_{\text{min}} = 12,400/V \text{Å}$$

2) Line or characteristic spectrum – It is produced when electron of the target material are dislodged from their orbits by the striking electrons. The spectrum consists K-, L– and M– series etc, depending on when electron jump ends.

Moseley’s Law

Moseley’s law states that the frequency of a spectral line in the characteristic x ray spectrum varies directly as the square of the atomic number of the element emitting it

X – ray absorption spectra, is contrast to optical spectra do not contain separate absorption lines. The coefficient of absorption of X – rays by a substance decreases with an increase in their frequency. This relationship is violated by jumps in the absorption coefficient (absorption edges) in the region of frequencies at which the energy of the X – ray quanta becomes sufficient to dislodge electrons from the $K_-, L_-, M_-$ etc, shell of te atom

$$\sqrt{\frac{V_{\text{min}}}{R}} = \alpha(Z - \sigma)$$

Where $R$ is Rydberg constant

$Z$ is atomic number of chemical element

$\sigma$ is screening constant, and

$\alpha$ is a constant depending upon the quantum number of the shells between which the transition occurs.

- Absorption of X – rays follows the exponential law

$$I = I_0 e^{-\mu x}$$

where $\mu$ is the absorption coefficient

- The linear absorption coefficient $\mu$ may be defined as the fractional decrease in the intensity of the x – rays per unit thickness of the absorber material.

- Due to Compton scattering, change in wavelength of the scattered X – rays is given by

$$\Delta \lambda = 0.024(1 - \cos \theta) \text{Å}$$

Molecular Spectra

The Boron – Oppenheimer Approximation

- We cannot classify molecular energy state according to the electron angular momentum L, which is not conserved in molecules.
• The energy of each of the vibrational and rotational motions is quantized with the result that there are many more energy levels in a molecule than in an atom.

• We can solve the complete molecular wave equation in the following way

Types of Molecular Spectra

1) **Electronic spectra** – These spectra are observed in emission and absorption in the visible and ultraviolet regions. The electronic spectra are observed for the heteronuclear as well as for the homonuclear diatomic molecules.

2) **Vibrational rotational spectra** – These spectra are observed in absorption, in the near infrared region \((1 \mu - 10^2 \mu)\). They are observed only for the heteronuclear molecules. The homonuclear molecules like \(H_2, N_2, O_2\) do not produce vibrational rotational band.

3) **Pure rotational spectra** – These spectra are observed in absorption in the far infrared \((10^2 \mu - 10^3 \mu)\) and observed only for the heteronuclear diatomic molecules.

Pure Rotational Spectra

Only molecules that have permanent electric dipole moments can absorb or emit electromagnetic radiation in such transition.

Homonuclear diatomic molecules such as \(H_2, O_2, N_2\); symmetric linear molecules such as \(CO_2\) and spherical top polyatomic molecules such as \(CH_4\) do not exhibit rotational spectra.

- The moment of inertia of the molecule as a rigid rotator

\[ I = \mu r^2 \]

\( \mu \rightarrow \) Reduced mass; \( r \rightarrow \) distance from the axis of rotation.

- Eigen values, \( E \) are

\[ E = \frac{\hbar^2}{8 \pi^2 I} J (K + 1) \]

\( J \rightarrow \) Rotational quantum number.

J = 0, 1, 2, 3, …

- In terms of wave number, the energy equation can be written as

\[ \frac{E}{\hbar c} = F(J) = BJ(J + 1) cm^{-1} \] with

\[ B = \frac{\hbar}{8 \pi^2 I c} \]

- Wave number \( \nu = 2B(J + 1) \)

with \( J = 0, 1, 2, … \)

\[ \nu = 2B, 4B, 6B, … \]

Thus, the absorption spectrum of a rigid rotator is expected to consist of a series of equidistant lines with constant separation \(2B\)

- The selection rule for rotational transitions is given by

\[ \Delta J = J' - J'' \equiv \pm 1 \]

Because a molecular which is symmetrical in its ground state does not possess resultant dipole moment will not interact with the radiation.

- For a non rigid rotator energy levels and given by

\[ E = \frac{\hbar^2}{8 \pi^2 I} J (J + 1) - \frac{\hbar^4}{32 \pi^4 r^2 k} J^2 (J + 1)^2 \]

or \( F(J) = \frac{E}{\hbar c} \)

\[ = BJ(J + 1) - DJ^2 (J + 1)^2 \]

where \( D \rightarrow \) centrifugal distortion constant.

- If the force were anharmonic, the expression becomes
\[ F(J) = BJ(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 + KJ^4(J + 1)^4 + \ldots. \]

\( H, k \text{etc, are small constants, dependent on the geometry of the molecules.} \)

- Using selection rule \( \Delta J = \pm 1 \)

The expression for transition is

\[ F(J + 1) - F(J) = v_r = 2B(J + 1) - 4D(J + 1)^3 \]

- Lines are no longer exactly equidistant but their separation decreases slightly with increasing \( J \).

### Vibrational Rotational Spectra

In the series of lines which are not equidistant, a line is missing in the centre of the band. The missing line is known as the ‘null line’ or zero gap’.

### The Molecule as a Harmonic Oscillator

The allowed energies for the harmonic oscillator

\[ E = \hbar \nu_{osc}(\nu + \frac{1}{2}) \]

where, \( \nu = 0,1,2 \ldots \ldots \)

- The vibrational terms

\[ G(\nu) = \frac{E}{\hbar c} = \frac{\nu_{osc}}{c}(\nu + \frac{1}{2}) \]

\[ = \omega(\nu + \frac{1}{2}) \]

where, \( \omega = \frac{\nu_{osc}}{c} \rightarrow \text{Vibrational constant} \)

- Vibrational transitions can only occur when the molecule has a permanent dipole moment which change with distance
- The spacing between the vibrational levels are considerably larger than the spacing between the rotational levels of a molecule, infact larger than \( kT \) at room temperature.
- Thus, the main vibrational transition in absorption is

\[ \nu = -1 \leftrightarrow \nu = 0 \]

\( \Delta \nu = \pm 1 \)

which indicates that each mode of vibration would yield one band only

- The vibrational spectrum is expected to consists of a single band at \( \omega \ \text{cm}^{-1} \)
- In the vibrational spectrum, the nuclei carrying out harmonic vibrations along the internuclear axis.

### Molecule as Anharmonic Oscillator

- The actual infrared spectrum is found to consists at an intense (fundamental) band at \( \omega \) plus a number of weak bonds (overtones) at slightly lesser and lesser than \( 2 \omega, 3\omega, \ldots \) The observation of overtones indicates that the selection rule \( \Delta \nu = \pm 1 \) is not strictly obeyed and transitions corresponding to \( \Delta \nu > 1 \) do take place.
- The selection rules for the anharmonic oscillator are found to be

\[ \Delta \nu = \pm 1, \pm 2, \pm 3, \ldots \]

For transitions

\[ \nu = 1 \rightarrow \nu = 0 \ \text{gives fundamentals Band} \]
\[ \nu = 2 \rightarrow \nu = 0 \ \text{gives first overtone (second harmonic)} \]
\[ \nu = 3 \rightarrow \nu = 0 \ \text{gives second overtone (Third harmonic)} \]

\[ \Rightarrow \ \text{Now for fundamental band} \]

\[ \nu_1 = (1 + 2x) \omega_e \]

For first overtone band

\[ \nu_2 = (1 - 3x)2 \omega_e \]

For second overtone band

\[ \nu_3 = (1 - 4x)3 \omega_e \]

\( \nu_1, \nu_2, \nu_3 \) are frequencies of the origin of fundamental first and second overtone bands respectively. To a good approximation, three spectral lines lie very close to \( \omega_e, 2\omega_e \) and \( 3\omega_e \)
The observation that the overtones appear not exactly at $2\omega, 3\omega, \ldots$ but at lesser and lesser values indicates that the vibrational energy levels are not exactly equally spaced but coverages slowly.

The corresponding term values are given by

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \ldots$$

$\omega_e x_e$→ the anharmonicity constant smaller than $\omega_e$ and always positive.

The vibrational frequency of anharmonic oscillator is

$$v_{osc} \sim c \left[ (\omega_e - \omega_e x_e) - 2 \omega_e x_e v \right]$$

The frequency

$$V_{osc} \left( -\frac{1}{2} \right) = c \omega_e \left[ v = -\frac{1}{2} \right]$$

is a hypothetical state.

$\omega_e$→ The vibrational frequency that anharmonic oscillator would have classically for an infinitesimal amplitude i.e. in imaginary state $v = -\frac{1}{2}$ at the very bottom of the potential curve

$$v_{osc} = c \omega_e \left( v = -\frac{1}{2} \right)$$

or $k_e = 4\pi^2 \mu c^2 \omega_e^2$

Isotope Effect on Vibrational Level

The vibrational levels of the heavier isotope are lower than the corresponding levels of the lighter isotope

$$G'(v) < G(v)$$

Molecule as Vibrating Rotator: Fine Structure of Infrared Bands

The near infrared spectra of molecules consists of ‘band’ (not lines) each band being composed of close lines arranged in a particular manner. This observed fine structure suggests that in a vibrational transition the molecules also changes its rotational energy state i.e. it must be treated as a vibrating rotator

• $B$, determines the spacing between the rotational levels, is different for different vibrational states.

• For a given vibrational transition, the rotational transitions $\Delta J = +1$ given one set of lines called the ‘R - branch’ while the rotational transitions $\Delta J = -1$ give the other set of lines called the ‘P - branch’

• $v_o = G(v') - G(v')$, is the wave number of the pure vibrational transition (for which $J' = J = 0$) which is unallowed ($\Delta J = 0$) and corresponds to the missing line in the band. $v_0$ is known as the wave number of the ‘band-origin’

• If we neglect vibration rotation interaction, then

$$v_R = v_o + 2B + 2BJ''$$ [Wave number of R branch]

$$v_p = v_o - 2B J''$$ [Wave number of P branch]

• The only case of a diatomic molecule for which a Q – branch (i.e. a central ‘line’) has been observed in the rotation – vibration infrared bands is that of nitric oxide NO.

Electronic Spectra: Franck – Condon Principle

• Each electronic states of the molecule has a different potential energy curve

• A single electronic transition in a molecule gives rise to a band system

Electronic Band Spectra in Absorption

The study of absorption spectra, as compared to emission spectra, gives more information, with less elaborate computation, regarding the excited electronic states of molecules.

• The absorption spectrum of $I_2$ molecule, show progressions corresponding to $v'' = 1$ and even higher, in addition to the progression $v'' = 0$, although with smaller intensity

• This P and R branch can be represented by a single parabolic equation

$$v = v_0 + (B'_o + B''_o)m + (B'_o - B''_o)m^2$$

where,
\[ m = J'' + 1 = 1, 2, 3, \ldots \]

for lines R (0), R (1), R (2)……

\[ m = 0 \]

for the and origin

- To a close approximation the total energy \( E \) of the molecule is given quantum state may be supposed to made up of the electronic energy \( E_e \), the vibrational energy \( E_v \) and the rotational energy \( E_r \), i.e.

\[ E = E_e + E_v + E_r \]

or \( \Delta E = \Delta E_e + \Delta E_v + \Delta E_r \)

or \( \frac{\Delta E}{hc} = \frac{\Delta E_e}{hc} + \frac{\Delta E_v}{hc} + \frac{\Delta E_r}{hc} \)

The orders of magnitude of these changes are approximately, given as –

\[ \frac{\Delta E_e}{hc} = \Delta E_v \times 10^3 cm^{-1} \]

\[ \approx \frac{\Delta E_r}{hc} \times 10^6 cm^{-1} \]

which clearly shows that vibrational energy changes will produce a ‘coarse’ and rotational changes a ‘fine structure’ in the electronic spectra.

- Since a pure rotation spectra are given by molecules having a permanent electric dipole moment and vibration spectra require a change of dipole during the motion, electronic spectra are given by all molecules since changes in the electron distribution are always accompanied by a dipole change.

\[ \begin{align*}
\text{Vibrational energy levels (e.g. XY line). The probability of transition between two given vibrational levels of states A and B are determined by Franck – Condon principle.}
\end{align*} \]

**Franck Condon Principle**

A vibrational transition will have a large Franck Condon factor only if one of the two turning points of a level of one electronic state lies at approximately the same intermuscular distance as one of the two turning point of a level of the other electronic state, except in case of \( v = 0 \) level for which the middle point of the level rather than the turning point must be substituted.

- The potential curves become increasingly asymmetric with increasing \( r \). This means that the nuclei spend more time in the extend phase \((r > r_e)\) than the contracted phase \((r < r_e)\). Hence according to Franck – Condon principle, transition will be more probable from (or to) the one side than the other.

\[ \therefore \text{for a system degraded to the red } (r' > r'') \text{ the right limb of the Condon parabola will be the stronger.} \]

- **Vibrational Coarse Structure**

Ignoring rotational energy changes, the energy change

\[ E' - E'' = (E''_e - E_e') + (E_v' - E_v') \]

In terms of frequency

\[ v_0 = \frac{E'_e - E''_e}{hc} + \frac{E'_v - E''_v}{hc} \]

\[ = V_e + \left\{ \left( v' + \frac{1}{2} \right) \omega' - \left( v' + \frac{1}{2} \right)^2 x' \omega' + \ldots \right\} - \left\{ \left( v'' + \frac{1}{2} \right) \omega'' - \left( v'' + \frac{1}{2} \right)^2 x' \omega'' + \ldots \right\} \]

\( v', \omega' \) - vibrational quantum number and equilibrium vibration frequency of molecule in initial state

\( v'', \omega'' \) – corresponding quantities in final state.

There is no selection rule for \( v \) which means \( \Delta v \) can assume any value.

- **Rotational Fine Structure of Electronic Spectra**
The change in total energy of an electronic spectra
\[ \Delta E_{total} = \Delta E_e + \Delta E_v \Delta (BJ(J + 1)) \]
The frequency corresponding to such change is
\[ v = v_0 + \Delta (BJ(BJ + 1)) \]
The selection rule
\[ \Delta J = 0 \text{ or } \pm 1 \]
(0 → 0 transition is excluded)

If \( B' \) and \( J' \) refer to the upper electronic state, \( B'' \) and \( J'' \) to the lower electronic state, the frequencies of radiation can be written as
\[ v = v_0 + BJ(J' + 1) - B''J''(J'' + 1) \]

General form
\[ v = v_0 + (B' + B'')m + \Delta (B' + B'')m^2 \]
where \( m = \pm 1, \pm 2, \ldots \)

- Positive \( m \) values giving rise to \( r \) branch (corresponding to \( \Delta J = J' = 1 \)) and negative values of \( m \) to \( P \) branch (corresponding to \( \Delta J = J'' = -1 \))
- It is to be seen that \( m \neq 0 \) since it correspond in \( P \) branch to \( J' = -1 \) which is impossible. It means that no line from \( P \) and \( R \) branch appears at the band origin \( v_0 \).

Case – I \( B' < B'' \)

Note –

1) \( P \) branch lines appear on the low wave number side of the band origin and the spacing between the lines increases with \( m \)

2) \( R \) branch lines appear on high number side of the band origin and the spacing between them decreases with \( m \), the point at which \( R \) branch separation becomes zero is termed as band head.

3) \( Q \) branch lines appear close to low wave number of the origin and their spacing increase with value of \( J'' \)

4) Band head appears in \( R \) branch on high wave number side of the origin and such a band is said to be degraded towards the red i.e. the tail of the band where intensity falls off point towards the red end.

Case – II \( B' > B'' \)

All the previous arguments of case \( B' < B'' \) are reversed

- Fortrat Diagram

For \( P, R \) branches \( (\Delta J = \pm 1) \) and for \( Q(\Delta J = 0) \) the frequency of lines in terms of variable parameters \( p \) and \( q \) are given respectively by

\[ v(\text{PR}) = v_0 + (B' + B'')p + (B' - B'')p^2 \]
\[ v(Q) = v_0 + (B' - B'')q + (B' - B'')q^2 \]

These two equations represent a parabola, \( p \) – taking both positive and negative values while \( q \) only positive values. These parabola are called fortratparabolate.

The position of vertex is given by

\[ \frac{dv(\text{PR})}{dp} = B' + B'' + 2(B'B'')p = 0 \]
\[ \text{or} p = \frac{(B' + B'')}{2(B' - B'')} \text{ for band head} \]

So, if \( B' < B'' \), the band head occurs at positive \( p \) values i.e. in \( R \) branch and if \( B' < B'' \), band head occurs in \( p \) branch.

- Raman Spectra

When a monochromatic radiation is scattered by a solid then the scattered light not only consists of the radiation of incident energy but also the radiations of frequencies above and below that of incident beam frequency. If \( v_i \) is the frequency of incident radiation, and \( v_s \) is that of light scattered by a given molecule, then the Raman shift.

\[ \Delta v = v_i - v_s \]

If \( \Delta v \) is positive, \( v_s < v_i \), then Raman spectrum consists of stroke lines when \( \Delta v \) is negative, \( v_s > v_i \), then Raman spectrum is said to be consisting of antistokes lines.
• Stokes lines have more intensity than the anti-Stokes lines $\Delta\nu$ normally lies in range 100 cm$^{-1}$ to 3000 cm$^{-1}$ which falls in near and far infrared region. Thus we conclude that the changes in energy of scattered light correspond to energy changes due to rotational and vibrational transitions.

**Probability of energy transition in Raman Spectra**

$$P_{mn}(x) = F_x a_{nx}^{\alpha} \int \psi_m^{*} \psi_n dz + \frac{F_x}{A} \beta_{xx} \int \psi_m^{*} \psi_n dz$$

where, $F_x =$ Field in $x$ - direction

$A =$ vibration amplitude

$\alpha_{xx} =$ equilibrium polarizability in $x$ - direction

$\beta_{xx} =$ rate of variation of polarizability in

**Note** –

i) The first term on r.h.s is zero except $m = n$ and gives the probability of Rayleigh scattering.

ii) For Raman scattering $m \neq n$, hence first term on r.h.s vanishes and Raman lines appear due to second term being finite. It means polarizability must change during molecular vibration to show the Raman effect.

iii) For Raman lines to appear it is necessary that even in case of molecular rotation the polarizability either in $x$, $y$ or $z$ direction must change.

**Vibrational Raman Spectra**

- the selection rule

  $$\Delta\nu = \pm 1$$

∴ Transition can take place only to adjacent vibrational state.

⇒ At ordinary temperature most if the molecules are in their lowest vibrational level i.e. $v = 0$ so the majority of transition are of type $v = 0$ to $v = 1$ of considerable intensity. A small number of molecules occupy initial level $v = 1$ which undergoes $v = 1$ to $v = 2$ transition (Stokes transition) or $v = 1$ to $v = 0$ transition (antistokes with weaker intensity)

⇒ At higher temperature a large number of molecules crowd the higher vibrational levels and results in the increase of intensity of antistokes lines.

Thus Raman spectrum consist of one strokes and one antistoke line.

$$\Delta\nu = (1 - 2x)\omega_c = v_0$$

$v_0 \rightarrow$ frequency of fundamental vibration band.

**Rotational Raman spectra**

- selection rule, $\Delta J = 0, \pm 2$ for diatomic molecule in ground state

The transition $\Delta J = 0$ gives no change in molecular energy i.e. Raman radiation will be of the same frequency as that of incident radiation.

- $\Delta J = +2$ gives Stokes lines (longer wave length side)

- $\Delta J = -2$ gives antistokes lines (shorter wave length side)

- Rotational Raman shift of Stokes lines

$$\Delta\nu = 2B(2J + 3)$$

And for antistokes rotational lines

$$\Delta\nu = -2B(2J + 3)$$

∴ Raman shift is as

$$\Delta\nu = \pm 2B(2B + 3)$$

Where, $J = 0, 1, 2, \ldots$

**QUESTIONS**

1. An atom emits a photon of wavelength $\lambda = 600$ nm by transition from an excited state of life time $8 \times 10^{-9}$ s. If $\Delta\nu$ represents the minimum uncertainty in the frequency of the photon, the fractional width $\frac{\Delta\nu}{\nu}$ of the spectral line is of the order of

   a) $10^{-4}$  
   b) $10^{-6}$  
   c) $10^{-6}$  
   d) $10^{-10}$
2. The shortest wavelength of Balmer series in hydrogen spectrum is given by the equation

\[ \lambda = R_H \left( \frac{1}{4} - \frac{1}{n^2} \right) \]

\[ \lambda = R_H \left( \frac{1}{2} - \frac{1}{\infty} \right) \]

\[ \lambda = R_H \left( 1 - \frac{1}{\infty} \right) \]

\[ \lambda = R_H \left( \frac{1}{4} - \frac{1}{\infty} \right) \]

\( R_H \rightarrow \) Rydberg constant for hydrogen

3. The constant for hydrogen is

a) \( 1.0961 \times 10^{-7} \) m
b) \( 1.0961 \times 10^7 \) m

c) \( 1.0961 \times 10^{-6} \) m

d) \( 1.0961 \times 10^6 \) m

4. The expression for the total energy with the principal quantum number \( n \) is the relativistic model of the atom is

a) \( -E_n \left\{ 1 + \frac{\alpha^2}{n^2} \left( \frac{n - \frac{3}{4}}{n_{\phi}} \right) \right\} \)

b) \( E_n \left\{ 1 + \frac{\alpha^2}{n^2} \left( \frac{n_{\phi} - \frac{3}{4}}{n} \right) \right\} \)

c) \( E_n \left\{ 1 + \frac{\alpha^2}{n^2} \left( \frac{n_{\phi} - \frac{3}{4}}{n} \right) \right\} \)

d) \( -E_n \left\{ 1 - \frac{\alpha^2}{n^2} \left( \frac{n_{\phi} - \frac{3}{4}}{n} \right) \right\} \)

where, \( \alpha = \frac{e^2}{2 \varepsilon_0 \hbar} \)

5. The maximum number of electrons in a sub shell with orbital quantum number \( l \) is

a) \( 2l + 1 \)  

b) \( 2l - 1 \)

c) \( 2(2l + 1) \)  

d) \( 2(2l - 1) \)

6. If \( v \) is the velocity of the electron in a stationary orbit of radius \( r \), the orbital frequency of the electron is

a) \( \frac{v}{2\pi r} \)  

b) \( \frac{v}{r} \)

c) \( \frac{v}{\pi r} \)  

d) \( \frac{2\pi r}{v} \)

7. One Bohr magneton is approximately

a) \( 10^{23} Am^2 \)  

b) \( 10^{-25} Am^2 \)

c) \( 10^{10} Am^2 \)  

d) \( 10^{-10} Am^2 \)

8. The root mean square velocity \( \bar{v} \) of helium atom at \( T \) degree K satisfies the relation

a) \( \bar{v} \propto \sqrt{T} \)  

b) \( \bar{v} \propto 1 \)  

c) \( \bar{v} \propto T \)  

d) \( \bar{v} \propto \frac{1}{T} \)

9. Which of the following transition is ruled out

a) \( 3_1 \rightarrow 2_1 \)  

b) \( 3_1 \rightarrow 2_2 \)

c) \( 3_2 \rightarrow 2_1 \)  

d) \( 3_3 \rightarrow 2_2 \)

10. The longest wavelength of the Lyman series in hydrogen spectrum is obtained educing the relation

a) \( \lambda = R_H \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \)  

b) \( \lambda = R_H \left( \frac{1}{1^2} - \frac{1}{\infty} \right) \)

c) \( \lambda = R_H \left( 1 - \frac{1}{\infty} \right) \)  

d) \( \lambda = R_H \left( \frac{1}{1^2} - \frac{1}{3^2} \right) \)

11. The magnetic moment associated with the first order in hydrogen atom is given by

a) \( \frac{\hbar}{4\pi m e} \)  

b) \( \frac{4\pi m e}{h} \)

c) \( \frac{e\hbar}{4\pi m} \)  

d) \( \frac{eh}{4\pi} \)

12. The length of the semi major axis of an electron in an elliptical orbit is determined

a) only by the principal quantum number  

b) only by the azimuthal quantum number  

c) both by principal quantum number and azimuthal quantum numbers  

d) none of these

13. When the azimuthal quantum number \( n_{\phi} \) is zero

a) the ellipse reduces to a straight line  

b) the ellipse reduces into a circle
c) the ellipse reduces to a parabola
d) none of these

14. If \( n_\phi \) and \( n \) for an electron is an elliptical orbit are 1 and 2 respectively, then the ratio of semi major axis and semi minor axis is
a) 2    b) 0.5    c) 1    d) 0.25

15. If the principal quantum number and the azimuthal quantum number is the relativistic model of the atom are 3 and 1 respectively, then the magnitude of the semi molar axis \( b \) in terms of the semi major axis \( a \) is given by
a) \( b = \frac{a}{3} \)    b) \( b = \frac{2a}{3} \)
c) \( b = \frac{a}{2} \)    d) \( b = a \)

16. If the wavelength of the first line of the Balmer series in the hydrogen spectrum is \( \lambda \), then the wavelength of the first line of the Lyman series is
a) \( \left( \frac{27}{5} \right) \lambda \)    b) \( \left( \frac{5}{27} \right) \lambda \)
c) \( \left( \frac{32}{27} \right) \lambda \)    d) \( \left( \frac{27}{32} \right) \lambda \)

17. If \( R_1 \) is the value of the Rydberg constant assuming mass of the nucleus to be infinitely large compared to that of an electron, and if \( R_2 \) is the Rydberg constant taking nuclear mass to be 7500 times the mass of the electron, then the ratio \( \frac{R_2}{R_1} \) is
a) a little less than unity
b) a little more than unity
c) infinitely small
d) infinitely large

18. In a stern Gerlach experiment, the magnetic field is in + Z direction. A particle comes out of this experiment in \( 1 + \frac{1}{2} \uparrow \) state. Choose the correct statement
a) the particle has a definite value of the y – component of the spin angular momentum
b) the particle has a definite value of the square of the spin angular momentum
c) the particle has a definite value of the x – component of spin angular momentum
d) the particle has definite values of x and y component of spin angular momentum

19. The Bohr model gives the value for the ionization potential of Li\(^{2+} \) ion as
a) 13.6 eV    b) 27.2 eV
c) 40.8 eV    d) 122.4 eV

20. In a stern – Gerlach experiment the atomic beam whose angular momentum state is to be determined must travel through
a) homogeneous radio frequency magnetic field
b) homogeneous static magnetic field
c) indigenous static magnetic field
d) inhomogeneous radio frequency magnetic field

21. Sodium atom has 11 electrons. If the sequence in which the energy levels are filled in 1s, 2s, 2p, 3s, 3p, 4s, 3d..... the ground state of sodium is
a) \(^3P_{1/2}\)    b) \(^2P_{1/2}\)    c) \(^1P_{1/2}\)    d) \(^2S_{1/2}\)

22. If the \( \phi \) dependent part of the eigen function of an electron in a hydrogen atom is \( e^{2i\phi} \) the minimum principal and orbital quantum numbers \( n \) and \( l \) respectively for the eigen function will be
a) \( n2,1,1 \)    b) \( n3,1,2 \)
c) \( n4,1,3 \)    d) \( n3,1,1 \)
23. Positronium is a hydrogen like bound state of a positron and an electron. If the \( n \)th energy level of hydrogen atom is given by \( E_n^H = \frac{1}{(4\pi\varepsilon_0)^2 2n^2\hbar^2} \) the \( n \)th energy level \( E_n^P \) of the Positronium will be equal to

a) \( \frac{1}{2} E_n^H \)  b) \( E_n^H \)

24. Suppose one bombards hydrogen gas to room temperature with electron of various energies. As the energy of the bombarding electron is increased, the wavelength of radiation first emitted from the gas will correspond to

a) Lyman series  b) shortest wavelength in Lyman series

c) longest wavelength in Lyman series  d) all series will appear together

25. Atoms with \( \frac{1}{2} \) nuclear spin cannot have

a) hyperfine structure  b) electric dipole interaction

c) fine structure  d) none of these

26. For an atom in the state of \( ^2D_{5/2} \) the Lande – g factor should be

a) 2  b) 1.75  c) 1.20  d) 1.33

27. The doublets observed in alkali spectra are due to

a) screening of the K electron  b) spin orbit interaction of the electrons

c) pressure of isotopes  d) none of these

28. Possible values of the total angular momentum quantum number of a single \( f \) electron are

a) \( j = \frac{7}{2}, \frac{5}{2} \)  b) \( j = \pm 3,2,1,0 \)

c) \( j = \frac{\pm 7}{2}, \frac{5}{2} \)  d) none of these

29. The de – Broglie wavelength associated with neutrons in thermal equilibrium with matter of 300 K, is

a) 1790 Å  b) 179 Å

c) 17.9 Å  d) 1.79 Å

30. The electronic configuration \((np)^2\) can have only which one of the following terms

a) \(^2D\), \(^3P\) or \(^1S\)  b) \(^1D\), \(^3P\) or \(^1S\)

c) \(^3D\), \(^3P\) or \(^2S\)  d) None of these

31. The total number of levels that could be formed by two electrons in the presence of an external magnetic field is

a) 6  b) 36  c) 60  d) 10

32. Which of the following has the order of increasing energy

a) \(^1D_2\), \(^3D_2\), \(^3F_2\)  b) \(^3F_2\), \(^3D_2\), \(^1D_2\)

c) \(^3D_2\), \(^3F_2\), \(^1D_2\)  d) \(^1D_2\), \(^3F_2\), \(^3D_2\)

33. The fluorine atoms has a nuclear spin \( \frac{1}{2} \). In a nuclear magnetic resonance of LiF, the fluorine nucleus will slow up as

a) one line  b) two lines

c) three lines  d) four lines

34. The mass of earth is about \( 6 \times 10^{27} \) gram and it is about \( 93 \times 10^6 \) miles from the Sun. Approximately what is the orbital angular momentum quantum number of the earth in its orbit around the sun

a) \( 10^{30} \)  b) \( 10^{39} \)  c) \( 10^{61} \)  d) \( 10^{71} \)
35. The values of the total angular momentum of a single of electrons are
   a) $\frac{5}{2}, \frac{7}{2}$  b) $\frac{3}{2}, \frac{5}{2}$  c) $\frac{1}{2}, \frac{3}{2}$  d) $0, \frac{1}{2}$

36. The average binding energy of a nucleon in a nucleus of an atom is
   a) 8eV  b) 80 eV  c) 8 MeV  d) 80 MeV

37. The different values for the total orbital quantum number of a two electron system with $L_1 = 3$ and $L_2 = 2$ are
   a) 5  b) 5, 1  c) 5, 4, 3, 2, 1  d) $\pm 5, \pm 4, \pm 3, \pm 2, \pm 1$

38. In outer atomic shell of atoms $4s$ level is filled first by electron then $3d$ level because
   a) $4s$ electron are less screened from the nucleus than $3d$ electrons
   b) spin spin interaction dominates for $3d$ level
   c) spin orbit interaction between the electrons is the different levels reduces energy of $4s$ electrons below that of $3d$ electrons
   d) none of these

39. The selection rule for orbital quantum number for electronic dipole transitions in a single electron atom is
   a) $\Delta l = 0, \pm 1$  b) $\Delta l = 0$
   c) $\Delta l = \pm 1$  d) $\Delta l = 1$

40. In M.K.S units Bohr magnetron is given by
   a) $\frac{eh}{4\pi m}$  b) $\frac{em}{4h}$  c) $\frac{e}{4mh}$  d) $\frac{mh}{2e\pi}$

41. The maximum change in energy of a $p$ – electron due to the processional motion of its orbit in a magnetic field of $3 \times 10^4$ gauss is of the order of
   a) $2 \times 10^{-8}$ ergs  b) $2 \times 10^{-16}$ ergs  c) $2 \times 10^{-12}$ ergs  d) $2 \times 10^{-10}$ ergs

42. If the magnitude of the charge of the proton and the electron in a hydrogen atom were doubled, the energy of quantum radiated by the atom as a result of a transition from $n = 2$ to $n = 1$ state will multiplied by
   a) 1  b) 4  c) 8  d) 16

43. Which of the interactions cause the non – conservation of orbital angular momentum of the electron in an atom
   a) spin - orbit interaction
   b) spin - spin interaction
   c) electrostatic interaction between electrons
   d) electrostatic interaction between electrons and nucleus

44. $S$ value for state $^2D_{3/2}$ is given by
   a) 0  b) $\frac{1}{2}$  c) 1  d) $\frac{3}{2}$

45. $L$ value for state $^2D_{3/2}$ is given by
   a) 0  b) 1  c) 2  d) 3

46. $J$ value for state $^6H_{5/2}$ is given by
   a) $\frac{1}{2}$  b) $\frac{3}{2}$  c) $\frac{5}{2}$  d) $\frac{7}{2}$

47. Multiplicity of the state $^2D_{3/2}$ is given by
   a) 1  b) 2  c) 3  d) 4
48. The sodium doublet lines are due to transitions from $^2P_{3/2}$ levels to $^2P_{1/2}$ level. On application of a weak magnetic field, the total number of allowed transitions becomes

a) 4  

b) 6  

c) 8  

d) 10

49. In a two-electron atomic system having orbital and spin angular momenta $I_1, I_2$ and $s_1, s_2$ respectively, the coupling strengths are defined as $\tau_{l_1 l_2}, \tau_{s_1 s_2}, \tau_{l_1 s_2}, \tau_{l_1 s_1}$. For the $jj$ coupling scheme to be applicable, the coupling strength MUST satisfy the condition

a) $\tau_{l_1 l_2}, \tau_{s_1 s_2} > \tau_{l_1 s_2}, \tau_{l_1 s_1}$

b) $\tau_{l_1 l_2} > \tau_{l_1 s_2}, \tau_{s_1 s_2}$

c) $\tau_{l_1 s_2} > \tau_{l_1 l_2}, \tau_{s_1 s_2}$

d) $\tau_{l_1 s_2}, \tau_{l_2 s_2} > \tau_{l_1 s_1}, \tau_{l_2 s_2}$

50. In hyperfine interaction, there is coupling between the electron angular momentum $\vec{J}$ and nuclear angular momentum $\vec{I}$, forming resultant angular momentum $\vec{F}$. The selection rules for the corresponding quantum number $F$ in hyperfine transitions are

a) $\Delta F = \pm 2$ only

b) $\Delta F = \pm 1$ only

c) $\Delta F = 0, \pm 1$

d) $\Delta F = \pm 1, \pm 2$

51. The principal series of spectral lines of lithium is obtained by transitions between

a) $nS$ and $2p, n > 2$

b) $nD$ and $2P, n > 2$

c) $nP$ and $2S, n > 2$

d) $nF$ and $3D, n > 3$

52. Pauli exclusion principle state that

a) two electron can have all the quantum numbers same

b) no tow electrons can have all the quantum numbers same

c) particles with integer and half integer spin cannot exist in the same state

d) none of the above

53. The spectral term for the atoms with 70% filled subshell and only $S = \frac{3}{2}$ is

a) $^3P_0$  
b) $^4F_{9/2}$  
c) $^3F_{1/2}$  
d) $^4P_{1/2}$

54. The hyperfine splitting of the spectral lines of an atoms is due to

a) the coupling between eh spines of two or more electrons

b) the coupling between eh spins and the orbital angular momentum of the electrons

c) the coupling between the electron spins and the nuclear spin

d) the effect of external electromagnetic field

55. What is the wavelength of the photon emitted by hydrogen atom in transition $2s \to 1s$

a) 2181 Å  
b) 1218 Å  
c) 1000 Å  
d) 2120 Å

56. The spectral terms for a certain electronic configuration are given by $^3D, ^1D, ^3P, ^1P, ^5S, ^3S$

The term with the lowest energy is

a) $^5S$  
b) $^3P$  
c) $^3D$  
d) $^3S$

57. The degeneracy of the spectral terms $^3F$ is

a) 7  
b) 9  
c) 15  
d) 21

58. The Lande g factor for the level $^3D_3$ is

a) $\frac{2}{3}$  
b) $\frac{3}{2}$  
c) $\frac{3}{4}$  
d) $\frac{4}{3}$
59. The L,S and J quantum numbers corresponding to the ground state electronic configuration of Boron (Z = 12) are

a) L = 1, S = \frac{1}{2}, J = \frac{3}{2}

b) L = 1, S = \frac{1}{2}, J = \frac{1}{2}

c) L = 1, S = \frac{3}{2}, J = \frac{1}{2}

d) L = 0, S = \frac{3}{2}, J = \frac{3}{2}

60. The degeneracies of the J – states arising from the 3P term with spin – orbit interaction are

a) 1, 3, 5  
b) 1, 2, 3  
c) 3, 5, 7  
d) 2, 6, 10

61. Assuming that the L – S coupling scheme is valid, the number of permitted transitions from 2P_{3/2} to 2S_{1/2} due to a weak magnetic field is

a) 2  
b) 4  
c) 6  
d) 10

62. The Lande g – factor for the 3P_{1} level of an atom is

a) \frac{1}{2}  
b) \frac{3}{2}  
c) \frac{5}{2}  
d) \frac{7}{2}

63. Under the LS coupling scheme, the possible spectral terms \(2s^{1}3s^{1}\) for the electronic configuration 2s\(1\)3s\(1\) are

a) \(2S_{1/2}, 2P_{3/2}^{2}P_{1/2}\)  
b) \(1^{2}S_{0}, 3S_{1}\)  
c) \(1S_{0}, 1S_{1}, 3S_{1}\)  
d) \(3S_{0}, 3S_{1}\)

64. Which of the following is the spectroscopic ground state \(2s^{1}L_{f}\) for Mn\(^{3+}\) ionic of electronic configuration

1s\(^{2}\) 2s\(^{2}\) 2p\(^{6}\) 3s\(^{2}\) 3p\(^{6}\) 3d\(^{4}\) predicted by Hund’s rules

a) \(^{5}D_{0}\)  
b) \(^{5}D_{4}\)  
c) \(^{5}D_{3}\)  
d) \(^{3}D_{2}\)

65. Which of the following states exist

a) \(^{2}3P_{1/2}\)  
b) \(^{2}2P_{3/2}\)  
c) \(^{2}2P_{5/2}\)  
d) \(^{2}2P_{7/2}\)

66. In Zeeman effect, a spectral line, upon the application of magnetic field, splits into more than three components because of

a) energy level split into 2J + 1 components  
b) in magnetic field \(\Delta M_{j} = 0, \pm 1\) no longer holds  
c) variation of Lande g factor from one level to another  
d) none of the above

67. The total number of Zeeman components observed in an electronic transition \(2D_{5/2} \rightarrow 2P_{3/2}\) of an atom in a weak field is

a) 4  
b) 6  
c) 12  
d) 10

68. The normal Zeeman effect is

a) observed only in atoms with an even number of electrons  
b) observed only in atoms with an odd number of electrons  
c) a confirmation of space quantization  
d) not a confirmation of space quantization

69. In Q. 88, the number of levels into which each of the above four terms split into respectively is

a) 6, 4, 10, 8  
b) 4, 6, 10, 12  
c) 11, 9, 6, 4  
d) 9, 5, 12, 10

70. The linear stark effect is possible in a hydrogen atom but not in a sodium atom because
a) the principal quantum number for the ground state of the sodium atom is different from that of the hydrogen atom in the ground state
b) spin orbit interaction is stronger in sodium than in hydrogen
c) the electronic energy levels of sodium that exhibit \( l - \) degeneracy
d) the electronic energy level of hydrogen exhibits \( l - \) degeneracy

71. A stable \( H_2 \) molecule is possible because (Choose incorrect)

a) the electronic ground state is a spin triplet
b) the magnitude of the electronic charge density is maximum in the inter nuclear region
c) the electronic charge density is depleted in the internuclear region
d) of strong spin orbit interaction in the molecule

72. The Compton effect experiment photons of energy \( h \nu \) around material of atomic number \( Z \). The change in wavelength can be

a) \( \nu \) is in visible region and \( Z \) is small
b) \( \nu \) is in x-ray region and \( Z \) is small
c) \( \nu \) is in x-ray region and \( Z \) is large
d) \( \nu \) is invisible region and \( Z \) is large

73. Which one of the following statements concerning the Compton effect is NOT correct

a) the wavelength of the scattered photon is greater than that or equal to the wavelength of the incident photon
b) the electron can acquire kinetic energy equal to the energy of incident photon
c) the energy of the incident photon equal to the kinetic energy of the electron plus the energy of the scattered photon
d) the K.E. acquired by the electron is largest when the incident and scattered photons move in opposite direction

74. If 50 kV is applied potential in an X ray tube, then the minimum wavelength of X-ray produced is

a) 0.2 nm  b) 2 nm  c) 0.2 Å  d) 0.2 Å

75. X-rays consists of

a) negatively charged particles
b) electromagnetic radiation
c) positively charged particles
d) a stream of neutrons

76. X-rays are produced when as element of high atomic weight is bombarded by high energy

a) protons  b) photons  c) neutrons  d) electrons

77. As the wavelength of X-rays is smaller than that of visible light, the speed of X-rays in vacuum is

a) same as that of visible light
b) larger than that of visible light
c) smaller than that of visible light
d) none of these

78. According to Moseley’s law, the frequency of the characteristic X-ray radiation is proportional to the square of

a) atomic weight of the element
b) atomic number of the element
c) both (A) and (B)
d) none of these
79. The constant $a$ in Moseley’s law is

a) screening constant
b) rydberg constant
c) atomic number
d) none of these

80. The constant $a$ in Mosely’s law related with Rydberg constant as

a) $R = \left(\frac{4a}{3c}\right)$
b) $R = \left(\frac{3c}{4d}\right)$
c) $R = \left(\frac{a}{2c}\right)$
d) $R = \left(\frac{2c}{a}\right)$

where, $c =$ velocity of light

81. The short wavelength limit of X–rays depend upon

a) nature of the target
b) p.d across the X ray tube
c) nature of the filament used
d) none of these

82. The variation of the intensity of X rays with the thickness of absorbing material is given by

a) $I = I_0 \exp(-\mu x)$
b) $I = I_0 \exp(\mu x)$
c) $I = I_0 \exp(-\frac{\mu}{x})$  
d) $I = I_0 \exp(\frac{\mu}{x})$

where, $\mu$ is the absorption coefficient

83. In an X ray experiment when we apply a voltage across an X ray tube, we find that there is a definite short wavelength limit to the continuous X–ray spectrum. This limit

a) depends upon the voltage across the tube only or is independent of the material of target
b) depends on the voltage across the tube and also depends on the material of the target
c) depends upon the material of target only
d) depends upon the ionisation potential of target atom

84. The ratio of the ionisation potential of ground state mu meson to the corresponding electron is about

a) $\frac{1}{200}$  
b) $\frac{1}{(200)^2}$  
c) $\frac{1}{(200)^4}$  
d) 200

85. The Bohr magneton is of the order of

a) $10^{-23}$ erg/gauses  
b) $10^{-20}$ erg/gauses  
c) $10^{-25}$ erg/gauses  
d) none of these

86. If the energy required to remove a second electron form L level be approximately equal to that of first electron, then kinetic energy $T$ of an Anger electron from an atom ionised in the L state will be given by

a) $T = E_k - E_L$  
b) $T = E_k + E_L$  
c) $T = 2E_k - 2E_L$  
d) $2E_k - E_L$

87. An electron is revolving in an orbit of radius 1A’ with the force of nuclear charge (+ 2) producing the centripetal acceleration. By taking classical model of the atom frequency of rotation will be about

a) $2 \cdot 27 \times 10^{20}$/sec  
b) $2 \cdot 27 \times 10^{16}$/sec  
c) $2 \cdot 27 \times 10^{10}$/sec  
d) $2 \cdot 27 \times 10^{18}$/sec

88. The continuous X – ray spectrum at constant voltage will have

a) a minimum wavelength  
b) a maximum wavelength  
c) a minimum frequency  
d) a maximum frequency

89. The shortest wavelength produce in an X – ray tube operated at 2 million volts will be
90. Radius of the H–mesic orbit of lead (Z = 82, A = 208, n = 1 nucleus of lead atom is a point charge) should be about

- a) $3 \cdot 08 \times 10^{-11}$ cm
- b) $3 \cdot 08 \times 10^{-12}$ cm
- c) $3 \cdot 08 \times 10^{-13}$ cm
- d) $3 \cdot 08 \times 10^{-18}$ cm

91. Characteristic or line X–ray spectra are not likely to be excited by the following

- a) electron bombardment
- b) irradiation by short X–rays
- c) proton bombardment
- d) neutron absorption

92. The $K_\beta$ of X–rays emitted from an atom with principal quantum numbers $n = 1, 2, 3, \ldots$ arises from the transition

- a) $n = 4 \rightarrow n = 2$
- b) $n = 3 \rightarrow n = 2$
- c) $n = 5 \rightarrow n = 2$
- d) $n = 3 \rightarrow n = 1$

93. The target of an X–ray tube is subjected to an excitation voltage $V$. The wavelength of the emitted X–rays is proportional to

- a) $\frac{1}{\sqrt{V}}$
- b) $\sqrt{V}$
- c) $\frac{1}{V}$
- d) $V$

94. The NMR spectrum of ethanol ($CH_3CH_2OH$) comprises to three bunches of spectral lines in the bunch corresponding to $CH_2$ group is

- a) 1
- b) 2
- c) 3
- d) 4

95. The short wavelength cut off the continuous X–ray spectrum form a nickel target is $0.0825$ nm. The voltage required to be applied to an X–ray tube is

- a) 0.15 kV
- b) 1.5 kV
- c) 15 kV
- d) 150 kV

96. X–ray were produced using cobalt (Z = 27) as target. It was observed that the X–ray spectrum contained a strong $k_\alpha$ line of wavelength $0.1930$ nm. Then, the weak $k_\alpha$ line is due to an impurity whose atomic number is

- a) 25
- b) 26
- c) 28
- d) 30

97. The energy $E$ of $k_\alpha$ X–ray emitted from target of different atomic number $Z$ varies as

- a) $Z^2$
- b) $Z^{2/3}$
- c) $Z$
- d) $Z^{1/2}$

98. The continuous X–ray spectrum is the result of the

- a) photoelectric effect
- b) inverse photoelectric effect
- c) Compton effect
- d) auger effect

99. The frequencies of lines of a line spectrum of X–ray emission depend on

- a) the kinetic energy of the electron
- b) the metal used for the anti–cathode
- c) the declination of the electron
- d) the shape of the continuous spectrum

100. Typical energy of the rotational modes in a polyatomic molecule like $NH_3$ is

- a) $10^6$ eV
- b) $10^3$ eV
- c) $10^4$ eV
- d) 1 eV
101. Which one of the following molecules does not exhibit a rotational spectrum
   a) $H_2$  b) CO  c) HCl  d) HBr

102. Resonance (NMR, ESR etc) studies in solids provide information about (Choose Incorrect)
   a) the electronic structure of single defects
   b) the motion of the spin or of the surroundings
   c) collective spin excitations
   d) external magnetic fields sampled by the spin

103. Infrared absorption can be observed in which of the following molecules
   a) $N_2$  b) $O_2$  c) HCl  d) $C_2$

104. The pure rotational levels of a molecule in the far infrared region follows the formula
   $F(J) = BJ(J + 1)$, where $F(J)$ is the energy of the rotational level with quantum number $J$ and $B$ is
   the rotational constant. The lowest rotational energy gap in rotational Raman spectrum is
   a) $2B$  b) $4B$  c) $6B$  d) $8B$

105. The vibrational spectrum of a molecule exhibits a strong line with P and R branches at a
   frequency $v_1$ and a weaker line at a frequency $v_2$. The frequency $v_3$ is not shown up. Its
   vibrational Raman spectrum shows a strong polarized line a frequency $v_3$ and no feature of
   $v_1$ and $v_2$
   a) the molecule could be linear
   b) the molecule lacks a center of inversion
   c) $v_1$ arises from a symmetric stretching mode
   d) $v_3$ arises from a bending mode

106. Three values of rotational energies of molecules are given below in different units
   P : $10 \text{ cm}^{-1}$; Q: $10^{-25}$ J, R = $10^4$ MHz
   Choose the correct arrangement in the increasing order of energy
   a) P, Q, R  b) R, Q, P
   c) R, P, Q  d) Q, R, P

107. Consider the following statement about molecular spectra
   P : $CH_4$ does not give pure, rotational Raman lines
   Q : $SF_6$ could be studied by rotational Raman spectroscopy
   R : $N_2$ show infrared absorption spectrum
   S : $CH_3CH_3$ shows vibrational Raman and infrared absorption lines
   T : $H_2O_2$ shows pure rational spectrum
   Choose the right combination of correct statements
   a) P and Q  b) P, R and T
   c) P, S and T  d) Q and R

108. All vibration producing a change in the electric dipole moment of molecule yield
   a) raman spectra  b) infrared spectra
   c) ultra violet spectra  d) X – ray spectra

109. Consider the pure rotational spectrum of a diatomic right rotor. The separation between
   two consecutive lines ($\Delta v$) in the spectrum
   a) is directly proportional to the moment of inertia of the rotor
   b) is inversely proportional to the moment of inertia of the rotor
   c) depend son the angular momentum,
   d) is directly proportional to the square of the interatomic separation

110. Light of wavelength $1 \cdot 5 \mu m$ incident of a material with a characteristic Raman
    frequency of $20 \times 10^{12}$ Hz results in a stokes
shifted line of wavelength \([\text{Given: } c = 3 \times 10^8 \text{ ms}^{-1}]\)

a) 1\cdot 47 \mu m  

b) 1\cdot 57 \mu m  

c) 1\cdot 67 \mu m  

d) 1\cdot 77 \mu m

111. In the microwave spectrum of identical rigid diatomic molecules, the separation between the spectral line is recorded to be 0\cdot 7143 cm\(^{-1}\). The moment of inertia of the molecules, in kg m\(^2\), is

a) 2\cdot 3 \times 10^{-36}  

b) 2\cdot 3 \times 10^{-40}  

c) 2\cdot 3 \times 10^{-42}  

d) 7\cdot 8 \times 10^{-46} 

112. A vibrational electronic spectrum of homonuclear binary molecule involving electronic ground state \(\epsilon''\) and excited state \(\epsilon'\), exhibit a continuum at \(\bar{\nu} \text{ cm}^{-1}\). If the total energy of the dissociated atoms in the excited state exceeds the total energy of the dissociated atoms in the ground state by \(E_{\text{ex}} \text{ cm}^{-1}\), the dissociation energy of the molecule in the ground state is

a) \(\bar{\nu} + E_{\text{ex}}/2\)  

b) \(\bar{\nu} - E_{\text{ex}}/2\)  

c) \(\bar{\nu} - E_{\text{ex}}\)  

d) \(\sqrt{\bar{\nu}^2 - E_{\text{ex}}^2}\)

113. For a diatomic molecule with the vibrational quantum number \(n\) and rotational quantum number \(J\), the vibrational level spacing \(\Delta E_n = E_n - E_{n-1}\) and the rotational level spacing \(\Delta E_1 = E_J - E_{J-1}\) are approximately

a) \(\Delta E_n = \text{constant}, \Delta E_J = \text{constant}\)  

b) \(\Delta E_n = \text{constant}, \Delta E_J \propto J\)  

c) \(\Delta E_n \ll n; \Delta E_J \propto J\)  

d) \(\Delta E_n \propto n; \Delta E_J \propto J^2\) 

114. The typical wavelengths emitted by diatomic molecules is purely vibrational and purely rotational transition are respectively in the region of

a) infrared and visible  

b) visible and infrared  

c) infrared and microwave  

d) microwave and infrared 

115. The separation of the lines in the far infrared spectrum of HBr is 16\cdot 90 \times 10^{-10} \text{ cm}, its moment of inertia should be around

a) 6\cdot 66 \times 10^{-40} \text{ g cm}^2  

b) 3\cdot 30 \times 10^{-38} \text{ g cm}^2  

c) 3\cdot 30 \times 10^{-38} \text{ g cm}^2  

d) 3\cdot 30 \times 10^{-40} \text{ g cm}^2  

116. In the band spectra of diatomic molecule which of the following characteristic is not true

a) formation of band does not occur in rotation vibration spectra  

b) the band head can occur towards the red end  

c) the band head can occur towards the violet end  

d) the band head must be formed at the transition between the same set of rotational quantum number

117. Pure rotational spectrum of a diatomic molecule consists of

a) two equally spaced lines  

b) three equally spaced line  

c) many equally spaced lines  

d) no regular pattern

118. The moment of inertia of two point masses about an axis through their centre of mass in a plane perpendicular to the massless rigid rod is given by

(given \(r_0 = \text{separation between point masses}\))

\(\mu = \text{reduced mass}\)
119. In Raman spectra Q branch is
a) absent     b) present
(c) presence of appearance depends on the state of polarization of the molecule
d) none of these

120. At ordinary temperature the molecules remain in their
a) lowest vibrational level     b) highest vibrational level
c) can remain in any vibrational level     d) does not show any type of vibration

121. A three level system of atoms has \( N_1 \) atoms in level \( E_1 \), \( N_2 \) in level \( E_2 \) and \( N_3 \) in level \( E_3 \) (\( N_2 > N_1 > N_3 \) and \( E_1 < E_2 < E_3 \)). Laser emission is possible between the levels
a) \( E_3 \rightarrow E_1 \)     b) \( E_2 \rightarrow E_1 \)
c) \( E_3 \rightarrow E_2 \)     d) \( E_2 \rightarrow E_3 \)

122. In Young’s double slit experiment with a helium neon laser beam of wavelength 632 nm, the first interference maximum will occur when
a) path difference is 948 nm     b) path difference is 316 nm
c) phase difference is \( 2\pi \) radian     d) phase difference is \( \pi \) radian

123. The number of photons emitted per second from a 1 Watt Ar – ion laser operating at 488\( \cdot \)0 nm is approximatley
a) \( 10 \cdot 23 \times 10^{19} \)     b) \( 2 \cdot 46 \times 10^{18} \)
c) \( 10 \cdot 23 \times 10^{17} \)     d) \( 2 \cdot 46 \times 10^{15} \)

124. Special line width of the He – Ne laser is \( 0 \cdot 01 cm^2 \). If the output power is 1 milli Watt, the radiation intensity per unit wavelength (in Watt/cm\(^2\)) is
a) \( 10^{10} \)     b) \( 10^{8} \)     c) \( 10^{-8} \)     d) \( 10^{-10} \)

125. A laser beam emerging from a laser tube operating at 80 nm has a cross sectional diameter of 2 mm. The diameter of the beam at a distance of 1 km is approximately given by
a) 10 m     b) 8 cm
(c) 80 cm     d) 10 m

126. The dependence of Doppler broadened line width of a laser transition on temperature \( T \) is given by
a) \( T \)     b) \( T^{-1/2} \)     c) \( T^{1/2} \)     d) \( T^2 \)

127. A laser beam of wavelength 600 nm with a circular cross section having a radius of 10 mm falls normally on a lens of radius 20 mm and focal length 10 cm. The radius of the focussed spot is approximately
a) 0\( \cdot \)3\( \mu m \)     b) 0\( \cdot \)6\( \mu m \)
c) 3\( \cdot \)0\( \mu m \)     d) 6\( \cdot \)0\( \mu m \)

128. There is no infrared absorption for nitrogen molecules because
a) its polarizabilty is zero     b) it has no vibrational level
c) it has no rotational level     d) its dipole moment is zero

129. The vibrational constant \( \omega_0 \) and \( \omega_0 x_0 \) of HCl are 2937\( \cdot \)5 cm\(^{-1}\) and 51\( \cdot \)6 cm\(^{-1}\). Then first Raman strokes line will be observed at (in cm\(^{-1}\))
130. The intensity of the electronic O – O band of a diatomic molecule is very intense when the minimum of a potential curve for the upper electronic state lies (here $r$ is the internuclear distance)

a) at the same value of $r$ as that of the lower potential curve
b) at the smaller value of $r$ than that of the lowest potential curve
c) at the larger value of $r$ then that of the lower potential curve
d) above the dissociation level of the lower potential curve

131. The total number of electrons in a subshell with orbital quantum number $'l'$ is

a) $R(l + 1)$  b) $2(l + 1)$
c) $2(2l + 1)$  d) $2l^2$

132. L – S coupling occurs often in

a) all atoms  b) lighter atoms
c) heavier atoms  d) occurs only in nuclei

133. The splitting of a spectral line in the presence of a electric field is called

a) stark effect  b) Zeeman effect
c) paschen back effect  d) raman effect

134. In a very strong magnetic field the splitting of a spectral line is normal, this effect is called

a) stark effect  b) Zeeman effect
c) paschen back effect  d) raman effect

135. Near infrared spectrum of diatomic molecule is known as

a) rotational spectrum  b) vibrational spectrum
c) rotational vibrational spectrum  d) electronic band spectrum

136. The effect used to study the energy levels of harmonic molecule is

a) stark effect  b) Zeeman effect
c) paschen back effect  d) raman effect

137. Raman effect is due to collision of

a) photon with electron  b) photon with molecule
c) electron with atom  d) electron with photon

138. The shortest wavelength of X rays emitted from X – ray tube depends on

a) current in the tube  b) the voltage applied to the tube
c) the nature of gas in the tube  d) the atomic number of target material

139. Characteristic X rays depend upon

a) only on nature of target material  b) only on operating voltage of X rays tube
c) both (A) and (B)  d) none of these

140. The precession frequency of an electron orbit in a magnetic field of 5 Tesla is

a) $1 \times 10^9$ sec$^{-1}$  b) $2 \times 10^9$ sec$^{-1}$
c) $4 \times 10^9$ sec$^{-1}$  d) $1 \times 10^9$ sec$^{-1}$
141. In metastable energy state molecule can stay upto
   a) $10^{-6}$ sec  b) $10^{-8}$ sec  
   c) $10^{-10}$ sec  d) $10^{-12}$ sec

142. In doublet splitting of the first excited $^2P_{3/2}$ - $^2P_{1/2}$ of H is $0\cdot365\text{cm}^{-1}$. The corresponding separation for Li$^{++}$
   a) $29\cdot6\text{cm}^{-1}$  b) $5\cdot85\text{cm}^{-1}$
   c) $24\cdot5\text{cm}^{-1}$  d) $11\cdot20\text{cm}^{-1}$

143. For infrared spectrum of diatomic molecules is known as
   a) rotational spectrum  b) vibrational spectrum
   c) rotational vibrational spectrum  d) electron band spectrum

144. With exciting line 2536 Å, a Raman line for a sample is observed at 2612 Å. The Raman shift is
   a) $2\cdot0 \times 10^{-5}\text{m}^{-1}$  b) $1\cdot0 \times 10^{-1}\text{m}^{-1}$
   c) $1\cdot15 \times 10^{-5}\text{m}^{-1}$  d) $3\cdot0 \times 10^{-5}\text{m}^{-1}$

145. Cut off wavelength of X – rays coming from a Coolidge tube depends on the
   a) target material  b) accelerating voltage
   c) separation between the target and the filament  d) temperature of the filament

146. The minimum voltage that must be applied to an x – ray tube to produce X – ray photon of $\lambda = 0 \cdot 1 \text{ Å}$ is
   a) $1\cdot25 \times 10^5$ volts  b) $3\cdot0 \times 10^6$ volts
   c) $4\cdot5 \times 10^6$ volts  d) $2\cdot25 \times 10^7$ volts

147. X –ray on a material
   a) exerts a force on it  b) transfer energy to it
   c) transfers momentum to it  d) all of these

148. The spectrum of sodium atom can be explain by considering
   a) J – J coupling  b) relativistic correction
   c) L – S coupling  d) heitler London theory

149. Pure vibrational spectrum of a diatomic molecule are when
   a) it has a centre of symmetry  b) it has a permanent dipole moment
   c) it exhibit change in polarisability due to electronic transition  d) it has no magnetic moment

150. In a Ruby Laser population inversion is achieved by applying
   a) magnetic field  b) electronic field
   c) both magnetic and electrostatic field  d) optical pumping

151. Angular momentum quantisation is directly established by
a) stern Gerlach experiment  
b) Pranch Hertz experiment  
c) Photo electric effect  
d) Dauison Gerner experiment

152. The spectral term for \( L = 2 \) and \( S = 1 \) is given by

a) \( 1P_{3/2} \)  
b) \( 3D \)  
c) \( 2s_{1} \)  
d) \( 3D_{5/2} \)

153. Line broadening is not due to

a) Doppler effect  
b) uncertainty principle  
c) rayleighs criterion  
d) pressure

154. For raman transitions, the selections rule are

a) \( \Delta J = 0, \pm 1; \Delta m \pm 1 \)  
b) \( \Delta J = \pm 1, \pm 2; \Delta m = \pm 1, \pm 2 \)  
c) \( \Delta J = 0, \pm 2; \Delta m = 0, \pm 1 \)  
d) \( \Delta J = \pm 2, \Delta m = \pm 1 \)

155. If \( 'R' \) is the distance between two hydrogen atoms, the Vander Waals interaction energy between them is proportional to

a) \( \frac{1}{R} \)  
b) \( \frac{1}{R^2} \)  
c) \( \frac{1}{R^3} \)  
d) \( \frac{1}{R^6} \)

156. The spectroscopic term \( 2F_{7/2} \) refers to an atomic system having total angular momentum \( J \), spin \( S \) and orbital angular momentum \( L \) given by

a) \( J = \frac{7}{2}, L = 3, S = \frac{1}{2} \)  
b) \( J = \frac{7}{2}, L = 4, S = 1 \)  
c) \( J = \frac{5}{2}, L = 2, S = \frac{1}{2} \)  
d) \( J = 2, L = 3, S = \frac{7}{2} \)

157. The Lyman series of hydrogen spectrum lies in the region

a) radio frequency  
b) infrared  
c) visible  
d) ultraviolet

158. In normal Zeeman effect the \( d \) – energy level is split into

a) 3  
b) 4  
c) 5  
d) 6

181. a. For a hydrogen atom in a uniform electric field

a) linear stark effect is possible in the first excited state  
b) only quadratic stark effect occurs  
c) stark effect occur only for the ground state  
d) the degeneracy of the first excited state is completely removed

182. If for a molecule \( E \) is the energy associated with the motion of a valence electron and \( E_v \) and \( E_r \) are vibrational and rotational energies for low modes, then

a) \( E_v \sim \frac{m}{M} E, E_r \sim \left(\frac{m}{M}\right)^{1/2} E \)  
b) \( E_v \sim \left(\frac{m}{M}\right)^{1/2} E, E_r \sim \frac{m}{M} E \)  
c) \( E_v \sim \left(\frac{m}{M}\right) E, E_v \sim \left(\frac{m}{M}\right)^2 E \)  
d) \( E_v \sim \left(\frac{M}{m}\right)^{1/2} E, E_r \sim \left(\frac{M}{m}\right) E \)

183. Which of the following will result symbolically the stimulate emission process (The asterisk indicates an excited condition)

a) atom + photon \( \rightarrow \) atom\*  
b) atom\* + photon \( \rightarrow \) atom\*  
c) atom\* \( \rightarrow \) atom + photon  
d) atom\* + photon \( \rightarrow \) atom + 2 photon
184. The maximum degeneracy of an energy level with principal quantum number \( n \) is

a) \( n \)  b) \( n^2 \)  c) \( 2n^2 \)  d) \( (2n^2 + 1) \)

185. Which one of the following experiment confirms

a) double slit experiment 
b) stern and gerlach experiment 
c) franck and hertz experiment 
d) Michelson and morley experiment

186. The relationship between the orbital quantum number \( l \) and azimuthal quantum number \( n_\phi \) is

a) \( l = n_\phi \)  b) \( l = n_\phi + 1 \)  c) \( l = n_\phi - 1 \)  d) \( l = n_\phi + 1 \)

187. According to vector atoms model

a) only the magnitude of orbital angular momentum is quantised 
b) both the magnitude and direction of orbital angular momentum and spin angular momentum are quantised 
c) the total spin angular momentum of many electron system is always \( \frac{h}{2} \) 
d) the total angular momentum of many electrons system has only two values

188. For the single electron system

a) all the energy levels are singlet 
b) all the energy levels are doublets 
c) the ground state is singlet and all the other energy levels are doublets 
d) the ground energy state is singlet and other energy state are multi states

189. Which transition is not possible

190. The intensity of spectral line will be maximum if

a) \( \Delta L = -1, \Delta J = 0 \)  b) \( \Delta L = +1, \Delta J = 0 \)  c) \( \Delta L = +1, \Delta J = -1 \)  d) \( \Delta L = -1, \Delta J = -1 \)

191. For the two electron system if \( l_1 = 2, l_2 = 1 \), the value of \( J \) according to L – S coupling will be

a) 3, 2, 1  b) 4, 3, 2, 1, 0  c) 4, 3, 2  d) 4, 3, 2

192. The difference between soft and hard X rays is of

a) velocity  b) intensity  c) frequency  d) polarisation

193. In an X-ray tube, X-ray are produced by the electrons accelerated by \( V \) volt. The maximum frequency of the X-rays is

a) \( e\hbar V \)  b) \( \frac{\hbar V}{e} \)  c) \( \frac{e\hbar}{V} \)  d) \( \frac{eV}{h} \)

194. And X-ray operates on 30 kV. The minimum wavelength of X-ray emitted is

a) 0.133 Å  b) 0.4 Å  c) 1.2 Å  d) 6.6 Å

195. For production of characteristic \( k_\alpha \) line of X-ray the electrons transition is from
a) $n = 2$ to $n = 1$

b) $n = 3$ to $n = 2$

c) $n = 3$ to $n = 1$

d) $n = 4$ to $n = 2$

196. In X-ray absorption spectra, the wavelength of K edge is $\lambda$. The accelerating voltage of the tube will be

a) $\frac{hc}{\lambda e}$

b) $\frac{e\lambda}{hc}$

c) $\frac{hc\lambda}{e}$

d) $\frac{e}{hc\lambda}$

197. A band has a sharp intense edge

a) on the longer wavelength side

b) in the middle

c) on the shorter wavelength side

d) nowhere

198. The energy change in an electronic transition is of the order of

a) $5 - 10$ eV

b) $10^{-2}$ eV

c) $0.1$ eV

d) 1 keV

199. The vibrational transition is a molecule are accompanied with an energy change as

a) 10 eV

b) $0.1$ eV

c) $0.05$ eV

d) 5 eV

200. In a molecule, the rotational transitions occurs by the absorption of energy of the order of

a) 5eV

b) $0.005$ eV

c) $0.05$ eV

d) 5 eV

201. The rotational energy levels of a diatomic molecule are

a) continuous

b) discrete and equispaced

c) discrete, but not equispaced

d) nothing can be said

202. The vibrational frequency of a diatomic molecule of reduces mass $\mu$ and force constant $k$

a) $2\pi \sqrt{\frac{\mu}{k}}$

b) $\frac{1}{2\pi \sqrt{\frac{\mu}{k}}}$

c) $\frac{1}{2\pi \sqrt{\frac{k}{\mu}}}$

d) $\frac{k}{\sqrt{\mu}}$

203. In HCl molecule, the energy gap between the two vibrational level is 0.36 eV. Its zero pint energy will be

a) 0

b) 0.18 eV

c) 0.36 eV

d) 0.54 eV