



Production of Courseware

- Contents For Post Graduate Courses

Paper No. : Atomic, Molecular and Laser Spectroscopy

Module: Spectra of Alkali Metals

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Description of Module	
Subject Name	Physics
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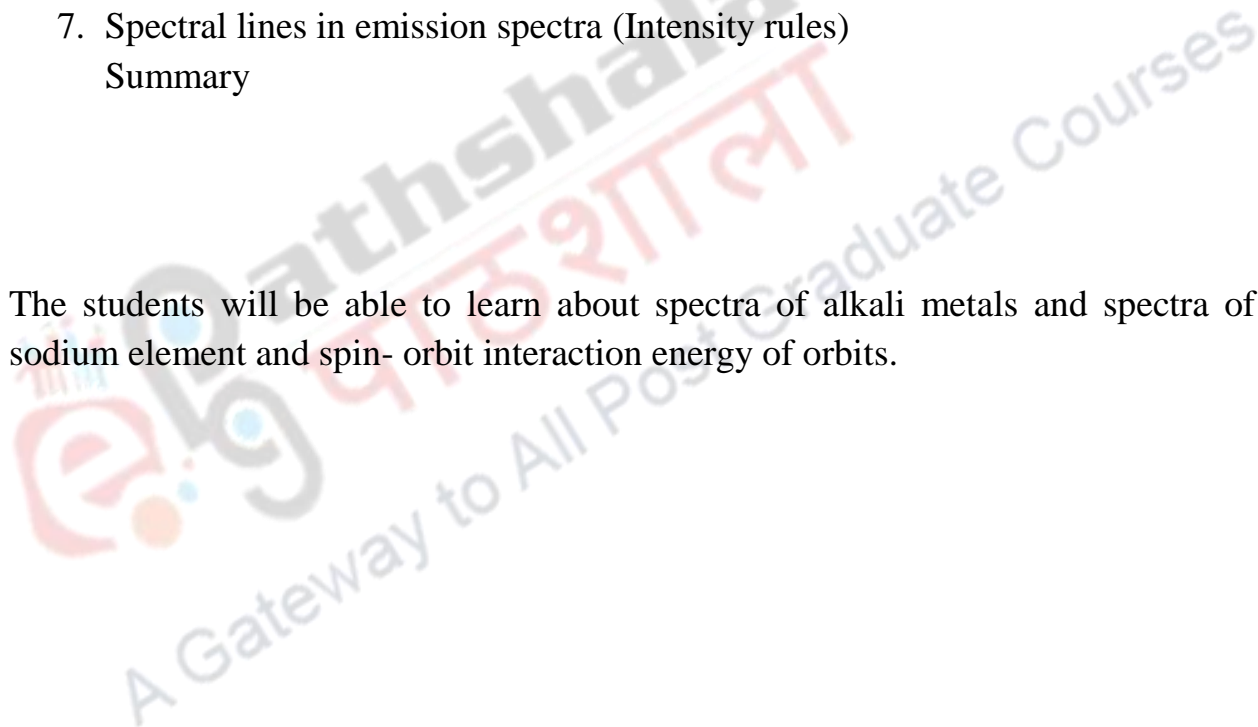




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The students will be able to learn about spectra of alkali metals and spectra of sodium element and spin- orbit interaction energy of orbits.



1. Spectra of Alkali Atoms : Introduction

The series of Alkali atoms contain Lithium ($Z=3$), Sodium($Z=11$), Potassium($Z=19$), Rubidium($Z=37$) and Cesium($Z=55$) and their configurations are $1s^2 2s$, $1s^2 2s^2 2p^6 3s$, $1s^2 2s^2 2p^6 3s^2 3p^4 4s$, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s$, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s$

This suggests that an alkali atom consists of one or more closed shells of electrons in its ground state and a single valence electron in a new shell in an ns orbit.

Now visualizing the two-particle system with a lone (valence) electron subjected to the Coulomb field of a point charge that is equivalent to a proton of the diameter

$\sim 10^{-15} \text{m}$ and is thus the simplest spectra.

The aim is to solve this two-body system exactly to find the wave functions and understand the meaning of the four quantum numbers n, l, m_l and m_s .

Keeping in mind the shell model to understand the structure of the alkali spectra and it is the fact that the fine structure and magnetic field splitting are smaller than the gross structure energies by a factor of about $Z^2 \alpha^2 = (Z^2 / 137)^2 \sim 10^{-4} Z^2$. Fine structure and the field splitting of the transitions (lines) can be understood after the gross structure of the spectrum.

So far, on the basis of the shell model, the atomic states are known.

1. *The electronic states are specified by four quantum numbers: n, l, m_l and m_s . and electrons with $l=0, 1, 2, 3, \dots$ are called s, p, d, f, \dots electrons, respectively.*

2. *The gross energy of the electron is determined by n and l .*

3. *In the absence of fine structure and external magnetic fields, all the states with the same values of n and l are degenerate. Each (n, l) term of the gross structure therefore contains $2(2l+1)$ degenerate levels.*

According to the Bohr model, radii of the principal atomic shells of normal sodium atom with atomic number 11 are 0.05 \AA (as 1s electron sees +11 nuclear charge)

OR valence electron of sodium is moving in a net field of $+1e$ charge (due to the core of finite size) apparently like a lone (valence) electron in hydrogen atom, moves around the proton (point charge). Therefore it is assumed that the spectra of sodium atom are expected to be analogous to that of the hydrogen as in both the

cases, respective valence electron moves in a net field of $+1e$ but with the difference that the field is from the finite size core in former whereas from a point charge (proton) field in the later case.

n(electrons)	l(orbital)	m_l	m_s	* $\sum m_l, \sum m_s$
1(2)	0(s)	0	$\pm \frac{1}{2}$	Zero
2(2 + 6)	0(s)	0	$\pm \frac{1}{2}$	Zero
	1(p)	-1, 0, +1	$\pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}$	Zero
3(2 + 6 + 10)	0(s)	0	$\pm \frac{1}{2}$	Zero
	1(p)	-1, 0, +1	$\pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}$	Zero
	2(d)	-2, -1, 0, +1, +2	$\pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}$	Zero

The closed shell has Zero Total angular momentum and Zero spin angular momentum and designated as 1S_0

The valence electron can be excited to various s,p,d,f,... Orbits those results in doublet terms.

2. Spectrum of Na: Quantum Mechanical View

As the potential energy in hydrogen atom is spherically symmetric, that is, it depends only on the radial coordinate 'r', its solution, like for all spherically symmetric systems, may be expressed as

$$\psi(r, \theta, \phi) = R(r) Y_{l,m}(\theta, \phi) \text{-----[1]}$$

where $Y_{l,m}(\theta, \phi)$ are spherical harmonics. Substitution of equation (1) in

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + \frac{2m_j}{\hbar^2} (E - V) \psi = 0$$

leads to radial equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left\{ \frac{2m}{\hbar^2} [E - V(r)] - \frac{l(l+1)}{r^2} \right\} R = 0 \quad \text{-----[2]}$$

and the angular equation

$$\mathbf{L}^2 Y_{l,m}(\theta, \phi) = \hbar^2 l(l+1) Y_{l,m}(\theta, \phi) \quad \text{-----[3]}$$

Where,

$$\mathbf{L}^2 = -\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \quad \text{-----[4]}$$

Orbital angular momentum operator has eigenvalues $l(l+1)\hbar^2$ corresponding to eigenfunction $Y_{l,m}(\theta, \phi)$.

The orbital angular momentum for a completely filled shell, according to Pauli's principle, is zero and therefore, their charge distribution is spherically symmetric. Accordingly, in the case of sodium atom (for that matter in case of all alkali atoms) charge distribution in $n=1$ & 2 shells (completely filled shells) is spherically symmetric and is known as the core of the atom. Valence electron $3s$ is, therefore, regarded as moving in a central force field (force that depends only on distance and is completely independent of the angular position) of the core.

Therefore, quantum mechanically also spectrum of sodium is expected to be similar to that of the hydrogen atom.

Experimental Observations

The transition of the electron from one energy level to another is governed by the selection rules $\Delta l = \pm 1$

Experimental findings reveal that emission spectra of the alkali atoms can be analyzed into four chief series with the peculiarities as given below.

First series consists of doublets; separation (in cm^{-1}) between the doublet components remains constant (say $\Delta\nu_s$) as far as the series extends. Series is termed as **Sharp series**.

This arises due to transition from $2S$ states to lowest $2P$ state. The lines are observed in visible and infrared regions and are quite narrow.

Second series consists of doublets; separation (in cm^{-1}) between the doublet components decreases rapidly as the series extends to higher members. Series is termed as **Principal series**. This arises due to transition from 2P state to 2S state. The lines are intense and are observed in absorption spectrum as most of the atoms are in ground state. The lines of this series are in ultraviolet region except one in visible region.

Third series initially consists of triplets (three components) followed by apparent doublets; separation (in cm^{-1}) between the outer components remains constant (say $\Delta\nu_d$) as far as the series extends. Series is termed as **Diffuse series**. This arises due to transition from 2D state to 2P state. The lines lie in the visible and infrared region. The lines of this series are diffused on one end or both the end of line.

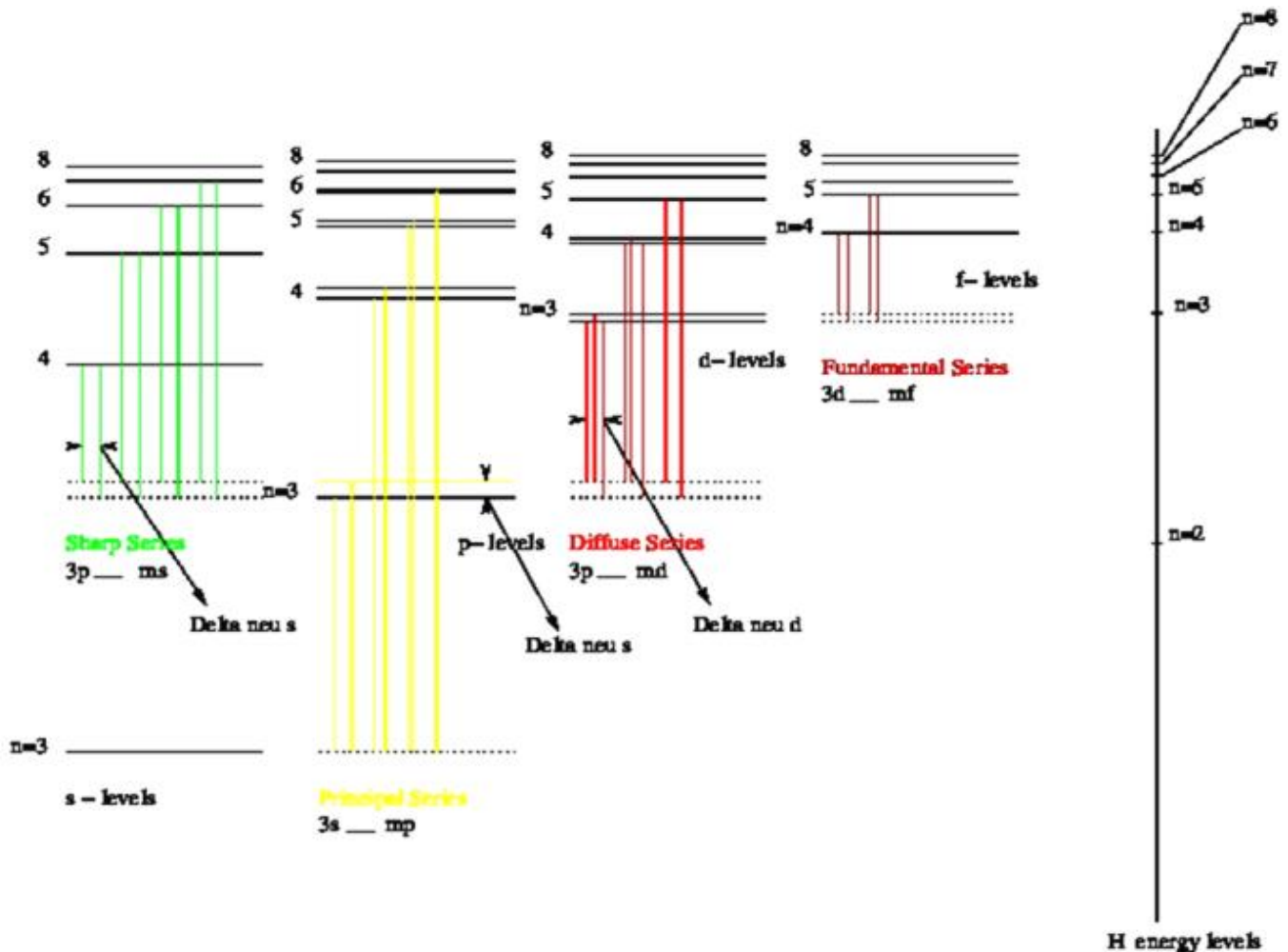
Fourth series, termed as **Fundamental series**, lies in far infra red region and consists of very close lying doublets. This arises due to transition from 2F state to the lowest 2D state. The lines of this series are in visible and infrared regions.

Remarks:

- The Sharp, Diffuse and Fundamental series occur in Emission spectra.
- The Sharp and Diffuse series have common limit, whose wave number is equal to the lowest P - term (converge to two limits corresponding to doublet components). Further, the difference between the convergence limits of sharp (or diffuse) series and the principal series is equal to wave number of the first member of the latter (Principal) series. This is referred as Rydberg Schuster law. This forms one of the basis for analysis of atomic spectra.
- The difference between the limit of Diffuse and Fundamental series is equal to the first line of Diffuse series.
- Each series in alkali atoms converge towards shorter wavelength similar to that of hydrogen.

- In absorption (spectrum) at moderately low temperature, only Principal series is observed implying lowest term is ns and the series appears similar to the Lyman series of hydrogen atom.

The figure shows the transitions forming four chief series.



The figure depicts the s, p, d and f series corresponding to various different values of n and l . Transitions are drawn in accordance with the selection rules (that is, principal quantum number, n can change by any value whereas l by unity only, i.e. $\Delta l = \pm 1$).

The alkali spectra comprises of series of lines (doublets) with successive decreasing separation and the intensity as well, in a fashion similar to that of hydrogen spectrum. The transitions forming the four chief series in alkali spectra may, therefore, be summarized as:

Sharp series: $n_0p \rightarrow ms$

Principal series: $n_0s \rightarrow mp$

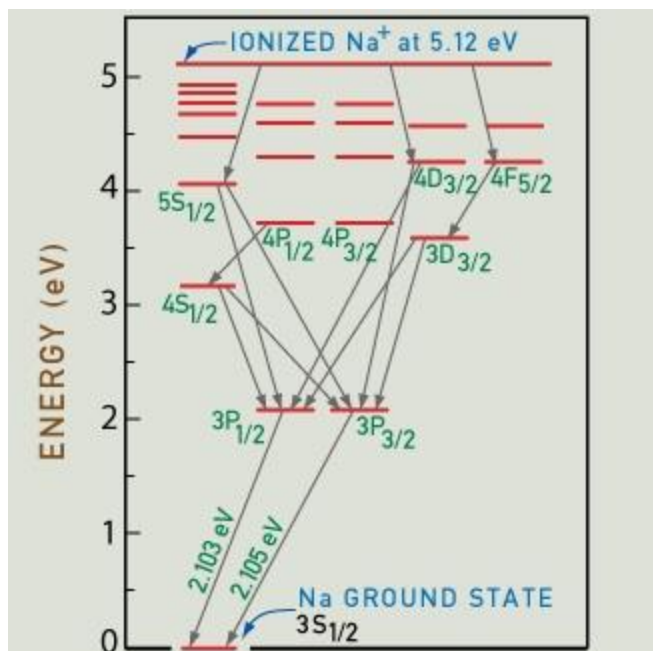
Diffuse series: $n_0p \rightarrow md$

Fundamental series: $n_0d \rightarrow ms$

Where m assumes running values.

Principal quantum number (measure of total energy) for the hydrogen atom is shown on the right hand side of the Fig.

Sodium alkali atom



Source: <http://www.webexhibits.org/causesofcolor/4AC.html>

The Comparison with the hydrogen atom leads to the fact that the energy levels of sodium lie lower on the energy scale. This suggests that the kinetic energy (and therefore, velocity) of exciting (valence) electron in sodium is greater than the corresponding value of the valence electron in hydrogen atom.

On the other hand, velocity of valence electron decreases with increase of its principal quantum number, n and increases with increase of effective charge, z in the field of which valence electron moves around the nucleus. The latter dependence makes it imperative that the valence electron, in case of sodium atom,

sees more than $+1e$ charge and this is possible only if the valence electron penetrates core of the atom; that is electron orbit is elliptical.

In addition, deviation of the potential from the Coulomb potential due to a point charge, causes the term value to depend on l and smaller the value of l , larger is the eccentricity. Thus, the penetration increases with the decrease of l value and hence the electron experiences more nuclear charge during its penetration. Therefore, the electron moves part of time in a field of greater effective charge. Also, close proximity of the electron distorts the core leading to electrostatic polarization.

Both these effects increase the force of attraction and hence lower the total energy.

Difference in energy is attributed to the various amounts of penetration into the core. Orbits that penetrate the core are called penetrating orbits and those does not are non-penetrating orbits.

Note: While describing through quantum mechanics, these effects are taken as first and second order perturbations, respectively.

Following Rydberg relation, lines of the sodium can be represented by a general formula:

$$\nu = \frac{R}{(m_1 + \mu_1)^2} - \frac{R}{(m_2 + \mu_2)^2}$$

m_1 is a fixed number, m_2 is a running number and μ_1 & μ_2 are known as Rydberg constants. On comparison with Balmer formula and the quantum number, n of the valence electron in sodium or of the alkali atom, one finds that n is greater than the Rydberg denominator. That is

$$n > m_1 + \mu_1$$

$$\text{Or } n - (m_1 + \mu_1) = \delta_1$$

$$n - \delta_1 = (m_1 + \mu_1)$$

Similarly,

$$n' - \delta_2 = (m_2 + \mu_2)$$

Substitution for $(m_1 + \mu_1)$ & $(m_2 + \mu_2)$ in the above equation gives,

$$\nu = \frac{R}{(n - \delta_1)^2} - \frac{R}{(n' - \delta_2)^2}$$

The equation has principal quantum number, n, δ'_s that measure the extent of penetration. It is inferred that larger the δ , greater is the penetration.

Considering the first member of the principal series ($3s \rightarrow 3p$) of sodium The experimentally observed first member is expressed analytically by the following transition:

$$\nu = \frac{R}{(1.637)^2} - \frac{R}{(2.117)^2} = \frac{R}{(1+0.637)^2} - \frac{R}{(2+0.117)^2}$$

The principal quantum number of the sodium valence electron is 3, the above equation could equally be written as:

$$\nu = \frac{R}{(3 - 1.373)^2} - \frac{R}{(3 - 0.883)^2} \text{-----}[8]$$

Thus, $1.373(=\delta_1)$ and $0.883(=\delta_2)$ are the quantum defects in $3s$ and $3p$ levels respectively. This means that the s-orbit is penetrating more than the p-orbit.

Similarly,

Sharp series:
$$\nu = \frac{R}{(3 - 0.883)^2} - \frac{R}{(4 - 1.357)^2},$$

Diffuse series:
$$\nu = \frac{R}{(3 - 0.883)^2} - \frac{R}{(3 - 0.010)^2},$$

Fundamental series:
$$\nu = \frac{R}{(3 - 0.010)^2} - \frac{R}{(4 - 0.001)^2}.$$

Conclusions:

1. For a given value of n , s-levels lie deepest followed by p, d and f levels. And Quantum defect, for a given value of n , is a function of l .

2. For a given value of n , eccentricity of the elliptical orbit decreases with the increase of the value of l . That is, as l approaches n , the orbit is tending to be circular.

Spectral lines may be rewritten in a general form like

$$\nu = R \left(\frac{1}{n^{*2}} - \frac{1}{n'^{*2}} \right)$$

where, $n^* = n - \delta_1$ and $n'^* = n' - \delta_2$. n^* are termed as effective quantum number.

It is observed that the quantum defect is constant within one term series, but is slightly larger for lowest term values. Relation between n^* and n , to a first approximation, may thus be written as

$$n^* = n - \alpha(l)$$

And, to take care of slightly higher value of quantum defect in lowest term values,

$$n^* = n - \alpha(l) - \beta(l)/n^2$$

Or $n^* = n - \alpha(l) + \beta'(l)T$ ($T = -R/n^2$ and use $\beta' = \beta/R$)

This relation is known as Rydberg-Ritz formula. α and β are normally positive and are constant within a series of term values. $\beta \ll \alpha$ and is therefore negligible.

3. Screening Constant

Lowering of term series is explained using the concept of quantum defect that itself measures the extent of penetration of the valence electron.

Valence electron, on penetration faces charge more than unity as it should while the electron moves well outside the atomic core (non-penetrating orbit). This has got the attention of using effective quantum number $n^* (< n)$. OR The empirical adaptation of the Balmer formula for the non-hydrogen like spectra can be made by using the effective nuclear charge, Z^* , in the numerator of the relation. Thus,

$$T_n = \frac{(Z - \sigma)^2}{n^2} R = \frac{Z^{*2}}{n^2} R \text{ ----- [12]}$$

Here σ is known as Screening Constant that measures the extent to which intervening electrons screen the nuclear charge. σ remains almost constant within an iso-electronic series. This helps to find screening constant and n as well by plotting $\sqrt{(T/R)}$ against Z that are known as Mosley's Graphs.

Note:

Penetration/ non-penetration of the spherically symmetric core can be visualized through quantum mechanics by plotting wave function, $\psi(r, \theta, \phi)$ against the distance from the nucleus. The most probable location of the electron can be found from the plot of the square of the Radial part (R_{nl}) of the wave function against distance as the Bohr's theory tells

exactly the orbit and the location of the electron, considering the Heisenberg Uncertainty principle.

Maximum (most probable location) in the curve moves to larger distance from the nucleus with the increase in value of n . However, Angular part ($Y_{l,m}(\theta, \phi)$) of the wave function provides the shape and the orientation of the orbital.

4. Doublet Structure of Sodium Series Lines (Spin-Orbit interaction)

The splitting of the levels and hence splitting of the lines is due to spin-orbit interaction on the valence electron of alkali atom.

All the energy levels of the valence electron of alkali atoms except $l=0$ are splitted into two. One level corresponding to a total angular momentum $J=l+ \frac{1}{2}$ and the other $J=l- \frac{1}{2}$ with the second lying lower than the first.

The Shift or the interaction energy ΔT (in cm^{-1}) is given by

$$\Delta T = -\frac{R\alpha^2 Z^4}{n^3} \frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+\frac{1}{2})(l+1)}$$

$$= -a \frac{j^*2 - l^*2 - s^*2}{2} = -\Gamma \text{ (say)}$$

where, $a = \frac{R\alpha^2 Z^4}{n^3 l(l+\frac{1}{2})(l+1)}$; $j^*2 = j(j+1)$, $l^*2 = l(l+1)$ & $s^*2 = s(s+1)$

When measured from the series limit, the term value of any fine structure component is given by $T = T_0 - \Gamma$, where T_0 is a hypothetical term for the center of gravity of the doublet and Γ gives the shift (in units of a) of the component from T_0 . Separation between the doublet components is given by the difference between their Γ values.

1. For an s-electron, $l=0$; thereby $j=s$ leading to $\Delta T=0$. Therefore, all levels in s-series are single.

2. Z is in the numerator of the equation and hence ΔT increases with the increase of atomic number.

$$\Delta T_{Li} < \Delta T_{Na} < \Delta T_{K} < \Delta T_{Rb} < \Delta T_{Cs}.$$

3. ΔT decreases with increasing n ,

4. ΔT decreases with increasing l ,

These are in agreement with the experimental findings.

5. Spin-Orbit interaction energy for non-penetrating orbits

The difference in the term values is attributed to polarization energy of the atomic core for the non-penetrating orbits. This deviation is understood by using the concept of quantum defect. The term values

$$T_n = \frac{RZ^2}{(n-\delta)^2} = \frac{RZ^2}{n_{eff}^2} \text{ cm}^{-1}$$

where Z is the effective charge and $=1$ for neutral one electron atomic system and $=2$ for singly ionized atoms and so forth.

Rewrite the above equation in terms of screening constant as

$$T_n = \frac{(Z-\sigma)^2}{n^2} R = \frac{Z^*2}{n^2} R \text{ cm}^{-1}$$

Applying the same reasoning, spin-orbit interaction energy (shift) for the non-penetrating orbit is

$$\Delta T = -\frac{R\alpha^2(Z-\sigma)^4}{n^3} \frac{j(j+1)-l(l+1)-s(s+1)}{2l(l+\frac{1}{2})(l+1)} \text{ cm}^{-1}$$

giving the separation between the doublet components as

$$\Delta\nu_{(l+\frac{1}{2}-l-\frac{1}{2})} = \frac{R\alpha^2(Z-\sigma)^4}{n^3 l(l+1)} \text{ cm}^{-1}$$

Example: Assuming that two 1s electrons screen (*i.e.* $\sigma=2$) the nuclear charge of Li (Atomic number 3),

$\Delta\nu = 5.84 \frac{(3-2)^4}{2^3 \cdot 1(1+1)} = 5.84/16 = 0.365 \text{ cm}^{-1}$ for the $2p$ - level against the experimental value of 0.338 cm^{-1} .

The relation was applied to number of Li- like atoms *e.g.* $Be^+, B^{++}, C^{+++}, N^{++++}$ and so on.

Calculated values were found to be smaller than the experimental values suggesting that the screening by two 1s electrons is less than the assumed value of 2.

This is understandable because with the increase of atomic number, l - orbit gets closer to the nucleus and this decreases the screening of the electrons and hence σ smaller than 2.

6. Spin–Orbit interaction energy for penetrating orbits

An electron in the penetrating orbit spends part of its orbital time period inside the core. It means that the orbit may be considered to be consisting of two segments, one well outside the core and the second is within the core.

Interaction energy is calculated, first considering that the electron is completely outside the core where it experiences effective nuclear charge Z_o ; then separately as if the orbit is completely inside the core and faces altogether different nuclear charge, say Z_i .

Both these interaction energies are combined taking time weighted contribution. As the time spent within the core is just a fraction of the time (say t) required to traverse the whole path of the orbit, one makes an assumption that time required to traverse segment outside the core, to a first approximation, is equal to t .

When the electron is well outside the core, from the above relation

$$\Delta\nu_o = \frac{R\alpha^2 z_o^4}{n_o^3 l(l+1)} \text{ cm}^{-1}$$

and when the electron is taken to be within the core, the relation is

$$\Delta\nu_i = \frac{R\alpha^2 z_i^4}{n_i^3 l(l+1)} \text{ cm}^{-1}$$

n_o & n_i are the respective quantum numbers.

Time period of the electron's motion is

$$t = \frac{n^3 h^3}{4\pi^2 m e^4 z^2}$$

Time required traversing when the orbit is outside

$$t_o = \frac{n_o^3 h^3}{4\pi^2 m e^4 z_o^2}$$

and when the orbit is within the core,

$$t_i = \frac{n_i^3 h^3}{4\pi^2 m e^4 z_i^2}$$

Resultant value of $\Delta\nu$, taking time weighted contribution, is $=\frac{t_o}{t}\Delta\nu_o+\frac{t_i}{t}\Delta\nu_i$, one obtains by approximation $t_o=t$

$$\Delta\nu=\frac{R\alpha^2 z_o^2}{n_o^3 l(l+1)}(z_o^2+z_i^2)cm^{-1}$$

When the valence electron penetrates deep into the core $z_i e \gg z_o e$, particularly for the heavy elements. The equation can, therefore, be approximated further to:

$$\Delta\nu=\frac{R\alpha^2 z_o^2 z_i^2}{n_o^3 l(l+1)}cm^{-1}$$

Inserting screening constants for each of the z's in the above equation, one arrives at

$$\Delta\nu=\frac{R\alpha^2(z-\sigma_o)^2(z-\sigma_i)^2}{n_o^3 l(l+1)}cm^{-1}$$

As Frequency, $f=(\text{linear velocity, } v)/2\pi r$. Using the relation for $v(=2\pi^2 e^2 z/nh)$ and $r(=n^2 h^2/4\pi^2 m e^4 z)$, one gets $f=4\pi^2 m e^4 z^2/n^2 h^2$ and using $t=1/f$, one obtains the relation.

The other alkali atoms are $Li(1s^2, 3s), K(3p^6, 4s), Rb(4p^6, 5s)$ & $Cs(5p^6, 6s)$.



7. Spectral Lines in Emission Spectra (Intensity rules)

Intensity of a spectral line is defined as a measure of the number of photons of exactly the identical energy arriving per second at a point that corresponds to the energy of the photons in the electromagnetic spectrum.

For a change $\Delta l \neq 0$ in the transition from one term to another in LS coupling the strongest lines are those for which Δj has the same sign as Δl . Of these, the intensities of the lines increase as the magnitude of j increases.

For a change $\Delta l = 0$, the weakest lines are those for which Δj and Δl have opposite sign. The lines with $\Delta j = 0$ are intermediate in intensity.

Let us apply these rules to fine structure transitions of First member of diffuse series. The transition is from ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$, $\Delta j = 0$ and $\Delta l = +1$ while for ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$ transition $\Delta j = 1$ and $\Delta l = +1$, that is, Δj and Δl have the same sign.

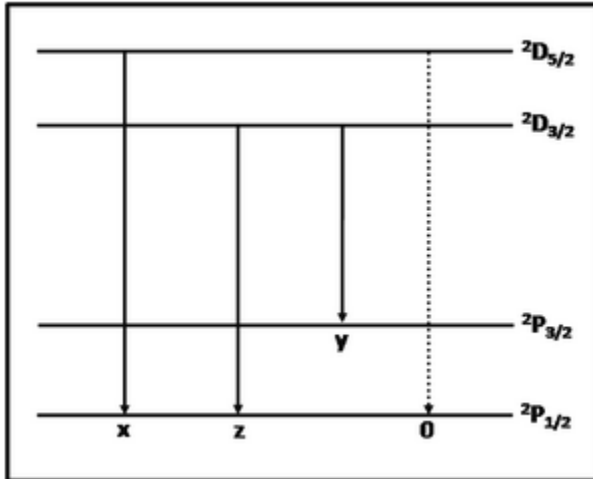
From this it is clear that the transition ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$ is stronger than ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$ as the former involve a larger value of j . The transition ${}^2D_{3/2} \rightarrow {}^2P_{3/2}$ is weakest as $\Delta j = 0$ though $\Delta l = 1$.

Quantitative rules for relative intensity from an initial level or to a final level of a multiplet is proportional to the statistical weight, $2j + 1$, of that level. The constant of proportionality is common to all levels of a given multiplet.

Conclusively: the transitions are ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$, ${}^2D_{3/2} \rightarrow {}^2P_{3/2}$, ${}^2D_{5/2} \rightarrow {}^2P_{1/2}$ (forbidden transition; zero intensity) and ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$

Wherein ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$, and ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$, $\Delta j = \Delta l = +1$, i.e. changes in j & l are in same way; therefore intense lines arising from these transitions. Out of these two, ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$ is more intense because it involves larger j . On the other hand, third allowed transition yields a weak line because changes in j & l are not in a similar manner.

All these transitions are shown in the figure:



Let the transitions ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$, ${}^2D_{3/2} \rightarrow {}^2P_{3/2}$, ${}^2D_{5/2} \rightarrow {}^2P_{1/2}$, and ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$ have intensities $x, y, 0$ and z respectively.

Applying sum rules,

$$x+y \propto 4; 0+z \propto 2 \text{ giving } x+y=2z$$

$$\text{Also, } x+0 \propto 6; y+z \propto 4 \text{ giving } 3y+3z=2x \text{ or } -2x+3y=-3z.$$

Solving for x, y & z , intensity ratio turns out to be as $x:y:z=9:1:5$.

$$x:y:z=9:1:5.$$

Remarks: The intensity rules may fail to explain the experimental results, particularly for the higher members of the series of the alkali spectra. The deviations have been understood to be due to the perturbations of the higher levels.

A Gate