

Lecture 10 : Title : ALKALI SPECTRA

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In the previous lecture we have learnt the quantum mechanical treatment of hydrogen atom.

The similar picture is not able to explain the alkali atoms, the other elements in the first group of periodic table.

Here, we will discuss the development of the theory to explain the alkali spectra.

We will also elaborate the concept behind the modification of the potential required to explain the observation in alkali atoms.

The absorption spectra of alkali vapors (Such as lithium, sodium) appear quite similar in many respects to the absorption spectrum of H atom. They are only displaced to a considerable extent, toward longer wavelengths. These spectra also consist of a series of lines with regularly decreasing separation and decreasing intensity.

⇒ It cannot, however, be represented by a formula completely analogous to the Bohr formula. On the other hand, since the lines converge to a limit, we must be able to represent them as differences between two terms.

Rydberg formula,

$$\nu = T_{PS} - \frac{R}{(m+p)^2} \quad \text{where } m = 2, 3$$

p is a constant, known as Quantum Defect. T_{PS} is known as series limit. This series is known as Principal series.

⇒ Other series, in addition to this, may be observed for the alkalis. They are diffuse, sharp and Bergmann series.

Sharp Series $\nu = T_{SS} - \frac{R}{(m+s)^2} \quad m = 2, 3$

Diffuse Series $\nu = T_{SS} - \frac{R}{(m+d)^2} \quad m = 3, 4$

Bergmann Series $\nu = T_{BS} - \frac{R}{(m+f)^2} \quad m = 4, 5$

Selection rules: $\Delta n = 0, 1, 2, 3$
 $\Delta \ell = \pm 1$

As an example, sodium energy levels and transitions are given in figure-10.1

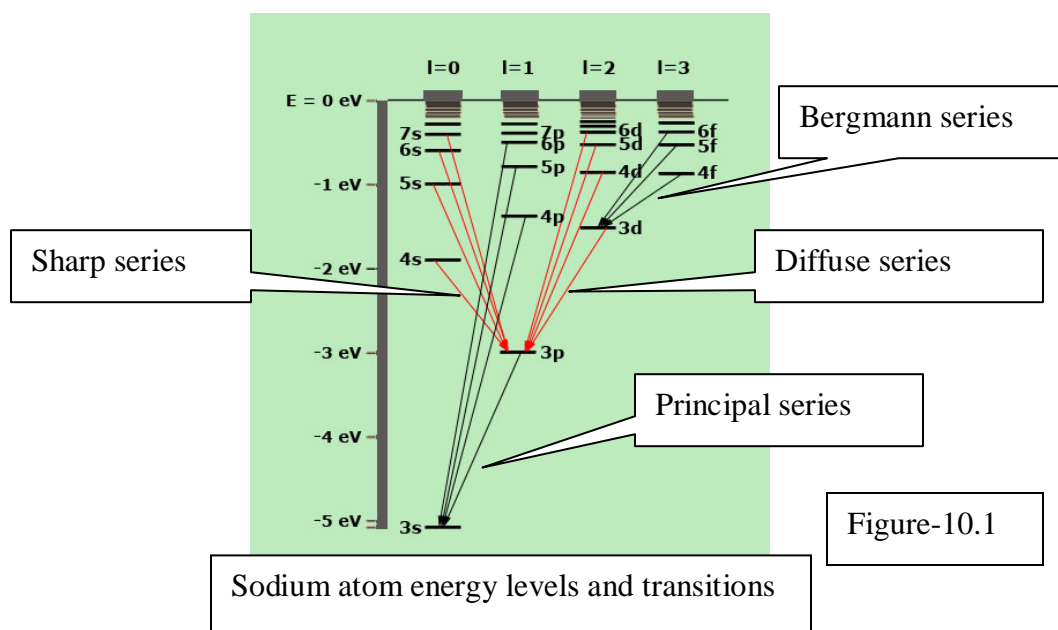


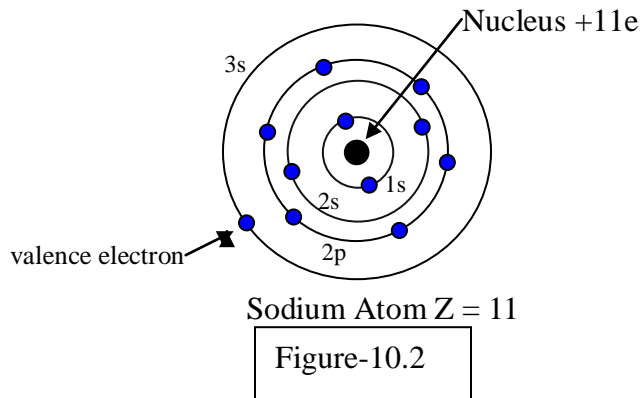
Figure-10.1

As a specific example, we consider the alkali metals such as lithium, sodium and potassium, which come from group I of the periodic table. They have one valence electron outside filled inner shells. They are therefore approximately one-electron systems, and can be understood by introducing a phenomenological number called the quantum defect to describe the energies.

Let us consider the sodium atom. The optical spectra are determined by excitations of the outermost 3s electron. The energy of each $(n; l)$ term of the valence electron is given by:

$$E_{n,l} = -\frac{R}{(n - \delta(l))^2} \quad \dots\dots\dots 10.1$$

Where $n \geq 3$, $\delta(l)$ is the quantum defect.



The quantum defect $\delta(l)$ was introduced empirically to account for the optical spectra. In principle it should depend on both n and l , but it was found experimentally to depend mainly on l as given in the following table.

Values of quantum defect for sodium				
l	$n = 3$	$n = 4$	$n = 5$	$n = 6$
0	1.373	1.357	1.352	1.349
1	0.883	0.867	0.862	0.859
2	0.010	0.011	0.013	0.011
3		0.000	-0.001	-0.008

The dependence of the quantum defect on l can be understood with reference to the figure where the radial probability densities for the 3s and 3p orbitals of a hydrogenic atom with $Z = 1$ are plotted with respect to normalized radial distance.

An individual electron in sodium atom experiences an electrostatic potential due to the Coulomb repulsion from all the other electrons in the atom. Ten out of eleven electrons are in closed sub-shells, which have spherically-symmetric charge clouds. The off-radial forces from electrons in these closed shells cancel because of the spherical symmetry.

Hydrogen radial probability distribution (figure-10.3) is expected to be a reasonable approximation for the single valence electron of sodium.

⇒ We see that both the 3s and 3p orbitals penetrate the inner shells, and that this penetration is much greater for the 3s electron.

⇒ The electron will therefore see a larger effective nuclear charge for part of its orbit, and this will have the effect of reducing the energies.

⇒ The energy reduction is largest for the 3s electron due to its larger core penetration.

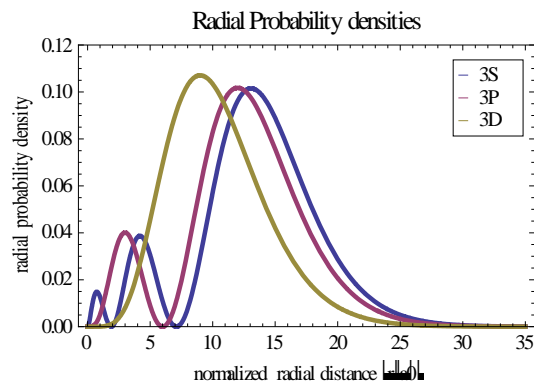
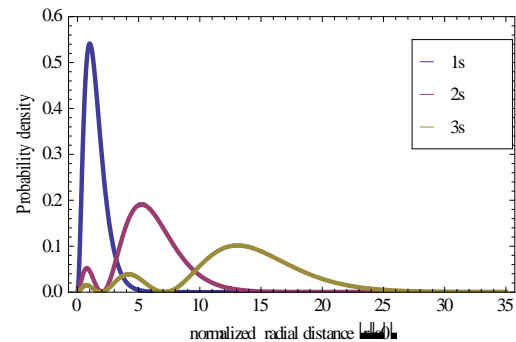
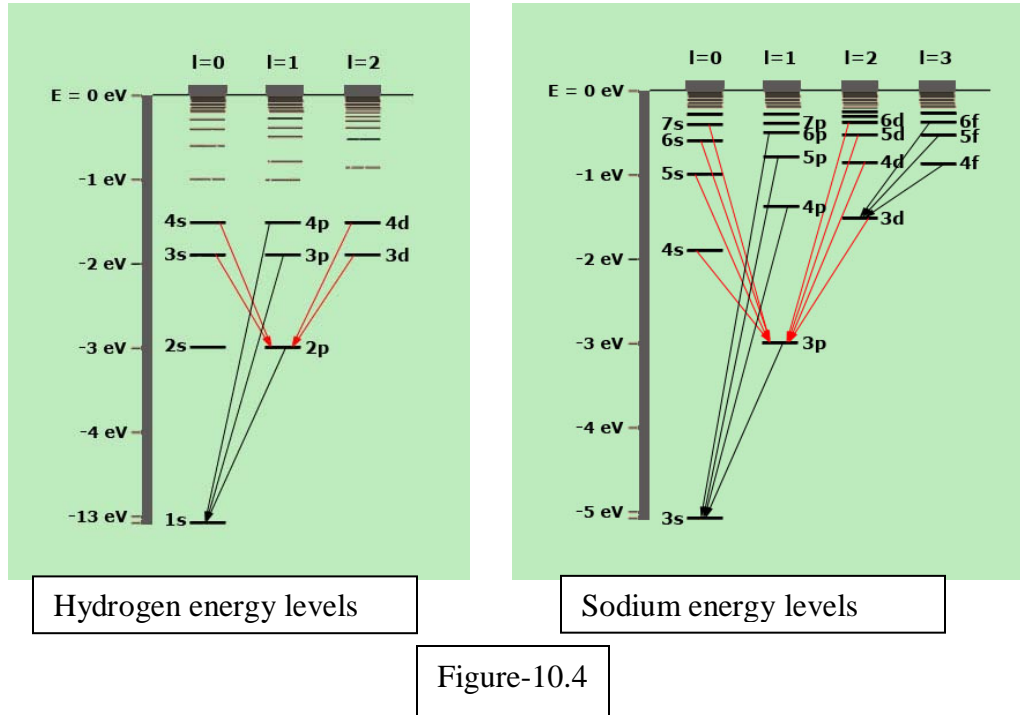


Figure-10.3

The effect of this penetration results in the shift of energy levels. A comparison with the hydrogen energy level is shown in figure-10.4.



We can draw the conclusions that,

⇒ Energy levels with different ℓ have different energies. In other words ℓ degeneracy removed.

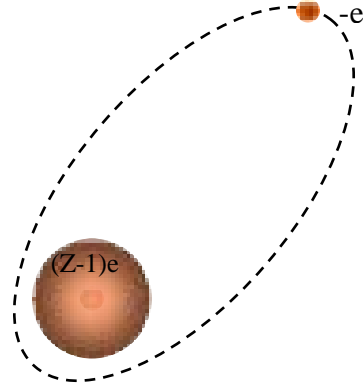
⇒ From the hydrogen atom energy levels, it cannot be described, because energy depends on “ n ” only.

Classical Explanation

Penetrating and Non-Penetrating Orbits as shown in figure-10.5:

1) Non-Penetrating orbits

The first is the case when the outer electron has a non penetrating orbit, as in the figure. If its accepted that the mean symmetry of the cloud formed by $(Z-1)$ electrons is similar, the electron experiences the electrostatic potential of the nuclear charge of Ze and of the spherical distribution of charge $(Z-1)$. The discussion presented for the hydrogen atom remains valid.



2) Penetrating orbit

On the other hand, if the orbit of the outer electron penetrates inside the core of the atom, the problem is much more complex, simple solution by Somerfield, is this,

$$V_{ext} = \frac{1}{4\pi\epsilon_0} \frac{e}{r} \quad "r" \text{ Large}$$

$$V_{in} = \frac{1}{4\pi\epsilon_0} \frac{Ze}{r} + Const. \quad "r" \text{ Small}$$

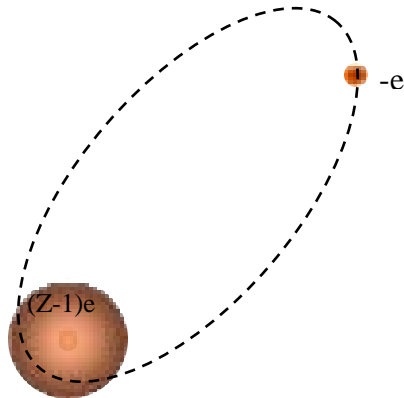


Figure-10.5

Quantum Mechanical Calculation

Form of the potential energy, $V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \left(1 + \frac{b}{r}\right)$ 10.2

This form represents the potential energy requirement at large distance,

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

and at small distance, $V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$

This potential with respect to radial distance is shown in figure-10.6

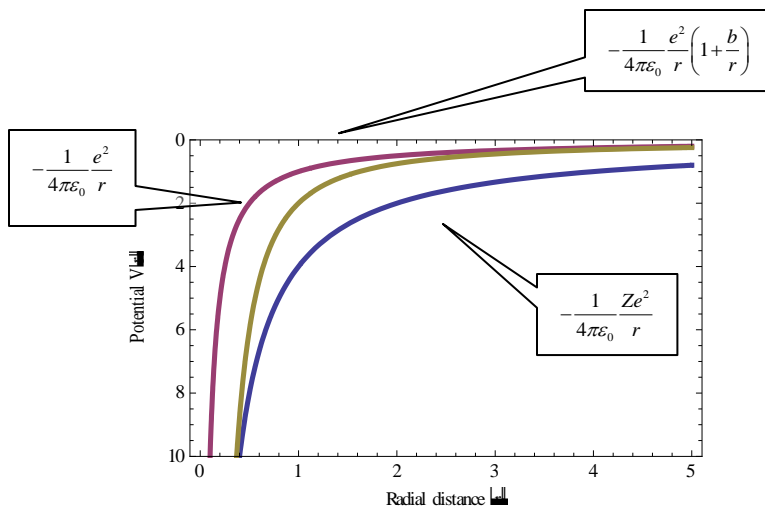


Figure-10.6

Since this is radial dependence and we need to solve only radial equation of the Schrödinger equation of hydrogen atom problem

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \left(1 + \frac{b}{r}\right)$$

$$= \frac{c}{r} \left(1 + \frac{b}{r}\right) \quad \text{where, } c = -\frac{1}{4\pi\epsilon_0} e^2$$

Now, the Hamiltonian for one electron atom,

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r)$$

$$= -\frac{\hbar^2}{2\mu} \nabla^2 + \frac{c}{r} \left(1 + \frac{b}{r}\right)$$

$$\Rightarrow -\frac{\hbar^2}{2\mu} \nabla^2 \psi + \frac{c}{r} \left(1 + \frac{b}{r}\right) \psi = E \psi$$

$$\Rightarrow \nabla^2 \psi + \frac{2\mu}{\hbar^2} \left[E - \frac{c}{r} \left(1 + \frac{b}{r}\right) \right] \psi = 0$$

.....10.3

The radial equation:

$$\frac{d^2 \chi}{dr^2} + \left[\frac{2\mu}{\hbar^2} E - \frac{2\mu c}{\hbar^2} \frac{1}{r} \left(1 + \frac{b}{r}\right) - \frac{\ell(\ell+1)}{r^2} \right] R(r) = 0$$

$$\Rightarrow \frac{d^2 \chi}{dr^2} - \left[-\frac{2\mu}{\hbar^2} E + \frac{2\mu c}{\hbar^2} \frac{1}{r} + \frac{2\mu c b}{\hbar^2} \frac{1}{r^2} + \frac{\ell(\ell+1)}{r^2} \right] R(r) = 0$$

.....10.4

Taking $A = -\frac{2\mu E}{\hbar^2}$; $B = -\frac{2\mu c}{\hbar^2}$ and substituting in equation 10.4

$$\frac{d^2 \chi}{dr^2} - \left[A - \frac{B}{r} + \frac{-Bb + \ell(\ell+1)}{r^2} \right] \chi = 0$$

$$\text{Let, } \ell^* (\ell^* + 1) = -Bb + \ell(\ell+1)$$

$$\text{So, } \frac{d^2 \chi}{dr^2} - \left[A - \frac{B}{r} + \frac{\ell^* (\ell^* + 1)}{r^2} \right] \chi = 0$$

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Same radial equation as in hydrogen atom, solution with n^* where $n^* = \ell^* + p + 1$

$$E = -\frac{R}{(n^*)^2} = -\frac{R}{(\ell^* + p + 1)^2}$$

$$n = \ell + p + 1$$

$$\text{So, } n^* = \ell^* + p + 1 = \ell^* - \ell + n$$

$$\Rightarrow n^* = n - (\ell - \ell^*) = n - \Delta\ell$$

Now,

$$\ell^*(\ell^* + 1) = \ell(\ell + 1) - Bb$$

$$\Rightarrow (\ell^2 - (\ell^*)^2) + (\ell - \ell^*) = Bb$$

$$\Rightarrow (\ell - \ell^*)(\ell + \ell^* + 1) = Bb$$

$$\begin{aligned}\Rightarrow \Delta\ell &= \frac{Bb}{\ell + \ell^* + 1} = \frac{Bb}{2\ell + 1} \\ &= \frac{\frac{B}{2}b}{\ell + \frac{1}{2}} = \frac{b}{a_1} \frac{1}{\ell + \frac{1}{2}}\end{aligned}$$

$$E_{n,\ell} = -\frac{Rhc}{\left(n - \frac{b}{a_1} \frac{1}{\ell + \frac{1}{2}}\right)^2}$$

Note that :

This energy expression is dependent on both n and l

Maximum l -> small correction

Small l -> correction term is large

$$E_{n,\ell} = -\frac{Rhc}{\left\{n - \frac{Bb}{2\ell+1}\right\}^2}$$

Now we know

$$E = h\nu$$

$$\nu = \frac{c}{\lambda} \quad \bar{\nu} = \frac{1}{\lambda}$$

$$E = \frac{hc}{\lambda} \Rightarrow \frac{1}{\lambda} (cm^{-1}) = \frac{E}{hc}$$

$$E_{n,\ell} = -\frac{R}{\left\{n - \frac{Bb}{2\ell+1}\right\}^2} cm^{-1}$$

Where $R = 109,728.7 cm^{-1}$

Conversion

	<i>ergs / molecule</i>	<i>Cal / molecule</i>	<i>electron volts</i>
$1 cm^{-1}$	1.9858×10^{-16}	2.8575	1.23954×10^{-4}

Take an example:

Lithium : ionization potential : $43,486 cm^{-1}$ or, $5.39 eV$

$$43486 = \frac{109728.7}{(2 - Bb)^2}$$

$$\Rightarrow (2 - Bb)^2 = 2.5233$$

$$\Rightarrow 2 - Bb = 1.588$$

$$\Rightarrow Bb = 0.41$$

$$E_{2,1} = \frac{109728.7}{\left(2 - \frac{0.41}{2}\right)^2} = 31603.8 cm^{-1}$$

$$E_{3,0} = \frac{109728.7}{(3 - 0.41)^2} = 16357.6 cm^{-1}$$

$$E_{3,1} = \frac{109728.7}{\left(3 - \frac{0.41}{3}\right)^2} = 13383.7 cm^{-1}$$

$$E_{4,0} = \frac{109728.7}{(4 - 0.41)^2} = 8513.9 \text{ cm}^{-1}$$

$$E_{4,1} = \frac{109728.7}{\left(4 - \frac{0.41}{3}\right)^2} = 7351.8 \text{ cm}^{-1}$$

$$E_{4,2} = \frac{109728.7}{\left(4 - \frac{0.41}{5}\right)^2} = 7148.1 \text{ cm}^{-1}$$

$$E_{4,3} = \frac{109728.7}{\left(4 - \frac{0.41}{7}\right)^2} = 7063.4 \text{ cm}^{-1}$$

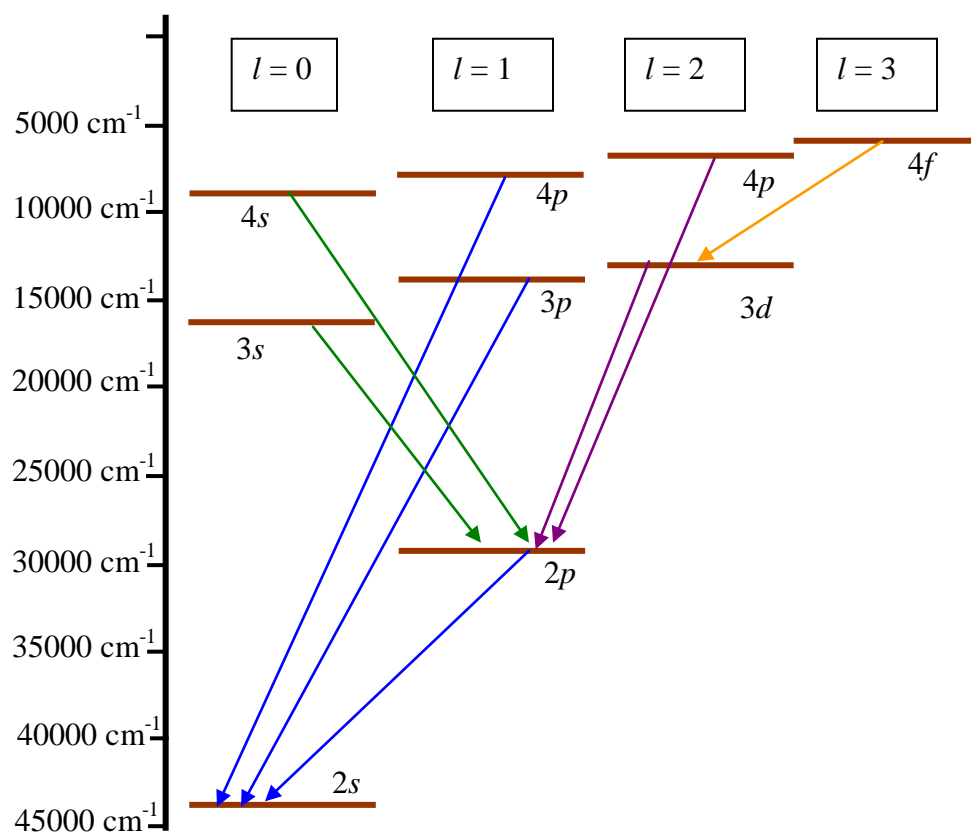


Figure-10.7

Recap

In this lecture, we have learnt that

⇒ The departure in the spectra of alkali atom from hydrogen such as lithium, sodium is that the energies are not only dependent on n but also l .

⇒ The modification of the potential of electron in such multielectronic atoms is that the energy correction term is large of small l values.