Notes For Bachelor of Science (TU)

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Sommerfeld Atom model

To overcome the Bohr's limitation, Sommerfeld introduced two main modifications in Bohr's theory

① According to Sommerfeld, the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of the foci. The circular orbits of Bohr's are a special case of this.

② The velocity of the electron moving in an elliptical orbit varies considerably at different parts of the orbit. This causes relativistic variation in the mass of the moving electron. Therefore we took into account the relativistic variation of the mass of the electron with velocity. Hence this is known as the relativistic atom-model.

Derivation :- elliptic orbits of Hydrogen :-

Let us consider the electron moving in an elliptical orbit around the Nucleus (N) and its position at any instant can be fixed in polar coordinates r and ϕ as showing fig. 1.

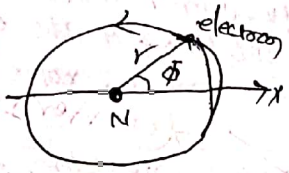


Fig. 1

In the case of circular orbits only ϕ varies periodically but in elliptical ϕ as well as r also varies periodically. We have now to quantise the momenta associated with both these co-ordinates (ϕ and r) in accordance with Bohr's quantum condition. The two quantisation conditions are

$$\int p_\phi d\phi = n_\phi h \quad \text{--- (I)}$$

$$\int p_r dr = n_r h \quad \text{--- (II)}$$

where n_r and n_ϕ is called radial quantum number and angular or azimuthal quantum number and both take only positive integral values, then $n_r + n_\phi = n$, where n is the principle quantum number and take integral values $1, 2, 3, \ldots$ etc.

To determine the allowed elliptical orbits, we have to evaluate the integrals in eq^n ① & ②

$$\int_0^{2\pi} p_\phi d\phi = n_\phi h \Rightarrow p_\phi = \frac{n_\phi h}{2\pi} \quad \text{--- (III)}$$

Now, Momentum along the radius

$$p_r = m v_r = m\frac{dr}{dt}$$

$$\therefore p_r dr = m\frac{dr}{dt}dr = m\left(\frac{dr}{d\phi}\frac{d\phi}{dt}\right)\frac{dr}{d\phi}d\phi$$

$$= m\left(\frac{dr}{d\phi}\right)^2 \frac{d\phi}{dt}d\phi$$

$$\therefore p_r dr = m\left(\frac{dr}{d\phi}\right)^2 \omega\, d\phi \quad \text{--- (IV)}$$

$\because p_\phi = mr^2\omega = mr^2\frac{d\phi}{dt}$

$\frac{1}{r^2}p_\phi = m\frac{d\phi}{dt}$

The eq^n of an ellipse in polar co-ordinate is $\frac{1}{r} = \frac{1+\varepsilon\cos\phi}{a(1-\varepsilon^2)}$, whereas a is the semimajor axis and ε is the eccentricity.

Taking log and differentiating w.r.to ϕ, we get

$$\frac{1}{r}\frac{dr}{d\phi} = \frac{\varepsilon\sin\phi}{1+\varepsilon\cos\phi}$$

Hence, $p_r dr = \left(\frac{\varepsilon\sin\phi}{1+\varepsilon\cos\phi}\right)^2 p_\phi d\phi$

$$\therefore \int_0^{2\pi} p_r dr = \int_0^{2\pi}\left(\frac{\varepsilon\sin\phi}{(1+\varepsilon\cos\phi)}\right)^2 p_\phi\, d\phi = n_r h$$

integrating by parts and substituting limit, we get

$$\frac{2\pi p_\phi}{(1-\varepsilon^2)^{1/2}} - 2\pi p_\phi = n_r h$$

$$\frac{n_\phi h}{(1-\varepsilon^2)^{1/2}} - n_\phi h = n_r h \quad \left(\because p_\phi = \frac{n_\phi h}{2\pi}\right)$$

$$n_r = \frac{n_\phi}{(1-\varepsilon^2)^{1/2}} - n_\phi \quad \text{or} \quad n_r + n_\phi = \frac{n_\phi}{(1-\varepsilon^2)^{1/2}}$$

comparing with $n_r + n_\phi = n$ then we get

$$n = \frac{n_\phi}{(1-\varepsilon^2)^{1/2}} \Rightarrow 1-\varepsilon^2 = \frac{n_\phi^2}{n^2} \quad \text{--- (V)}$$

For an ellipse $1-\varepsilon^2 = b^2/a^2$, where a and b are semi-major and semi-minor axis respectively.

Hence, $\frac{b^2}{a^2} = \frac{n_\phi^2}{n^2}$ or $\frac{b}{a} = \frac{n_\phi}{n}$ --- (VI)

This is the condition that determines the allowed elliptical orbits. (X)

(a) First orbit $n=1$, $n_\phi = n_r = 1$, $\varepsilon = 0$, $a = b = 1$ — $\frac{b}{a}$ — orbits becomes Circular,

(b) For 2nd orbit, $n=2$, $n_r + n_\phi = 2$, $n_\phi = 1$ or 2, either $n_r = 1, 0$

Hence,
(i) $n_\phi = 2, n = 2$ ($b = a$) ⊗ or $n_\phi = 2$
(ii) $n_\phi = 1, n = 2$, ($b = a/2$)
one circular, one elliptical

(c) $n = 3$, $n_\phi = 3, 2, 1$, $b = a, \frac{a}{2}, \frac{a}{3}$
$n_r = 0, 1, 2$, 1 circular, 2 elliptical.

(X) since, n_ϕ can't be greater than n, since b is always less than a. Hence, for a given value of n, n_ϕ can assume only n different values, there can be only n elliptical orbits of different eccentricities

(9)

Total Energy :-

The total energy E_n of a single electron $E_n = P.E + K.E$. Then, the $P.E = \frac{-Ze^2}{4\pi\varepsilon_0 r}$

$$K.E = \frac{1}{2}m\left[\left(\frac{dr}{dt}\right)^2 + \left(r\frac{d\phi}{dt}\right)^2\right] = \frac{1}{2}m\left(v_r^2 + v_\phi^2\right)$$

where $\frac{dr}{dt}$ is the radial component of the velocity and $r\left(\frac{d\phi}{dt}\right)$ is the transverse component of the velocity. Hence,

$$E_n = \frac{-Ze^2}{4\pi\varepsilon_0 r} + \frac{1}{2}m\left[\left(\frac{dr}{dt}\right)^2 + \left(r\frac{d\phi}{dt}\right)^2\right]$$

After derivation, E_n can be obtained that

$$E_n = -\left(\frac{me^4Z^2}{8\varepsilon_0^2h^2}\right)\frac{1}{n^2}$$ which is same as the Bohr's, which means no new energy levels introduces by elliptical orbits. so that fine structure (multiplicity) of orbits would not explin on this basis.

Sommerfeld's relativistic Correction in Energy

Sommerfied proceeded to find the solution to the problem of fine structure of spectral lines, on the basis of the variation of the mass of the electron with velocity. The velocity of the electron in a circular orbit is constant But the velocity of the electron in an elliptical orbit varies, being a maximum at the perihelion (ϕ); and a minimum at the aphelion. Therefore sommerfield modified his theory, taking account variation of the mass of the electron with velocity. According to this theory, the mass of a particle moving with velocity v is related to its rest mass by $m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$ — (1)

Sommerfield showed the relativistic eq^n describing the path of an electron is $\frac{1}{r} = \frac{1 + \varepsilon\cos\psi\phi}{a(1-\varepsilon^2)}$ — (2)

where $\psi^2 = 1 - \frac{Z^2e^4}{16\pi^2\varepsilon_0^2 p^2 c^2}$. Here $p = p_\phi$ = constant, for the non-relativistic case ($c \to \infty$), $\psi = 1$ and r returns to the same value when ϕ changes by 2π. So that it has the same periodicity as ϕ. However, when $\psi < 1$ as in the relativistic case, r does not return to the same value when ϕ changes by 2π and it has now, a different periodicity from ϕ. In fact, in this case, the value of r becomes the same only when ϕ changes by $\frac{2\pi}{\psi} > 2\pi$.

Taking the effect of relativistic precession into account Sommerfeld calculated the total energy of the electron to be

$$E_n = \frac{mZ^2e^4}{8\varepsilon_0^2n^2h^2}\left[1 + \frac{Z^2\alpha^2}{n^2}\left(\frac{n}{n_\phi} - \frac{3}{4}\right)\right]$$ — (3)

where $\alpha = \frac{e^2}{2\varepsilon_0 ch} = \frac{1}{137}$ is a dimensionless quantity and is called the fine-structure constant.

The first term in eq^n (3) is the energy of the electron in the orbit with the principal quantum number n. The second term is the Sommerfield relativity correction, shows that the energy does not depend on the azimuthal quantum number n_ϕ. This results in a splitting of the energy levels of the atom for a given value of n.

(chapter 12 page 27)

Fine Sturcture splitting of the H_α line

H_α line of the Balmer series is due to the transition from $n = 3$ to $n = 2$, state of the hydrogen atom. According to sommerfield's relativistic theory, the upper level $n = 3$ splits into three sub-levels with $n_\phi = 1, 2, 3$, while the lower level with $n = 2$ splits 2 sub levels with $n_\phi = 1$ and 2 as shown in the fig. 1.

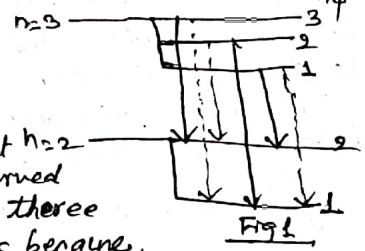


Fig 1

Theoritically, six transitions are possible as shown but actually, the observed H_α line has only three components. It is because, some of the transitions are forbidden, only those transitions can occur for which n_ϕ can change only by 1 unit. ie $\Delta n_\phi = \pm 1$. this is known as selection rule. which are shown by the full lines and the forbidden transitions are shown by broken lines. i.e. $+2, +1, 0$.

Drawbacks / Limitations :- ① could not explain the complex spectra of alkali metals like sodium ② could not explain Zeeman, stark effect. ③

(9)

Sommerfeld Atom model

To overcome the Bohr's limitation.

Now, Momentum along the radius

(2) The Vector Atom Model :- The atom model based on these quantised vectors is called the vector atom model. XXX (P.T.O)

In order to explain the complex spectra of atoms and their relation to atomic structure, the vector atom model was introduced. two distict features of the vector atom model are:

(i) the conception of spatial quantisation.

(ii) the spinning electron hypothesis (electron spin)

(I) :- Spatial quantisation :-

According to Bohr's theory, the orbits are quantised as regards their magnitude (i.e their size and form) only. But according to quantum theory, the direction or orientation of the orbits in space also should be quantised. The idea of space quantisation leads to an explanation of zeeman effect. An excellent proof of the space quantisation of atoms is provided by Stern-Garlach experiments

(II) Spinning electron :- To account for the observed fine structure of spectral lines and to explain the anomalous zeeman effect, the concept of spinning electron was introduced by Uhlenbeck and Goudsmit in 1926. According to their hypothesis, the electron spins about an axis of its own, while it also moves round the nucleus of the atom in its orbit. According to the quantum theory, the spin of the electron also should be quantised. Hence, a new quantum number called the spin quantum number (S) is introduced. The atoms have a single valance electron outside completely filled subshells is called one-electron, otherwise called many electrons systems.

(XXX continue)

Quantum Numbers Associated with the Vector Atom model →

(1) The principal quantum number (n) :- The serial number of the shells starting from the innermost is designated as its principal quantum number (n). It can take only integral values excluding zero i.e $n = 1, 2, 3, 4, \ldots$ corresponds to K, L, M, N and so on.

(2) The orbital (azimuthal) Quantum number (l) :- Orbital Quantum number is identical to the azimuthally Quantum number n_ϕ, l is related with n_ϕ as $l = n_\phi - 1$. Thus, it may take any integral value $0, 1, 2, 3 \ldots (n-1)$. This Quantum number is introduced to specify the electrons in different sub shells. The electron with $l = 0, 1, 2, 3$, are corresponds to s, p, d, f, ... electrons sub shells respectively. The orbital Quantum number determine the orbital angular momentum of an electron which is given by $P_l = \frac{h}{2\pi}\sqrt{l(l+1)}$

(3) Spin Quantum number (S) :-

To describe the spin motion of electron, a Quantum number called Spin Quantum number 'S' is defined which has only one value equal to $\frac{1}{2}$. Due to spin motion of electron, it possesses a spin angular momentum, given by $P_s = \frac{h}{2\pi}\sqrt{s(s+1)}$

(4) Total angular momentum Quantum number (J)

The resultant of the orbital and spin angular momentum represent the total angular momentum Quantum number. Hence, it is equal to the numerical value of the vector sum of $\vec{l}$ and $\vec{s}$, i.e $\vec{J} = \vec{l} \pm \vec{s} \Rightarrow l \pm \frac{1}{2}$ with restriction that J is positive.

where the +ve sign for $\vec{l}$ & $\vec{s}$ are parallel each other

-ve sign for $\vec{l}$ & $\vec{s}$ are antiparallel each other.

"cease to learn"

sommerfeld ...
modifications in Bohr's theory
① According to sommerfeld, the path of an electron around the nucleus, in general, is an ellipse

The total angular momentum of electron is given by $P_j = \sqrt{j(j+1)}\,\hbar$.

④ ⑤ Magnetic orbital Quantum number (m_ℓ)
The projection of the orbital Quantum number ℓ on the magnetic field direction is called the magnetic orbital Quantum number m_ℓ. The possible value of m_ℓ are $(2\ell+1)$ from $-\ell$ to $+\ell$ including zero. The permitted orientations of the ℓ vector relative to the direction of B is $(2\ell+1)$ ranging from ℓ, $(\ell-1)$, $(\ell-2)$, $(\ell-3)$ ---- 1, 0, -1, -2, ---- $-(\ell-2)$, $-(\ell-1)$, $-\ell$.

⑥ Magnetic spin quantum number (m_s):-
The Quantum number which gives the estimation of the direction of the spin of an electron with respect to the magnetic field. It is numerically equal to the projection of the spin vector on the direction of B. m_s can take only two values i.e $m_s = \pm 1/2$ as the spin angular momentum (s) assumes only two possible positions with respect to the magnetic field. It may be parallel to it or antiparallel.

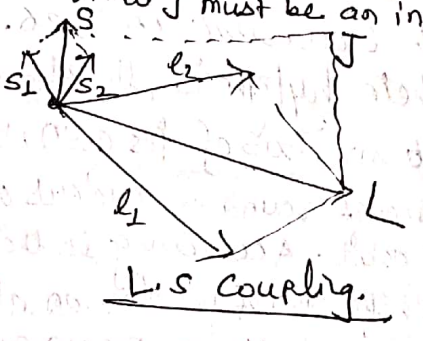
⑦ Magnetic total angular momentum Quantum number (m_j):-
it is the projection of total angular momentum vector j on the direction of the magnetic field B. Since, for a single electron, j can have only odd half integral values ($\because j = \ell \pm 1/2$). Hence, m_j must have only odd half-integral values, m_j can have only $(2j+1)$ values, from $+j$ to $-j$, zero excluded.

In conclusion, the state of an electron in an atom is completely specified by the four quantum numbers n, ℓ, m_ℓ and m_s. In Spectroscopic notation, small letters, ℓ, s, j and s, p, d, f, g etc are used to describe the state of the electrons and capital letters L, S, J and S, P, D, F, G etc. are used to describe the state of the atom as a whole.

Coupling Schemes ②

The method of Combination, in an atom having two or more electrons, depends on the interaction or coupling between the orbital and spin angular momenta.
There are two types of coupling Scheme have been developed
① the Russel-saunders coupling OR L-S coupling
② the j-j Coupling

① L-S Coupling :- All the orbital angular momentum vectors of the various electrons combine to form a resultant L and independently, all their Spin angular momentum vectors combine to form a resultant S. These resultant L and S then Combine to form the total angular momentum J of the atom. This scheme may be Summarised as follows $L = \Sigma l_i$; $S = \Sigma s_i$. $J = L+S$.
Where L is always an integer including zero, S is integer for an even number of electron and odd multiple of 1/2 for an odd number of electrons, And J must be an integer.



L-S Coupling.

If S is an integer and J must be an odd multiple of 1/2 if S is an odd multiple of 1/2.