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01

Date: 18/02/2025
Time: 01 pm

MPHY CC 10 — 12

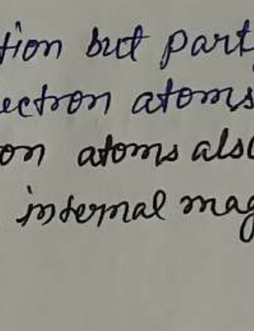
Fine structure in Hydrogen spectral lines were explained by Sommerfeld considering relativistic variation of mass of electron moving in elliptic orbit. It was perfectly explained considering spin-orbit interaction as well as relativity correction into account

Spin orbit interaction :–

Spin-orbit interaction is an interaction between electron's spin magnetic dipole moment and the internal magnetic field of the atom arises from orbital motion of the electron through the nuclear electric field. Since the internal magnetic field is associated with electron's orbital angular momentum. Hence it is termed as spin-orbit interaction. It is weak interaction but partly responsible for fine structure of the excited state of one electron atoms.

* Spin-orbit interaction occurs in multielectron atoms also but in these atoms it is reasonably strong because the internal magnetic field is quite strong.

$\vec{E}$ (electric field) in which the e^- is moving can be written as gradient of a potential function $V(r)$
r = distance b/w e^- & nucleus.



$$\vec{E} = \text{grad}\, V(r) = \frac{dV(r)}{dr}\frac{\vec{r}}{r} \quad \left[\frac{\vec{r}}{r} = \hat{r} \text{ unit vector}\right] \quad -(1)$$

magnetic field in a reference frame fixed with the electron arising from the orbital motion of the electron with velocity $\vec{v}$ in the electric field $\vec{E}$ (due to the nucleus)

$$\vec{B} = \frac{1}{c^2}(\vec{E} \times \vec{v})$$

$$\vec{B} = \frac{1}{c^2 r}\frac{dV(r)}{dr}[\vec{r} \times \vec{v}] \quad \ldots \quad (2)$$

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Orbital angular momentum of the electron $\vec{l} = m\vec{r}\times\vec{v}$ — (3)

using (3) in (2)

$$\vec{B} = \frac{1}{mc^2 r}\frac{dV(r)}{dr}\vec{l} \quad \cdots \quad (4)$$

The e^- & its spin magnetic moment μ_s can take different orientation in the internal magnetic field $\vec{B}$ of the atom. Hence magnetic potential energy for e^- is different for different orientations

magnetic potential energy for electron is

$$\Delta E_{ls} = -\vec{\mu}_s \cdot \vec{B} \quad \cdots \quad (5)$$

$$\vec{\mu}_s = -g_s\left(\frac{e}{2m}\right)\vec{S} \quad , \quad g_s = 2 \quad \cdots \quad (6)$$

using (6) in (5) we will have

$$\Delta E_{l,s} = \frac{e}{m}\vec{S}\cdot\vec{B} \quad \cdots \quad (7)$$

using (4) in (7) we will have

$$\Delta E_{l,s} = \frac{e}{m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}\cdot\vec{l} \quad \cdots \quad (8)$$

energy in expression (8) is the energy in a frame of reference in which the electron is at rest. On relativistic transformation in which the nucleous is at rest, the energy will be reduced by factor '2'. This is known as Thomas precession. Taking this into account the spin-orbit interaction energy can be written as

$$\Delta E_{l,s} = \frac{e}{2m^2c^2 r}\frac{dV(r)}{dr}\vec{S}\cdot\vec{l} \quad \cdots \quad (9).$$

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$$\vec{J} = \vec{l} + \vec{s} \quad \text{--} \quad (10)$$

Taking self product of the above eqn

$$\bar{J}\cdot\bar{J} = (\vec{l}+\vec{s})\cdot(\vec{l}+\vec{s})$$

$$\bar{J}\cdot\bar{J} = \vec{l}\cdot\vec{l} + \vec{s}\cdot\vec{s} + \vec{s}\cdot\vec{l} + \vec{l}\cdot\vec{s} \qquad \bar{l}\cdot\bar{s} = \bar{s}\cdot\vec{l}$$

$$\bar{J}\cdot\bar{J} = l^2 + s^2 + 2\bar{s}\cdot\bar{l}$$

$$\bar{s}\cdot\bar{l} = \frac{J^2 - l^2 - s^2}{2}$$

$$\bar{s}\cdot\bar{l} = \frac{1}{2}\left[J(J+1) - l(l+1) - s(s+1)\right]\frac{h^2}{4\pi^2} \quad \text{--} \quad (11)$$

using (11) in eqn (9)

$$\Delta E_{l,s} = \frac{e h^2}{16 m^2 \pi^2 c^2}\left[J(J+1) - l(l+1) - s(s+1)\right]\overline{\frac{1}{r}\frac{dV(r)}{dr}} \quad - (12)$$

For Hydrogen like atom

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze}{r}$$

$$\frac{dV(r)}{dr} = \frac{1}{4\pi\epsilon_0}\frac{Ze}{r^2} \quad \text{---} \quad (13)$$

using (13) in (12)

$$\Delta E_{l,s} = \frac{Z e^2 h^2}{4\pi\epsilon_0 (16\pi^2 m^2 c^2)}\left[J(J+1) - l(l+1) - s(s+1)\right]\overline{\frac{1}{r^3}} \quad -(14)$$

$$\overline{\frac{1}{r^3}} = \frac{Z^3}{a_0^3 n^3 l(l+\frac{1}{2})(l+1)} \qquad l > 0 \quad \text{--} \quad (15)$$

$$a_0 = 4\pi\epsilon_0 \frac{h^2}{4\pi^2 m e^2} \quad \text{---} \quad (16)$$

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using (15) & (16) in (14)

$$\Delta E_{l,s} = \frac{Ze^2h^2}{4\pi\varepsilon_0(16\pi^2 m^2c^2)\,a_0^3 n^3 l(l+\frac{1}{2})(l+1)}\left[J(J+1)-l(l+1)-s(s+1)\right] \quad \text{--- (17)}$$

$$R_\infty = \text{Rydberg's constant} = \frac{me^4}{8\varepsilon_0^2h^3c} \quad \text{--- (18)}$$
for only heavy nucleus

$$\& \ \alpha = \frac{e^2}{2\varepsilon_0 hc} = \text{fine structure constant} \quad \text{--- (19)}$$

using eqn (18) & (19) in (17) we will have

$$\Delta E_{l,s} = \frac{R_\infty \alpha^2 Z^4 hc}{2n^3 l(l+\frac{1}{2})(l+1)}\left[J(J+1)-l(l+1)-s(s+1)\right] \quad \text{--- (20)}$$

The term shift due to spin orbit interaction

$$\Delta T_{l,s} = -\frac{\Delta E_{l,s}}{hc} = \frac{-R_\infty \alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})(l+1)}\left[J(J+1)-l(l+1)-s(s+1)\right] \quad \text{--- (21)}$$

For Hydrogen like atom $s=\frac{1}{2}$, $J = l \pm s = l+\frac{1}{2}, l-\frac{1}{2}$

$$\left.\begin{aligned} J(J+1)-l(l+1)-s(s+1) &= l \quad \text{for } j = l+\tfrac{1}{2} \\ &= -(l+1) \quad \text{for } J = l-\tfrac{1}{2} \end{aligned}\right] \quad \text{--- (22)}$$

Term shift for $J=(l+\frac{1}{2})$ & $s=\frac{1}{2}$

$$\Delta T_{l,s}' = -\frac{R_\infty \alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})(l+1)} \cdot l \quad \text{--- (23)}$$

Term shift for $J=(l-\frac{1}{2})$ $s=\frac{1}{2}$

$$\Delta T_{l,s}'' = \frac{R_\infty \alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})(l+1)}(l+1) \quad \text{--- (24)}$$

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The spin orbit interaction causes each term of given 'l' to split into two terms of different 'j's one displaced upward and the other downward. (24) - (23)

$$\Delta T = \Delta T_{l,s}' - \Delta T_{l,s}$$

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})(l+1)}(2l+1)$$

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{\cancel{2} n^3 l\cancel{(l+\frac{1}{2})}(l+1)}\cancel{2}\cancel{(l+\frac{1}{2})}$$

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3 l(l+1)} \quad \text{--- (25)}$$

$R_\infty = 1.097 \times 10^7 \, m^{-1}$

$\alpha = \frac{1}{137}$ using in (25)

$$\Delta T = \frac{584 \, Z^4}{n^3 l(l+1)} \, m^{-1}$$

or $$\boxed{\Delta T = \frac{5.84 \, Z^4}{n^3 l(l+1)} \, cm^{-1}}$$

$\Delta T \propto Z^4$, $\Delta T \propto \frac{1}{n^3}$