Doublet structure of Alkali spectra:

Careful examination of the spectra of alkali metals shows that each member of some of the series are closed doublets. For example, sodium yellow line, corresponding to $3p \rightarrow 3s$ transition, is a close doublet with separation of $6\AA^0$ while potassium (K) has a doublet separation of $34\AA^0$ and so on. Further investigations show that only the S-terms are singlet, while all the other terms P, D, F etc. are doublets. Such doublet structure in energy is observed for all the atoms possessing a single valence electron i.e., in the outer most shell. Usually the doublet spacing is small compared to the term difference (for Na the main D line is cantered at $5893\AA^0$; $D_2 = 5890\AA^0$ and $D_1 = 5896\AA^0$) and hence it is called fine structure. To explain this feature Uhlenback and Goudsmith first proposed the hypothesis of electron spin, which was later on obtained as a natural consequence of Dirac’s relativistic theory.

Spin is essentially a quantum phenomenon. The spin of the electron is found to be $\frac{1}{2}\hbar$ and $S^2 = s(s+1)\hbar^2$ where $s = \frac{1}{2}$, the quantum number for spin.

Explanation of doublet structure of alkali atom:

The Hamiltonian for the lone electron of an alkali atom relative to the atomic core is given by,

$$\hat{H}_0 = \frac{\vec{p}^2}{2\mu} + V(r) \quad \text{.........(1)}$$

Where, $\vec{p} = $ momentum of the lone electron and $V(r) = $ Potential. $r. = $ Distance of the lone electron from the centre of the atomic core, i.e., nucleus.

Now considering the spin orbit interaction the total Hamiltonian is given by,

$$\hat{H} = \frac{\vec{p}^2}{2\mu} + V(r) + \hat{H}^{\text{s-o}} \quad \text{.........(2)}$$

Where $\hat{H}^{\text{s-o}} = $ spin orbit interaction term
An electron with orbital angular momentum $\vec{l}$ and spin $\vec{s}$ will behave a total angular momentum

$$\vec{j} = \vec{l} + \vec{s}$$

Which gives the quantum numbers for $\vec{j}$ as $j = (l + s),(l + s - 1),\ldots,(l - s)$. Since for a single electron $s = \frac{1}{2}$ or $-\frac{1}{2}$, $j = l + \frac{1}{2}$ and $l - \frac{1}{2}$, for $l = 0; j = \frac{1}{2}$ only.

The coupling of spin with orbital angular momentum gives rise to the fine structure splitting of spectral lines and it gives a full account of the doublet structure of alkali spectra. This interaction is called spin orbit interaction.

The existence of electron spin and the doublet structure comes as a natural consequence of the relativistic theory but classical electrodynamics gives a non-realistic description.

Consider an electron of charge $-e$ moving with velocity $\vec{v}$ at a distance $\vec{r}$ from the nucleus of charge $Z\varepsilon$ (or an entire atomic configuration of effective charge $Z\varepsilon$).

Viewed from electrons rest frame the entire atomic configuration (consisting of the nucleus and the rest of the electronic charge cloud be taken as rigid core) is moving with a velocity of $-\vec{V}$ and their effective field also moves with the same velocity. Associated with the moving electric field arising from relativistic transformation equation. To first order in $\frac{\vec{v}}{c}$, the magnetic field is

$$\vec{B} = \frac{1}{c} \vec{E} \times \vec{v}$$

and, $\vec{E} = -\vec{\nabla} \phi$; $\phi = $ scalar potential

$$\therefore \vec{B} = -\frac{1}{c} \vec{\nabla} \Phi \times \vec{v}$$

$$= +\frac{1}{ec} \vec{\nabla} \nabla \times \vec{v}$$

where $\nabla = -e\phi = $ potential.

Now for a spherical symmetric potential

$$\vec{\nabla} \phi = \frac{dV}{dr} \frac{\hat{r}}{r}$$

$$\therefore \vec{B} = \frac{1}{ec} \frac{1}{r} \frac{dV}{dr} \hat{r} \times \vec{v}$$

$$= \frac{1}{mec} \frac{1}{r} \frac{dV}{dr} \hat{r} \times \vec{p} \quad [\vec{p} = m\vec{v}]$$

$$= \frac{1}{mec} \frac{1}{r} \frac{dV}{dr} \hat{l} \quad [\hat{l} = \hat{r} \times \hat{p} = \text{angular momentum.}]$$
If the coordinate system is fixed with the atom the effective magnetic field is to be multiplied by a factor $\frac{1}{2}$. This is known as **Thomas correction** obtained from a spinning top model of the electron.

$$\therefore \mathbf{B} = \frac{1}{2me_c} \frac{1}{r} \frac{dV}{dr} \mathbf{l}$$

The interaction energy of the electronic magnetic moment with the magnetic field due to the motion of the charge particle is

$$\left[ \mathbf{H}^{s-o} = -\mathbf{\mu}_s \cdot \mathbf{B} \right]$$

$$= \frac{e}{mc} \frac{1}{2mc} \frac{1}{r} \frac{dV}{dr} l_s$$

$$\left[ \mathbf{\mu}_s = -\frac{e}{mc} \mathbf{s} \right]$$

This equation holds in the rest frame of both electron and the nucleus as to first order in $\frac{V}{c}$, the energy is same. There is no term proportional to $l^2$ as in the rest frame of the electron; there is no orbital magnetic moment.

Now we can write using quantum mechanical operator for $\mathbf{l}$ and $\mathbf{s}$ \((as \ h\mathbf{l} \ and \ h\mathbf{s})\).

$$\therefore \left[ \mathbf{H}^{s-o} = \frac{\hbar^2}{2mc^2} \frac{1}{r} \frac{dV}{dr} l_s \right]$$

$$= \xi(r) \mathbf{l}_s \quad \ldots\ldots(2)$$

Where $\mathbf{l}$ and $\mathbf{s}$ are dimensionless vector operators,

$$\xi(r) = \frac{\hbar^2}{2mc^2} \frac{1}{r} \frac{dV}{dr}$$

The total Hamiltonian of the alkali atom considering spin orbit interaction is given by,

$$\left[ \mathbf{H} = \frac{\mathbf{p}^2}{2\mu} + V(r) + \xi(r) (l_s) \right] \quad \ldots\ldots(3)$$

For a pure Coulombic potential,

$$V(r) = -\frac{Ze^2}{r}$$

$$\therefore \frac{1}{r} \frac{dV}{dr} = \frac{Ze^2}{r^3}$$

$$\therefore \xi(r) = \frac{\hbar^2 Ze^2}{2mc^2} \frac{1}{r^3} \quad \ldots\ldots(4)$$

Now the spin orbit term can be considered as perturbation term. The contribution of the spin orbit term can be calculated by considering its expectation value. (here we consider only the first order correction)
\[ \therefore \Delta E = \langle \psi \left| H^{S-O} \right| \psi \rangle \]  \hspace{1cm} \text{(5)}

Where \( \psi \) is the ground state wave function of the effective one particle system.

In an atom the total angular momentum \( \vec{j} \) is always conserved even if individual \( \vec{l} \) and \( \vec{s} \) may not be conserved. Hence we can work in a representation or system where \( \left[ H^{S-O} \right] \) is diagonal. Also we choose \( \left| nl, m_j \right\rangle \) representation, where individual \( \vec{l} \) and \( \vec{s} \) are combined to form the conserved quantity \( \vec{j} \).

Thus,

\[ \Delta E = \left\langle \psi_{nlj_m} \left| H^{S-O} \right| \psi_{nlj_m} \right\rangle 
\]

\[ = \left\langle \psi_{nl} \left( r \right) \xi \left( r \right) \right| \psi_{nl} \left( r \right) \right\rangle \left\langle \psi_{lsjm} \left| \vec{l} \cdot \vec{s} \right| \varphi_{lsjm} \right\rangle 
\]

\[ = \zeta_{nl} \left\langle \vec{l} \cdot \vec{s} \right\rangle \] \hspace{1cm} \text{..........................(5).}

Where,

\[ \zeta_{nl} = \left\langle \psi_{nl} \left( r \right) \xi \left( r \right) \right| \psi_{nl} \left( r \right) \right\rangle 
\]

\[ = \int_0^\infty R_{nl}^2 \left( r \right) \xi \left( r \right) r^2 dr 
\]

\[ = \frac{2m^2 \hbar^2}{Ze^2 c^2} \int_0^\infty R_{nl}^2 \left( r \right) \frac{1}{r^3} r^2 dr 
\]

\[ = \frac{Ze^2 \hbar^2}{2m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle 
\]

We have,
\[
\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{n^3l(l+1)\left(l + \frac{1}{2}\right)}a_0^3; \quad a_0 = \frac{\hbar^2}{me^2}
\]

\[
\therefore \text{We can write, } \zeta_{nl} = R_y\alpha^2\frac{Z^4}{n^3l(l+1)\left(l + \frac{1}{2}\right)}
\]

Where, \( R_y = \frac{me^4}{2\hbar^2} \) = Rydberg constant and

\[
\alpha = \frac{e^2}{\hbar c} = \text{fine structure constant.}
\]

To calculate the angular term \( \left\langle \vec{l}\cdot\vec{s} \right\rangle \) we proceed as follows:

\[
\vec{l}\cdot\vec{s} = \frac{1}{2}\left[j^2 - l^2 - s^2\right]
\]

\[
\therefore \left\langle \psi_{lsjm} \left| \vec{l}\cdot\vec{s} \right| \psi_{lsjm} \right\rangle = \left\langle \vec{l}\cdot\vec{s} \right\rangle
\]

\[
= \frac{1}{2}\left[j^2 - l^2 - s^2\right]
\]

\[
= \frac{1}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]
\]

\[
= \frac{1}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right] \quad \therefore s = \frac{1}{2}
\]

Here for a given \( l\), \( j = l + \frac{1}{2} \) and \( l - \frac{1}{2} \).

Thus each level split into two sublevels with \( j = l + \frac{1}{2} \) and \( l - \frac{1}{2} \).
For $\hat{j} = l + \frac{1}{2}$

$$\langle \hat{j}\hat{s}\rangle = \frac{1}{2} \left[ \left( l + \frac{1}{2} \right) \left( l + \frac{3}{2} \right) - l(l+1) - \frac{3}{4} \right]$$

$$= \frac{1}{2} \left[ \frac{3}{4} + \frac{3}{2} - l^2 - l - \frac{3}{4} \right]$$

$$= \frac{l}{2}$$

For $\hat{j} = l - \frac{1}{2}$

$$\langle \hat{j}\hat{s}\rangle = \frac{1}{2} \left[ \left( l + \frac{1}{2} \right) \left( l + \frac{3}{2} \right) - l(l+1) - \frac{3}{4} \right]$$

$$= \frac{1}{2} \left[ \frac{1}{4} - l^2 - l - \frac{3}{4} \right]$$

$$= -\frac{1}{2}(l+1)$$

Thus the energy levels are given by,

$$E_1 \left( \hat{j} = l + \frac{1}{2} \right) = E_0 + \zeta_{nl} \frac{l}{2} \text{ and}$$

$$E_2 \left( \hat{j} = l - \frac{1}{2} \right) = E_0 - \zeta_{nl} \frac{(l+1)}{2}$$

The separation is given by,

$$\Delta E = E_1 - E_2 = \zeta_{nl} \left( l + \frac{1}{2} \right)$$

Thus the splitting of energy levels i.e., separation between the two levels for each value of $l$ is $\frac{1}{2}(2l+1)\zeta_{nl}$. This is the so called fine structure of spectral lines for spin orbit interaction of energy levels.

Now we may draw the energy level diagram for the non relativistic theory then the correction to the energy levels due to relativistic variation of mass and at last correction to the energy level due to the presence of spin orbit interaction.
Now for \( l = 0, j = \pm \frac{1}{2} \) but \( j \) can never be \(-\text{ve}\). Hence \( j = + \frac{1}{2} \). Therefore \( 1s \) level doesn’t split up for \((\text{S-O})\) interaction.

For \( l = 1, j = \frac{3}{2}, \frac{1}{2} \)

\( l = 2, j = \frac{5}{2}, \frac{3}{2} \)

\( l = 3, j = \frac{7}{2}, \frac{5}{2} \) and so on

Thus except \( l = 0 \) (which has no \( S-O \) interaction) the other energy levels split up into two levels (doubles) as shown below due to \( S-O \) interaction.

The mechanism responsible to the doublet splitting is \( S-O \) interaction. Each energy level has got a spin multiplicity \( \left( 2s+\frac{1}{2} \right) = \frac{3}{2} + 1 = 2 \).
In spectroscopic notation, each energy level is represented as,

$$\frac{2s+1}{n} L_j$$

$n$ = Principal quantum number.
$L$ = Orbital angular momentum quantum number.
$J = \text{Total angular momentum quantum number} = l + s$
$2s + 1 = \text{spin multiplicity.}$

$l = 0, 1, \ldots, n - 1$
$m_l = -l, \ldots, +l$

$j = l + s$

$j = (l + s), (l + s - 1), \ldots, (1 - s)$. 

Alkali spectra