

Vector model of the atom

(1)

(Coupling of angular momentum)

The total angular momentum of an atom results from the combination of the orbital and spin angular momentum of the electron.

$$\text{Let } |\vec{L}\rangle = \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{l(l+1)} \frac{h}{2\pi} \text{ --- (1)}$$

$$L_z = m_l \frac{h}{2\pi} \text{ --- (2)}$$

$$m_l = l, (l-1) \dots -l+1, -l$$

orbital quantum no

$$\text{Similarly } |\vec{S}\rangle = \sqrt{s(s+1)} \frac{h}{2\pi} = \sqrt{s(s+1)} \frac{h}{2\pi} \text{ --- (3)}$$

its z-component $S_z = m_s \frac{h}{2\pi}$ --- (4)

$$m_s = +\frac{1}{2}, -\frac{1}{2} \checkmark$$

magnetic spin quantum no

Let $\vec{J} \rightarrow$ Total angular momentum

$$\vec{J} = \vec{L} + \vec{S} \text{ --- (5)}$$

using the quantization condition

$$|\vec{J}\rangle = \sqrt{j(j+1)} \frac{h}{2\pi} \text{ --- (6)}$$

$$J_z = m_j \frac{h}{2\pi} \text{ --- (7)}$$

$J \rightarrow$ inner quantum number

$$m_j = j, (j-1) \dots -j+1, -j \text{ --- (8)}$$

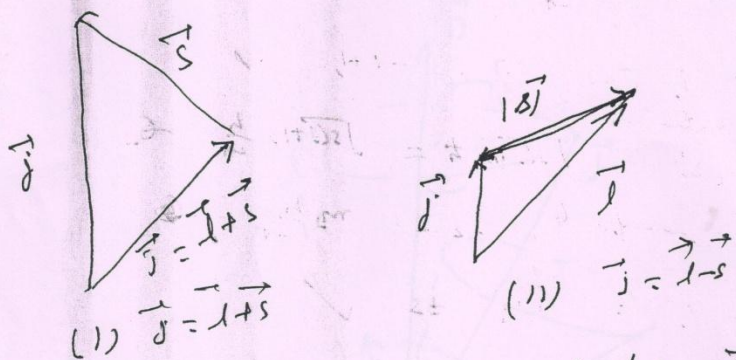
Since J_z, L_z and S_z are scalar quantities

$$J_z = L_z \pm S_z \text{ --- (9)}$$

this can be written as $m_l \pm m_s$

Since \vec{J} , \vec{L} and \vec{S} are all quantized, they can have only certain relative orientations. In case of one electron atom, there are only two relative orientations possible, as

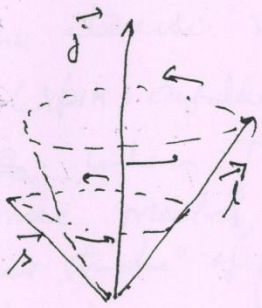
$$\begin{aligned} \vec{J} &= \vec{L} + \vec{S} & [|\vec{J}| > |\vec{L}|] & \text{--- (12)} \\ \vec{J} &= \vec{L} - \vec{S} & [|\vec{S}| < |\vec{L}|] & \text{--- (13)} \end{aligned}$$



The angular momenta of the electron \vec{S} & \vec{L} interact mechanically, \Rightarrow spin-orbit interaction. The exert torques on each other.

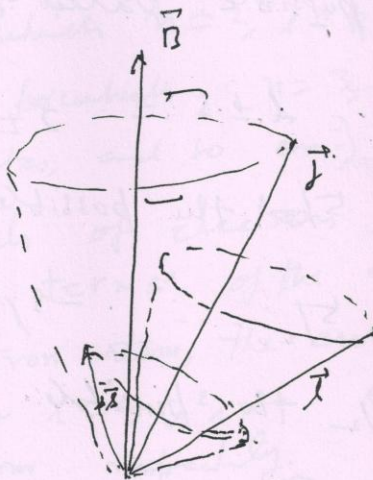
$$|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 + 2|\vec{L}||\vec{S}| \cos(\vec{L}, \vec{S})$$

$$\cos(\vec{L}, \vec{S}) = \frac{|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2}{2|\vec{L}||\vec{S}|}$$



$$= \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}} \text{--- (15)}$$

In vector model \vec{L} and \vec{S} precess around \vec{J} , when the atom is placed in an external magnetic field \vec{B} , then \vec{J} precess about the direction of \vec{B} ~~and \vec{L} and \vec{S}~~ . while \vec{L} and \vec{S} continue precessing about \vec{J} . The discrete orientations of \vec{J} relative to \vec{B} , which involves slightly different energies, give rise to anomalous Zeeman effect.



like electron, the atomic nuclei also have smaller intrinsic (spin) angular momentum and magnetic moment. When these vectors are added to the atomic model, the experimentally observed "hyperfine structure" of the spectral lines is explained.

① write down the values of the quantum nos. l and s for the d -electrons and enumerate for the possible values of the quantum number J and m_J .

Sol. for d -electron
 $l = 2, s = 1/2$.

The two possible values of J are

$$J = l \pm s = 2 \pm \frac{1}{2} = 5/2 \text{ \& } 3/2$$

For $J = 5/2$ the possible values of m_J are

$$m_J = 5/2, \dots, -5/2$$

For $J = 3/2$ the possible values of m_J are

$$m_J = 3/2, \dots, -3/2$$

Spectroscopic Terms and their Notations

(5)

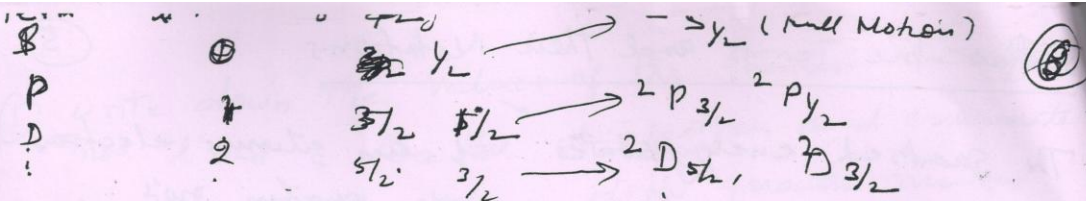
The quantised energy states of an atomic electron are described in terms of the quantum no's n, l, s and j . The electrons having the orbital quantum number $l = 0, 1, 2, 3, \dots$ are named as s, p, d, f... electrons. The atomic states in the atom are specified by writing the ~~orbital~~ principal quantum number along with these letters. [Thus an electron for which $n=2, l=0$ is a 2s atomic state, and one for which $n=3, l=2$ is in a 3p atomic states, and so on.]

The energy levels of electrons of an atom are called the terms of the atom.

For one-electron atom, the energy levels corresponding to $l=0, 1, 2, \dots$ are called s, p, d, f, g... term respectively.

By spin-orbit interaction, each energy level of a given l is split into two sub-levels corresponding to $j = l + s = l + \frac{1}{2}$ and $j = l - s = l - \frac{1}{2}$

The number of different possible orientations of \vec{l} and \vec{s} and hence the number of different possible values j is known as the multiplicity of the terms and is $2s+1$. Thus the multiplicity of the terms of one electron atom $2 \times \frac{1}{2} + 1 = 2$ it is added as a left superscript of the term symbol: $2s, 2p, 2d, \dots$. These are called the "Doublet terms". In addition to this, j value is added as a right subscript.



Spin-orbit Coupling and Fine structure

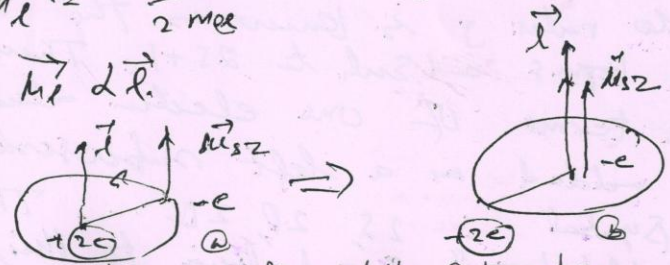
Now we will discuss why the energy levels of the H atoms with $l > 0$, split into two components, which could not be explained by the Schrodinger theory. Since this splitting is very small and can be only resolved with high resolution spectrographs, where the hydrogen lines appear as the fine substructure, it was named Fine structure.

We start here with a semiclassical model, treating the angular momenta as vectors with quantized absolute value and quantized z components.

We know that electron with charge $-e$, moving with orbital angular momentum \vec{l} on a circle around the nucleus, produces a magnetic moment.

$$\vec{\mu}_l = \frac{-e}{2m_e} \vec{l} = -(\mu_B/\hbar) \cdot \vec{l}$$

i.e. $\vec{\mu}_l \propto \vec{l}$



Vector model of spin-orbit interaction
 (a) → Vector model of electron circulating around nucleus when the electron

According to the Biot-Savart law, the magnetic field \vec{B}_l is

$$\vec{B}_l = \frac{\mu_0 z e}{4\pi r^3} (\vec{v} \times (-r)) \quad (7)$$

$$\vec{B}_l = - \frac{\mu_0 z e}{4\pi r^3} \vec{v} \times \vec{r} \quad (8)$$

$$\vec{B}_l = \frac{\mu_0 z e}{4\pi r^3 m_e} \vec{L} \quad \left[\begin{array}{l} \vec{L} = m_e \vec{v} \times \vec{r} \\ \vec{L} = m_e (\vec{v} \times \vec{r}) \end{array} \right] \quad (9)$$

because the angular momentum of the electron in a coordinate system where the electron moves around the proton at rest is $\vec{L} = m_e (\vec{v} \times \vec{r})$.

The magnetic spin moment of the electron has two spatial orientations in this field according to the two spin directions, $S_z = \pm \hbar/2$. This causes an additional energy (in addition to the Coulomb energy)

$$\Delta E = -\vec{\mu}_s \cdot \vec{B}_l = g_s \mu_B \frac{\mu_0 z e}{4\pi m_e r^3} (\vec{S} \cdot \vec{L})$$

$$\Delta E = -\vec{r} \times \frac{e\vec{h}}{2m_e} \times \frac{\mu_0 z e}{4\pi m_e r^3} (\vec{S} \cdot \vec{L}) \quad \left[\vec{\mu}_s = -g_s \left(\frac{\mu_B}{\hbar} \right) \vec{S} \right]$$

$$= \frac{\mu_0 z e^2}{4\pi m_e^2 r^3} (\vec{S} \cdot \vec{L}) \quad \left[\begin{array}{l} g_s = 2, \\ \mu_B = \frac{e\hbar}{2m_e} \end{array} \right]$$

Taking the effect of the Thomas factor which is due to the fact that electrons spin in the rest-frame of the nucleus precesses when moving around the nucleus (Thomas) $\Rightarrow \frac{1}{2}$

Then $\Delta E = \frac{1}{2} \times \frac{\mu_0 2e^2}{4\pi m_e^2 r^3} (\vec{J} \cdot \vec{L})$ — (6)

$E_{n,l,s} = E_n - \mu_B \vec{L} \cdot \vec{S} = E_n + \frac{\mu_0 2e^2}{8\pi m_e^2 r^3} (\vec{L} \cdot \vec{S})$ — (7)

$\vec{L} \cdot \vec{S} \rightarrow$ may be positive or negative.

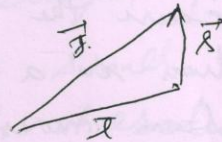
depending the orientation of the spin relative to the orbital angular momentum

let us introduce the total angular momentum

$\vec{J} = \vec{L} + \vec{S}$ with $|\vec{J}| = \sqrt{J(J+1)} \hbar$ — (8)

So $\vec{J} = \vec{L} + \vec{S}$

$J^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$



$\vec{L} \cdot \vec{S} = \frac{1}{2} \hbar^2 [J(J+1) - L(L+1) - S(S+1)]$ — (9)

In operator notation this is written as

$\vec{L} \cdot \vec{S} \psi_{n,l,s,m_j} = \frac{\hbar^2}{2} [J(J+1) - L(L+1) - S(S+1)] \psi_{n,l,s,m_j}$

with this relation equation (9) can be written as

$E_{n,l,s} = E_n + \frac{a}{2} [J(J+1) - L(L+1) - S(S+1)]$ — (10)

with $a = \frac{\mu_0 2e^2 \hbar^2}{8\pi m_e^2 r^3}$ — (11)

coupling with

Note: The fine structure may be regarded as Zeeman splitting due to the interaction of the magnetic spin moment with the internal magnetic field generated by the motion of the electron

For $s = 1/2$ the energy level splits, depending on the orientation of the spin, into two components with $J = l + 1/2$ or $J = l - 1/2$

Note: Fine structure splittings are observed only for $l > 0$, p, d, f, \dots

Relativistic effects

(9) (a)

$$\sum_n E_n = \frac{p^2}{2m} + E_{pot}$$

Using the relativistic energy relation

$$E = \sqrt{m_0^2 c^4 + p^2 c^2} - m_0 c^2 + E_{pot} \quad (12)$$

In hydrogen atom, the velocity of electron is
 (11) small compared to the velocity of light

$$\left(1 + \frac{p^2}{m_0^2 c^2}\right)^{1/2} = 1 + \frac{1}{2} \frac{p^2}{m_0^2 c^2} - \frac{1}{8} \frac{p^4}{m_0^4 c^4} + \dots$$

$$E = c \cdot m_0 c \left(1 + \frac{1}{2} \frac{p^2}{m_0^2 c^2} - \frac{1}{8} \frac{p^4}{m_0^4 c^4}\right) - m_0 c^2 + E_{pot}$$

$$E = \frac{p^2}{2m_0} - \frac{p^4}{8m_0^3 c^2} + E_{pot}$$

$$= \left(\frac{p^2}{2m_0} + E_{pot}\right) - \frac{p^4}{8m_0^3 c^2}$$

$$E = \frac{E_{nr}}{1} - \frac{p^4}{8m_0^3 c^2} = E_{nr} - \Delta E_r \quad (13)$$

$\Delta E_r =$ relativistic correction

$$\Delta E_r = \frac{p^4}{8m_0^3 c^2} \int \psi_{n,l,m}^* \nabla^4 \psi_{n,l,m} d\tau$$

$$\Delta E_r = \left[-E_{nr} \frac{2^2 \cdot 2}{n} \left(\frac{3}{4n} - \frac{1}{n(n+1/2)} \right) \right] \left[R_Y = \frac{m_0 c^4}{8\hbar^2 a_0^2} \right]$$

$a_0 = \frac{\hbar^2}{4\pi m_0 e^2}$

Total energy of an electron in hydrogen atom

$$E_{nr} = -R_Y \frac{2^2 \cdot 2}{n^2} \left[1 - \frac{2^2 \cdot 2}{n} \left(\frac{3}{4n} - \frac{1}{n(n+1)} \right) \right]$$

(corrected the mistake)

If we consider both the effect of relativistic correction and spin-orbit coupling (12)

$$E_{nj} = E_n \left[1 + \frac{2^2 \alpha^2}{n} \left(\frac{j+1/2}{4n} - \frac{3}{4n} \right) \right]$$

$$R_y = \frac{m e^4}{8 \epsilon_0^2 h^2}$$

$$\Delta E_r = + \left(\frac{m z^2 e^4}{8 \epsilon_0^2 h^2 n^4} \right) \left(\frac{\alpha^2 z^2}{n} \right) \left(\frac{3}{4n} - \frac{1}{l+1/2} \right)$$

$$= - E_{nr} \frac{\alpha^2 z^2}{n} \left(\frac{3}{4n} - \frac{1}{l+1/2} \right)$$

Where $E_{nr} = - \frac{m z^2 e^4}{8 \epsilon_0^2 h^2 \cdot n^2} = \frac{R_y z^2}{n^2}$

with $R_y = \frac{m e^4}{8 \epsilon_0^2 h^2}$

Total energy of an ^{Fig 10} ~~Fig 10~~ state for H atom

$$E = E_{nr} - \Delta E_r$$

$$= - \frac{R_y z^2}{n^2} + \frac{R_y z^2}{n^2} \left(\frac{\alpha^2 z^2}{n} \right) \left(\frac{3}{4n} - \frac{1}{l+1/2} \right)$$

$$E = - \frac{R_y z^2}{n^2} \left[1 - \frac{\alpha^2 z^2}{n} \left(\frac{3}{4n} - \frac{1}{l+1/2} \right) \right]$$