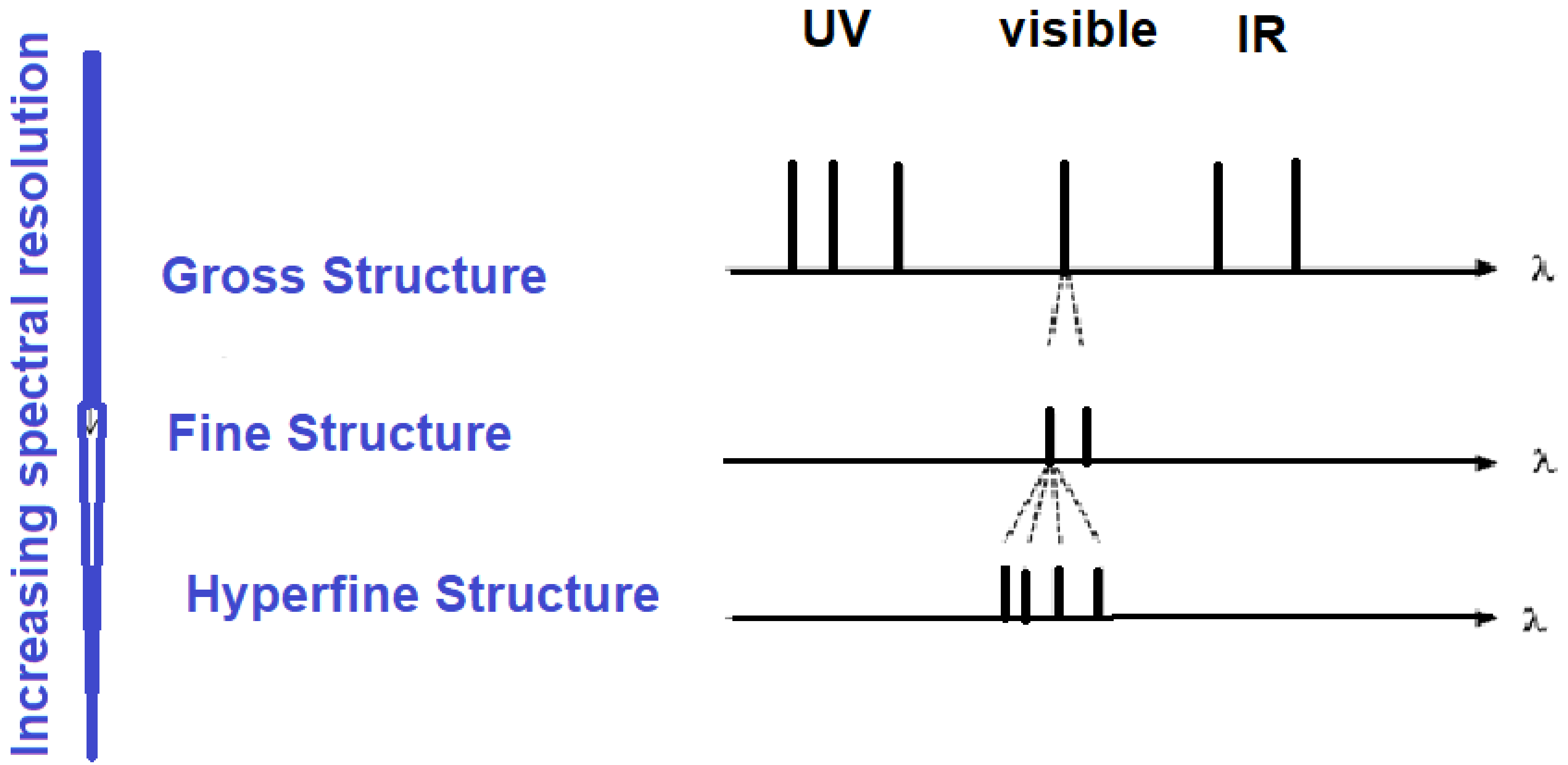
Hyperfine Structure


Increasing spectral resolution
UV
visible
IR
Gross Structure
Fine Structure
Hyperfine Structure
λ
λ
λ

	Energy (eV)	Effects
Gross structure of spectral lines	1-10	electron-nuclear attraction Electron kinetic energy Electron-electron repulsion
Fine structure of spectral lines	0.001 - 0.01	Spin-orbit interaction Relativistic corrections
Hyperfine structure	10^{-6} - 10^{-5}	Nuclear interactions

Hyperfine structure (hfs)

(1) Due to different isotopes (Isotope effect)

atoms of a chemical element with the same atomic number and nearly identical chemical behaviour but with different atomic masses and physical properties.

$$R = \frac{2\,\pi^2 e^4 (mM)}{ch^3 (M + m)}$$

$$\bar{\upsilon} = \frac{1}{\lambda} = \mathrm{R}\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right]$$

different isotopes of same element have slightly different spectral lines

Hfs => discovered for atoms with only one isotope

=> hypothesis abandoned

(2) Due to interaction of nuclear magnetic moment with total angular momentum

Later => Pauli and Russell => hfs due to interaction between I and J

Finally => hfs due to both (1) and (2)

Nucleus has magnetic moment μ_I

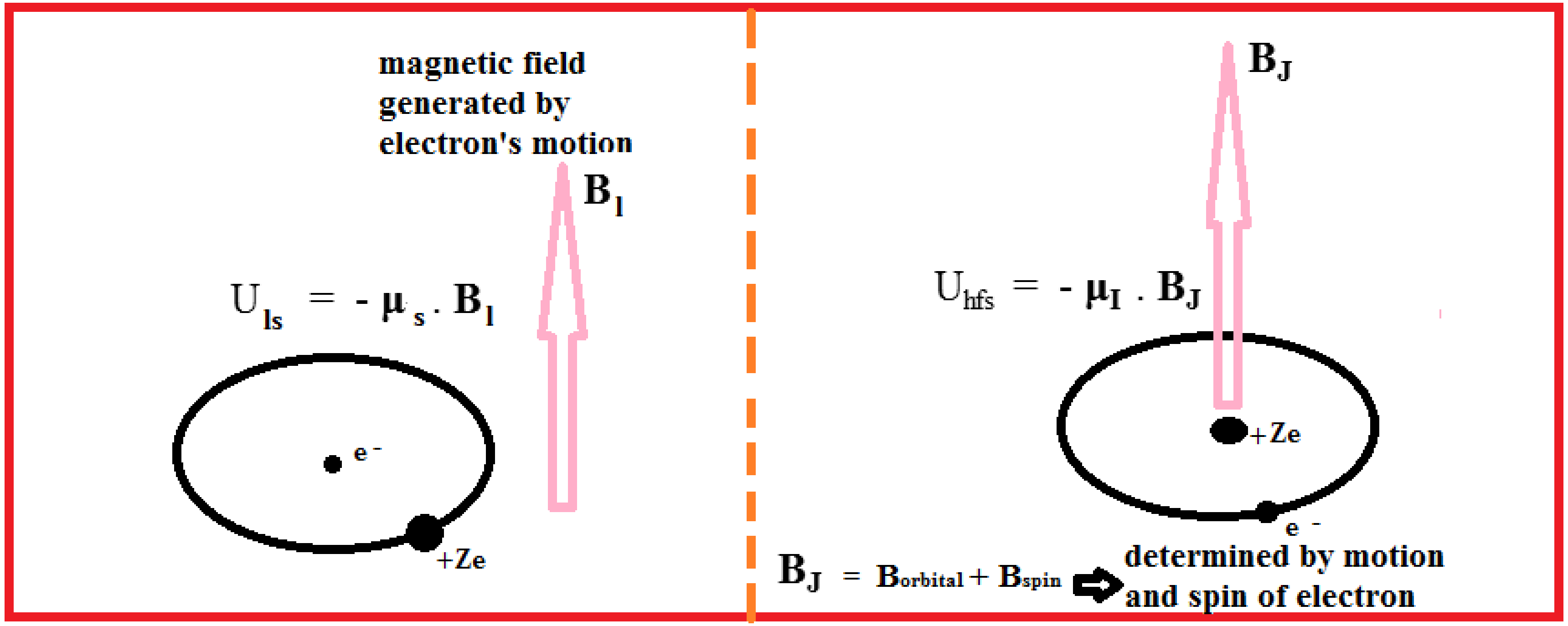
$\Rightarrow$ The interaction between μ_I and the magnetic field B_J generated by the electrons at the site of the nucleus.

$\Rightarrow$ $U_{hfs} = - \boldsymbol{\mu}_\mathbf{I} \cdot \mathbf{B}_\mathbf{J}$

=> Atoms with one isotope can produce hfs.

Spin –orbit interaction

Hf interaction



Nucleus has intrinsic spin I

$| I | = \sqrt{I(I+1)}\ \hbar$

$I_z = m_I \hbar$; $m_{I} =$ -I ------- + I

Nuclear magnetic moment $\boldsymbol{\mu_I = g_I \frac{\mu_N}{\hbar}}\ \mathrm{I}$

$$\boldsymbol{\mu_N = \frac{e\hbar}{2m_p}}$$

μ_N =5.050783699(31)×10^{-27} J/T

$$\boldsymbol{\mu_N = \frac{\mu_B}{1836} <<< \mu_B}$$

μ_B = 9.274009994(57)×10^{-24} J/T

=> $U_{hfs} <<< U_{ls}$

=> There is small effect on energy levels because of hyperfine splitting

Isotope structure => hfs due to different isotopes of the same element.

Eg. Tungsten (3 isotopes)

Explanation

Transition n=4 -> n=2

$$\bar{\upsilon} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

λ = 4861.33 Å

If it is seen through h.r.p. instrument it shows hfs.

Why????

$$R = \frac{2\,\pi^2 e^4 (mM)}{ch^3 (M+m)}$$

=> Different isotopes have different values of R.

In the case of hydrogen

$$\overline{\upsilon_H} = \frac{1}{\lambda_H} = R_H \left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

$$\overline{\upsilon_D} = \frac{1}{\lambda_D} = R_D \left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

$$\overline{\upsilon_T} = \frac{1}{\lambda_T} = R_T \left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

OR $\dfrac{\lambda_D}{\lambda_H} = \dfrac{R_H}{R_D}$

$$\frac{\lambda_D - \lambda_H}{\lambda_H} = \frac{R_H - R_D}{R_D}$$

$\Delta\lambda$ = -1.32 Å

λ_D = 4860.01 Å

Hyperfine structure due to a nuclear magnetic and mechanical moment

Example – Tantalum (eight components)

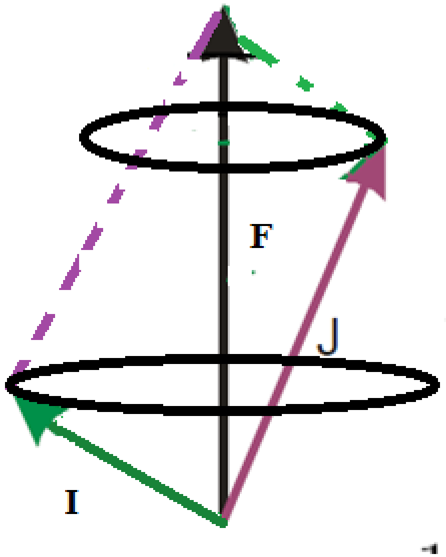
Experimental observation by Back and Interpretation by Goudsmit

Revealed for the first time that a new quantum vector should be added to the atom model and the Lande interval rule for the fine structure also applies to hfs.

The total mechanical moment of all extranuclear electrons J^* (j^* for one electron) is coupled with the quantum vector I^* representing the total mechanical moment of the nucleus ($I^* \hbar$) to form a resultant F^*

=> Total mechanical momentum of the atom is $F^* \hbar$.

$\bar{F} = \bar{I} + \bar{J}$



Goudsmit and Back has shown that just as the interaction energy between L^* and S^* Is proportional to the cosine of the angle between them, so the interaction energy between the nuclear moment I^* and the electron moment J^* is given by

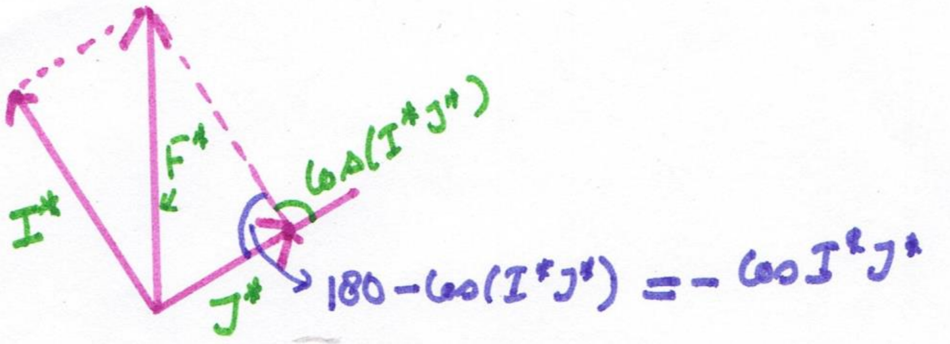
$$\Gamma_F = A' I^* J^* \cos (I^* J^*)$$

Where $A' I^* J^*$ is constant for each given fine structure level J, and A' is a measure of the strength of coupling between I^* and J^*.

I takes 0 (even N even Z) half (even Z odd N or odd Z even N) or whole integral values (odd Z odd N)

F=> I - J to I +J when $I \geq J$ and from $J - I$ to $J + I$ if $J \geq I$

$$\Gamma_F = A' I^* J^* \cos\,(I^* J^*)$$



$$-\cos(I^* J^*) = \frac{I^{*2} + J^{*2} - F^{*2}}{2 I^* J^*}$$

$$I^* J^* \cos(I^* J^*) = \frac{F^{*2} - I^{*2} - J^{*2}}{2}$$

$$\Gamma_F = \frac{A'}{2}\left[F^{*2} - I^{*2} - J^{*2}\right]$$

$$= \frac{A'}{2}\left[F(F+1) - I(I+1) - J(J+1)\right]$$

Spacing – Lande Interval rule

The spacing between consecutive levels of a hfs multiplet is proportional to (F+1) ie. Larger F value involved.

$$\Gamma_{F+1} - \Gamma_F = A' (F+1)$$

$$\Delta \Gamma = A' (F+1)$$

Hyperfine Structure of 3 $^2P_{3/2}$

Observed value of I =3/2

First calculate value of F

Value of Γ_F

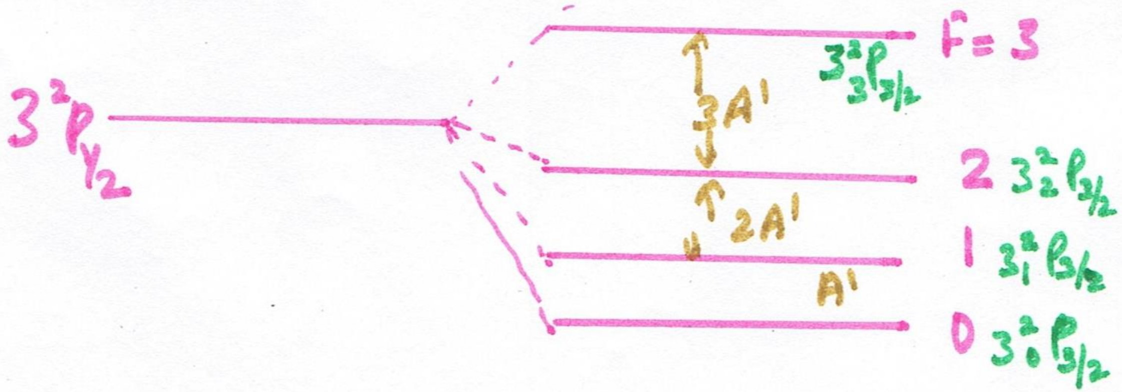
Hyperfine Structure of $3\,^2P_{3/2}$ level of Sodium

Observed values of $I = \frac{3}{2}$

$J = \frac{3}{2}$

$F = \frac{3}{2} + \frac{3}{2}$ to $\frac{3}{2} - \frac{3}{2} \Rightarrow 3$ to 0

$3, 2, 1, 0$



$\Gamma_F = \frac{9}{4} A'$

$= -\frac{3}{4} A'$

$= -\frac{11}{4} A'$

$= -\frac{15}{4} A'$

splitting of $6p^3\ {}^2D_{5/2}$ term in Bismuth atom

$I = \frac{9}{2}$, $J = \frac{5}{2}$ $L = 2$ $S = \frac{1}{2}$

$F = \frac{9}{2} + \frac{5}{2}$ to $\frac{9}{2} - \frac{5}{2}$ $\Rightarrow$ 7 to 2

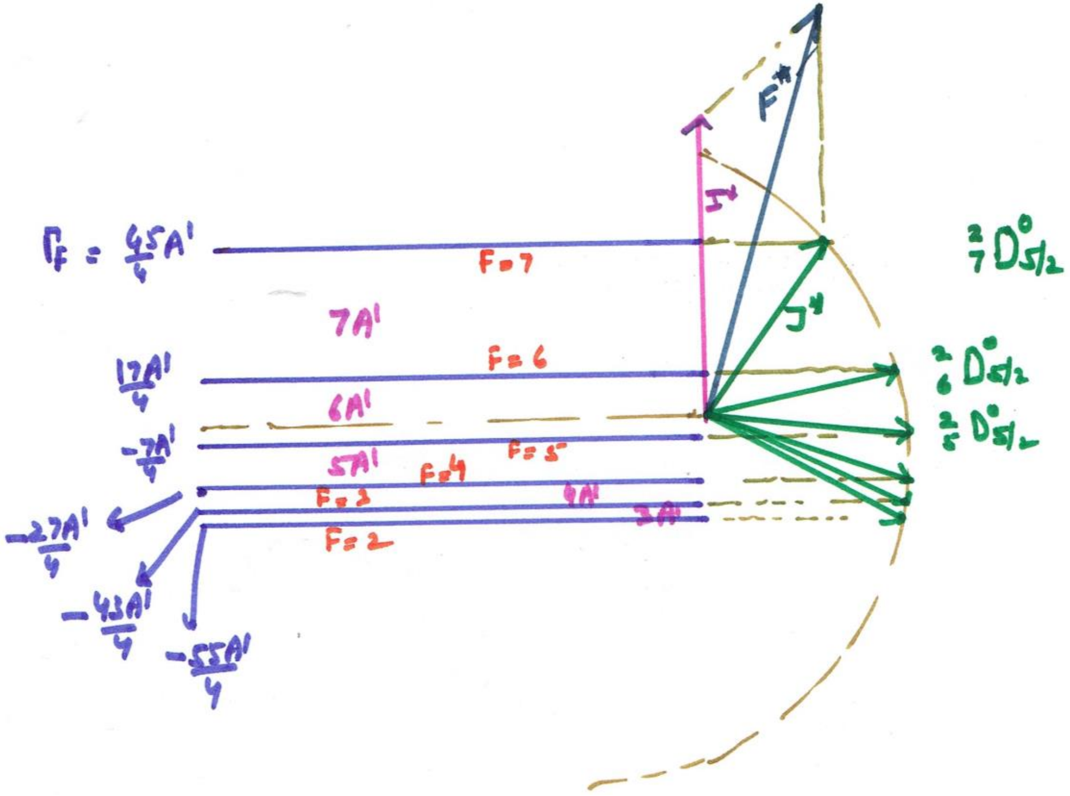
$F = 7, 6, 5, 4, 3, 2$

Γ_F for $F = 7$

$$\Gamma_F = \frac{A'}{2}\left[7\times 8 - \frac{9}{2}\times\frac{11}{2} - \frac{5}{2}\times\frac{7}{2}\right]$$

$$= +\frac{45A'}{4}$$

F	Γ_F
7	$+45/4\ A'$
6	$+17/4\ A'$
5	$-\frac{7}{4} A'$
4	$-\frac{27}{4} A'$
3	$-45/4\ A'$
2	$-55/4\ A'$



The difference between levels are 3A', 4A', 5A', 6A' & 7A' values proportional to the larger F values.

Since the value of I for a given atom is the same for all terms in all states of ionization, F is usually written by a small subscript to the left of the term.

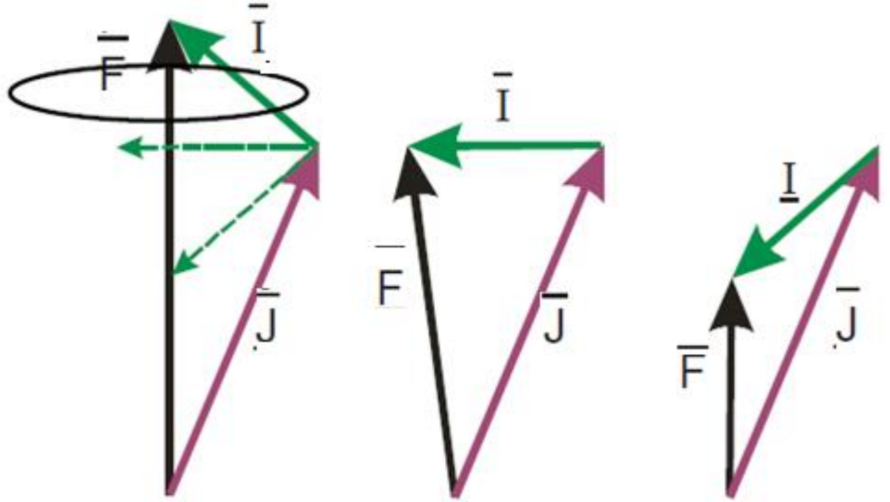
'O' → oddness of the electron configuration and terms.

All spectrum terms arising from an electron configuration for which the sum of l values = even → (even terms)

" " " → odd → (odd terms)

Vector model of nuclear interaction

$\bar{F} = \bar{I} + \bar{J}$



$$\bar{I} \cdot \bar{J} = \frac{1}{2}\{\bar{F}^2 - \bar{I}^2 - \bar{J}^2\}$$

$\bar{I}$ and $\bar{J}$ precess areound their resultant $\bar{F}$

$\bar{I} \cdot \bar{J} =$ IJ cos (IJ)

Normal and Inverted terms

A normal term is defined as one in which hfs level with the smallest F(J) lies deepest on the energy level diagram
And an inverted term is one in which the largest F(J) lies deepest on the energy level diagram

For normal terms A' = +ve

For inverted terms A' = - ve

The selection rule for F in hfs are just the same as those for J in the fine structure

$\Delta F = 0, \pm 1$

If $I \leq J$; the level will split into $2I + 1$ hfs levels

If $J \leq I$; the level will split into $2J + 1$ hfs levels

Interaction of a single valence e^- with the nucleus

may be divided into 2 parts

(1) Int. of l^* with I^* $\quad W_{Il}$

(2) Int. of s^* with I^* $\quad W_{Is}$

W_{Il}

Acc. to classical electromagnetic theory, the electric field at the nucleus due to the electron at a distance r is given by

$$\bar{E} = \frac{e}{r^2}\hat{r}$$

$$= \frac{e\bar{r}}{r^3}$$

the mag. field at the nucleus due to the orbital motion of the electron is

$$\bar{H} = \frac{\bar{E} \times \bar{v}}{c}$$

$$= \frac{e}{cr^3}\bar{r} \times \bar{v}$$

$$\because \quad \frac{l^* h}{2\pi} = m\bar{r} \times \bar{v}$$

$$\Rightarrow \bar{r} \times \bar{v} = \frac{l^* h}{2\pi m}$$

$$H = \frac{e}{cr^3}\frac{l^* h}{2\pi m}$$

$$H = \frac{e}{mc}\frac{l^* h}{2\pi}\left(\frac{1}{r^3}\right)$$

$\because$ $r \rightarrow$ not const in any orbit

$\Rightarrow \left(\frac{1}{r^3}\right)$ must be averaged.

nucleus with a mechanical moment $I^*\frac{h}{2\pi}$ and a magnetic moment μ_I tends to carry out a Larmor precession around the field with an angular velocity ω_L given by the product of the field strength H and the ratio between the magnetic and mechanical moment

I

$$\frac{\mu_I}{I^*\frac{h}{2\pi}} = g_I \frac{e}{2mc}$$

$g_I \Rightarrow$ nuclear g factor

processional ang. velocity –

$$\omega_L = H \cdot \frac{\mu_I}{I}$$

$$= \frac{e}{mc}\,\frac{l^* h}{2\pi}\,\overline{\left(\frac{1}{r^3}\right)}\, g_I \frac{e}{2mc}$$

$$\omega_L = g_I \frac{e^2}{2m^2c^2}\,\frac{l^* h}{2\pi}\,\overline{\left(\frac{1}{r^3}\right)}$$

The interaction energy is given by the product ω_L and the projection of the nuclear mechanical moment $I^*\frac{h}{2\pi}$ on l^*.

$$W_{Il} = \omega_L \times \text{projection of } \frac{I^* h}{2\pi} \text{ on } l^*$$

$$= g_I \frac{e^2}{2m^2c^2}\,\frac{l^* h}{2\pi}\,\overline{\left(\frac{1}{r^3}\right)}\,\frac{I^* h}{2\pi}\cos(I^* l^*)$$

Since l^* precess around j^* and j^* and I^* in turn precess around their resultant F^*, the above cosine ie $\cos(I^* l^*)$ must be averaged.

$$\cos(I^* l^*) = \cos(I^* j^*)\cos(l^* j^*)$$

W_{Is}

Acc. to classical electromagnetic theory the mutual energy of two magnetic dipoles with moments μ_I & μ_s and at a distance r apart is equal to

$$W_{Is} = \frac{\mu_I \mu_s}{r^3}\left\{\cos(\mu_I \mu_s) - 3\cos(\mu_I r)\cos(\mu_s r)\right\}$$

where $\mu_s = -2\frac{e}{2mc}\frac{s^* h}{2\pi}$

mean value by the use of direction cosines

$$-\frac{1}{2}\cos(I^* j^*)\left\{\cos(j^* s^*) - 3\cos(j^* l^*)\cos(s^* l^*)\right\}$$

Inserting the value

$$W_{Is} = +g_I \frac{e}{2mc}\frac{I^* h}{2\pi}\cancel{2}\frac{e}{\cancel{2}mc}\frac{s^* h}{2\pi}\overline{\left(\frac{1}{r^3}\right)}\frac{1}{2}\cos(I^* j^*)\left\{\cos(j^* s^*) - 3\cos(j^* l^*)\cos(s^* l^*)\right\}$$

$$= g_I \frac{e^2 h^2}{2m^2c^2}\frac{I^* h}{2\pi}\frac{s^* h}{2\pi}\overline{\left(\frac{1}{r^3}\right)}\frac{1}{2}\cos(I^* j^*)\left\{\cos(j^* s^*) - 3\cos(j^* l^*)\cos(s^* l^*)\right\}$$

Adding two interaction energies

$$\Gamma_F = W_{Il} + W_{Is}$$

$$W_{Il} = g_I \frac{e^2}{2m^2c^2} \frac{l^* h}{2\pi} \overline{\left(\frac{1}{r^3}\right)} \frac{I^* h}{2\pi} \cos(I^* j^*) \cos(l^* j^*)$$

$$W_{Is} = g_I \frac{e^2 h^2}{2m^2c^2} \frac{I^* h}{2\pi} \frac{s^* h}{2\pi} \overline{\left(\frac{1}{r^3}\right)} \frac{1}{2} \cos(I^* j^*) \left[\cos(j^* s^*) - 3\cos(j^* \cos(s^* l^*)\right]$$

$$\Gamma_F = g_I \frac{e^2 h^2}{2m^2c^2} \frac{I^*}{4\pi^2} \cos(I^* j^*) \overline{\left(\frac{1}{r^3}\right)} \left[l^* \cos(l^* j^*) + \frac{s^*}{2} \left\{ \cos(j^* s^*) - 3\cos(j^* l^*) \cos(s^* l^*) \right\} \right]$$

$$= g_I \frac{e^2 h^2}{8\pi^2 m^2 c^2} I^* \cos(I^* j^*) \overline{\left(\frac{1}{r^3}\right)} \left[l^* \cos(l^* j^*) + \frac{s^*}{2} \left\{ \cos(j^* s^*) - 3\cos(j^* l^*) \cos(s^* l^*) \right\} \right]$$

$$= \underbrace{g_I \frac{e^2 h^2}{8\pi^2 m^2 c^2} \overline{\left(\frac{1}{r^3}\right)} \left[\frac{l^*}{j^*} \cos(l^* j^*) + \frac{s^*}{2j^*} \cos(j^* s^*) - \frac{3s^*}{2j^*} \cos(j^* l^*) \cos(s^* l^*) \right]}_{a'} I^* j^* \cos(I^* j^*)$$

$$\Gamma_F = a' I^* j^* \cos(I^* j^*)$$

$$= \frac{a'}{2} \left[F^{*2} - I^{*2} - J^{*2} \right]$$ (more than one e^-)

$$\overline{\left(\frac{1}{r^3}\right)} = \frac{Z^3}{a_1^3 n^3 l (l+\frac{1}{2})(l+1)}$$

$$a_1 = \frac{h^2}{4\pi^2 m e^2}$$

a' can also be written as $\Rightarrow a' = g_I \frac{Rch\alpha^2 Z^3}{n^3 l(l+\frac{1}{2})(l+1)} \{ \}$

For a given spectral term i.e. given s, l & j, a' is constant

Fermi et.al. had shown from a quantum mechanical treatment and Goudsmit had shown from classical theory of energy sums

$\{\ \} \xrightarrow[\text{can be replaced}]{} \dfrac{l^{*2}}{j^{*2}}$

$$\Rightarrow a' = g_I \frac{Rch\alpha^2 Z^3}{n^3 l(l+\frac{1}{2})(l+1)} \times \frac{l(l+1)}{j(j+1)}$$

$$= g_I \frac{Rch\alpha^2 Z^3}{n^3(l+\frac{1}{2})j(j+1)}$$

dividing by hc a' in cm^{-1}

$$a'(cm^{-1}) = g_I \frac{R\alpha^2 Z^3}{n^3 l(l+\frac{1}{2})j(j+1)}$$

If $g_I = +ve$ $a' \Rightarrow +ve$ hfs $\Rightarrow$ Normal

$g_I = -ve$ $a' \Rightarrow -ve$ hfs $\Rightarrow$ inverted

Applications of hfs

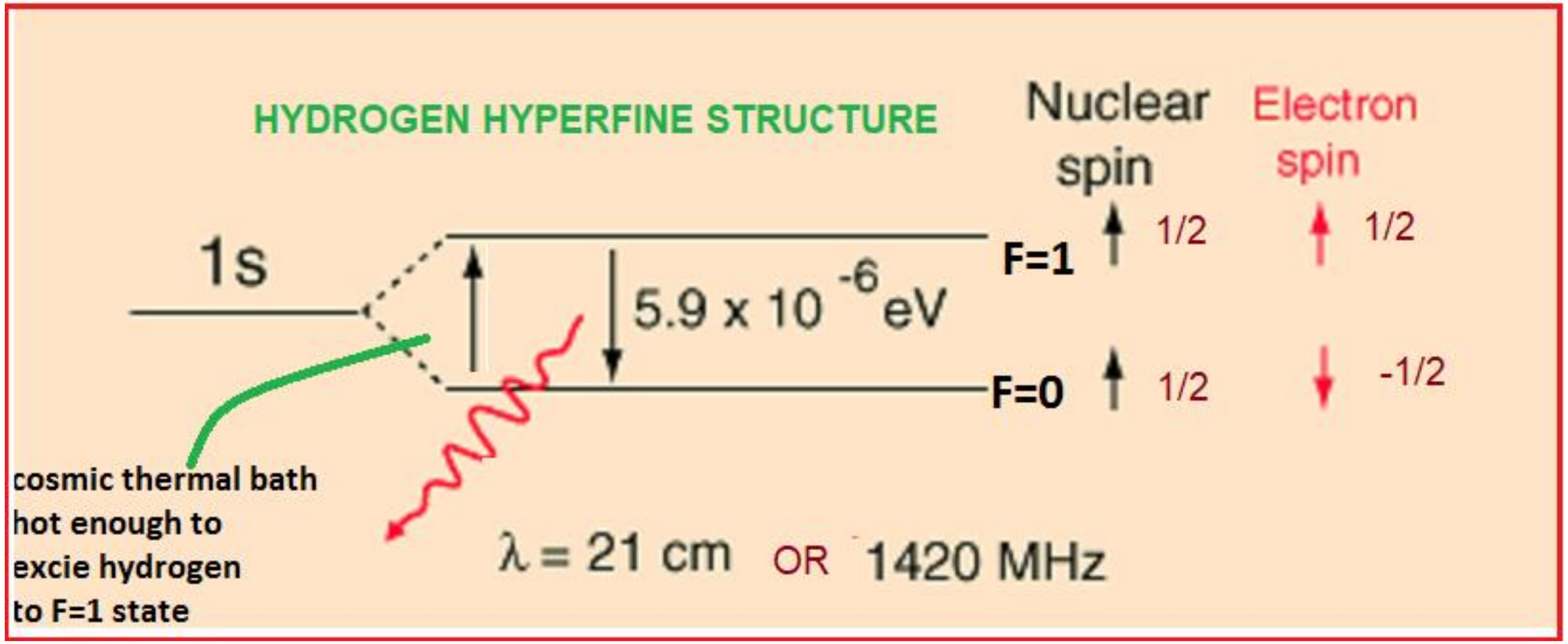
* Provides a straight test of QED and hf splitting of hydrogen and muonium have been used to measure the value of α.

* The hf transition can be used to make a microwave notch filter with very high stability

* In astrophysics $\Rightarrow$ As hf splittings are v. small the transmitted freq usually are not optical but in the range of radio and microwave freq.

21 cm transition in hydrogen $\rightarrow$ used for mapping the sky.

For atomic hydrogen in the ground state I = ½; j= ½ =» F= 0,1



The intensity of the 21-cm emission line depends on the density of the neutral atomic hydrogen along your line of sight.

The hydrogen in our galaxy has been mapped by the observation of the 21-cm wavelength line of hydrogen gas. At 1420 MHz, this radiation from hydrogen penetrates the dust clouds and gives us a more complete map of the hydrogen than that of the stars themselves since their visible light won't penetrate the dust clouds.

Problems

1.Consider an atom whose nuclear spin is I= 2. Draw an energy level diagram and the involved hyperfine components of the transition $^2D_{3/2} \rightarrow {}^2P_{1/2}$

2. Nuclear spin of bismuth atom is 9/2. Find the number of levels into which a $^2D_{5/2}$ term of bismuth splits due to I-J interaction. If the separation of $^2{}_7D_{5/2}$ term from $^2{}_6D_{5/2}$ is 70 cm^{-1} , calculate the separation between Other adjacent levels.