EPR Course
NTU Fall 2001
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October 24, 2001
Lecture 3

Zeeman Interaction

Interaction of unpaired electron(s) with magnetic field

Hamiltonian for Zeeman Interaction

$$\mathcal{H}_Z = -\vec{\mu}_S \cdot \vec{H} - \vec{\mu}_L \cdot \vec{H} = -\mu_J \cdot \vec{H}$$

Now

$$\vec{\mu}_S = -g_S \beta \vec{S} = -2.0023 \beta \vec{S}$$

$$\vec{\mu}_L = -g_L \beta \vec{S} = -1.000 \beta \vec{L}$$

where β = Bohr magneton $= \dfrac{e\hbar}{2m_e c}$

EXAMPLES

(1) Spin only atom or ion, e.g. Hydrogen atom

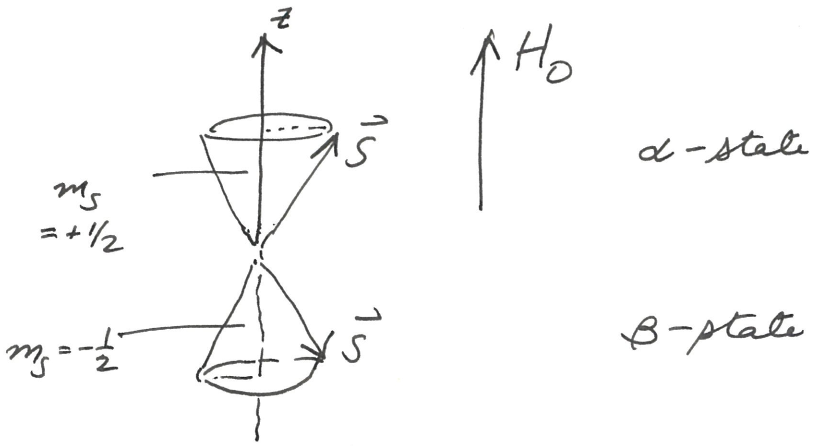
$1s^1$ ground electron configuration

$S = \frac{1}{2}, \quad L = 0 \qquad \therefore \quad {}^2S_{1/2}$

So $|\mu_L| = 0$ in this case

or $\mathcal{H}_Z = -\vec{\mu}_S \cdot \vec{H} = +g_S \beta \vec{S} \cdot \vec{H}$

Let the direction of $\vec{H}$ define the axis of quantization of electron spin



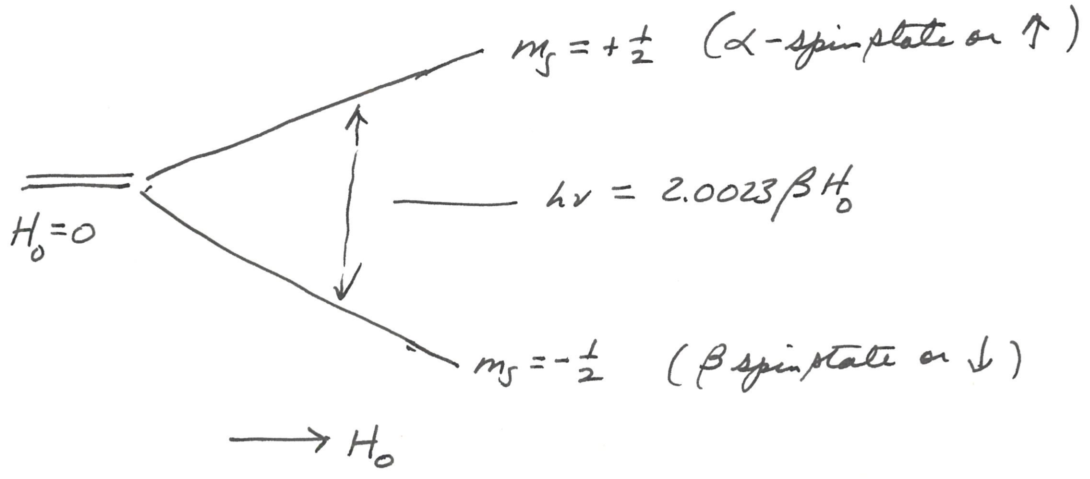
Then

$$\mathcal{H}_Z = g_S \beta S_z H_0$$

and the energy levels for the spins are given by

$$W_Z = g_S \beta m_S H_0 \qquad \text{with } m_S = \pm\frac{1}{2}$$

Energy level diagram



If experiment is done by varying ν to observe magnetic resonance at magnetic field H_0, then $h\nu_{\text{resonance}} = 2.0023\beta H_0$

If magnetic resonance is observed by varying the magnetic field to achieve resonance at EPR frequency ν_0, then

$$h\nu_0 = 2.0023\,\beta H_{resonance}$$

EPR spectrum is usually obtained by fixing the frequency of observation (ν_0)

$\nu_0 = 9 \times 10^9$ Hz, $\quad \frac{\nu_0}{c} = \frac{9\times10^9}{3\times10^{10}}$ cm^{-1} $= 0.3$ cm^{-1}

or $\lambda = \frac{c}{\nu_0} \simeq 3$ cm (μ-wave; X-band)

$\nu_0 = 35 \times 10^9$ Hz, $\quad \frac{\nu_0}{c} = \frac{35\times10^9}{3\times10^{10}}$ cm^{-1} $\cong 1$ cm^{-1}

or $\lambda = 1$ cm (μ-wave; Q-band)

$\nu_0 = 3\times10^9$ Hz, $\quad \frac{\nu_0}{c} = \frac{3\times10^9}{3\times10^{10}}$ cm^{-1} $= 0.1$ cm^{-1}

or $\lambda = \frac{c}{\nu_0} = 10$ cm (μ-wave; S-band)

$\nu_0 = 90\times10^9$ Hz, $\quad \frac{\nu_0}{c} = \frac{90\times10^9}{3\times10^{10}}$ cm^{-1} $= 3.0$ cm^{-1}

or $\lambda = 0.3$ cm (mm-wave; L-band)

or 3 mm

and varying H_0 to achieve resonance

X-Band H_0 = 3400 Gauss for $\nu_0 = 9.5 \times 10^9 Hz$

3300 Gauss for $\nu_0 = 9.2 \times 10^9 Hz$

Q-Band 12,500 Gauss for $\nu_0 = 35 \times 10^9 Hz$

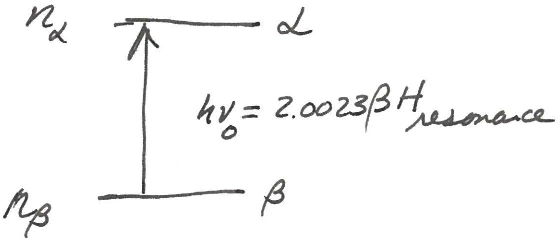
S-Band 1100 Gauss for $\nu_0 = 3.1 \times 10^9 Hz$

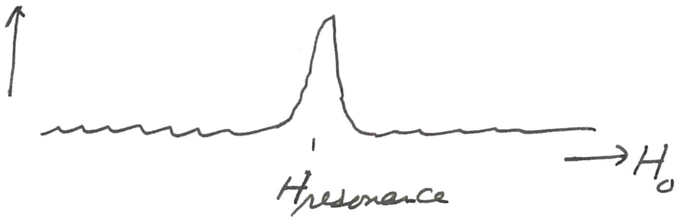
L-Band 3 Tesla for $\nu_0 = 90 \times 10^9 Hz$

or 90 GHz

1 Tesla $= 10^4$ Gauss

EPR or ESR

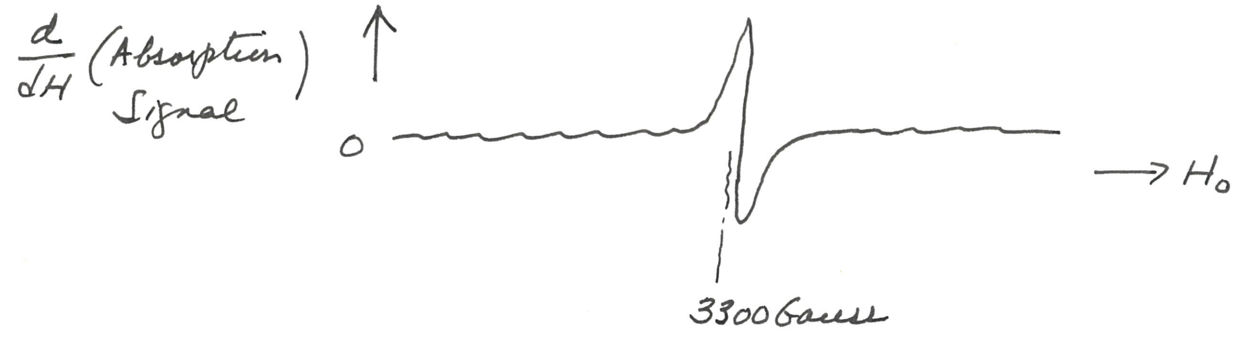




$= 3300$ Gauss for $\nu_0 = 9.2$ GHz

$$\boxed{I_{ESR} \propto (n_\beta - n_\alpha)}$$

Since in EPR spectroscopy, one typically modulates the applied $\vec{H}$ (in order to obtain an a.c. signal for amplification), the derivative of the absorption is recorded.



The above result could, of course, be obtained using the Landé g-factor.

$$\mathcal{H}_Z = -\vec{\mu}_S\cdot\vec{H} - \vec{\mu}_L\cdot\vec{H} = -\vec{\mu}_J\cdot\vec{H} = g_J\beta\vec{H}\cdot\vec{J}$$

where $g_J = \left\{1 + \dfrac{(J)(J+1) - L(L+1) + S(S+1)}{2J(J+1)}\right\}$

For $^2S_{1/2}$, $J=\frac{1}{2}$, $L=0$, $S=1/2$

$$\therefore\ g_J = \left\{1 + \frac{(\frac{1}{2})(\frac{3}{2}) - 0 + (\frac{1}{2})(\frac{3}{2})}{2(\frac{1}{2})(\frac{3}{2})}\right\} = 2$$

so that $\mathcal{H}_Z = 2\beta\vec{J}\cdot\vec{H}$ and $\boxed{W_Z = 2\beta m_J H_0 \quad \text{where } m_J = \pm\frac{1}{2}}$

(2) A more complicated example

N atom

Electronic configuration (ground state) $1s^2 2s^2 2p^3$

half-filled shell $(L=0)$ $\boxed{^4S_{3/2}}$

3 unpaired e^-, all ↑

$2S+1 = 2\times\frac{3}{2}+1 = 4$

$$g_J = 2$$

$$W_z = 2\beta m_J H_0 \,, \quad \text{but } m_J = \pm 3/2, \; \pm 1/2$$

(3) Another example

Trivalent rare-earth ions

Ce^{3+} electronic configuration $4f^1$

$L = 3$
$S = 1/2$

$^2F_{\frac{5}{2},\, 3/2}$

$^2F_{5/2}$ ground state

$$g_J = \left\{ 1 + \frac{(\frac{5}{2})(\frac{7}{2}) - (3)(4) + (\frac{1}{2})(\frac{3}{2})}{2(\frac{5}{2})(\frac{7}{2})} \right\} = 1 + \frac{(-10)}{70} = \frac{6}{7}$$

$$|\mu_J| = g_J \beta \sqrt{J(J+1)} = \frac{6}{7}\beta\sqrt{\frac{35}{4}} = 2.54\,\beta$$

$$|\mu_J|_{expt} = 2.51\,\beta$$

(4) Fine structure in 3p → 3S transition of Na

Elaborate on last lecture

For isolated atoms or ions

$$\mathcal{H}_{electronic} = \underset{\text{Kinetic energy of electrons}}{\sum_i \frac{p_i^2}{2m_e}} - \underset{\text{Coulomb attraction}}{\sum_i \frac{Ze^2}{r_i}} + \underset{\text{Electron repulsion}}{\sum_{i>j} \frac{e^2}{r_{ij}}}$$

$$+ \sum_i \zeta\, l_i \cdot s_i \nwarrow \text{spin-orbit interaction}$$

If ζ_i's are small (true for low Z atoms)

Then $L = \sum_i l_i$
$S = \sum_i s_i$ are good quantum #'s

So electronic wavefunction of atom or ion could be adequately described by

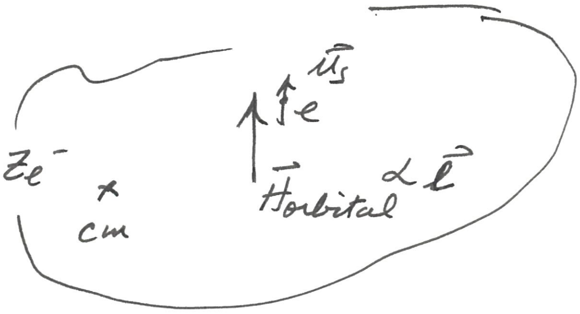
$$\psi = |\alpha L S M_L M_S\rangle$$

and atomic levels are described by TERMS ^{2S+1}L

$L =$	0	1	2	3	4
	S	P	D	F	G

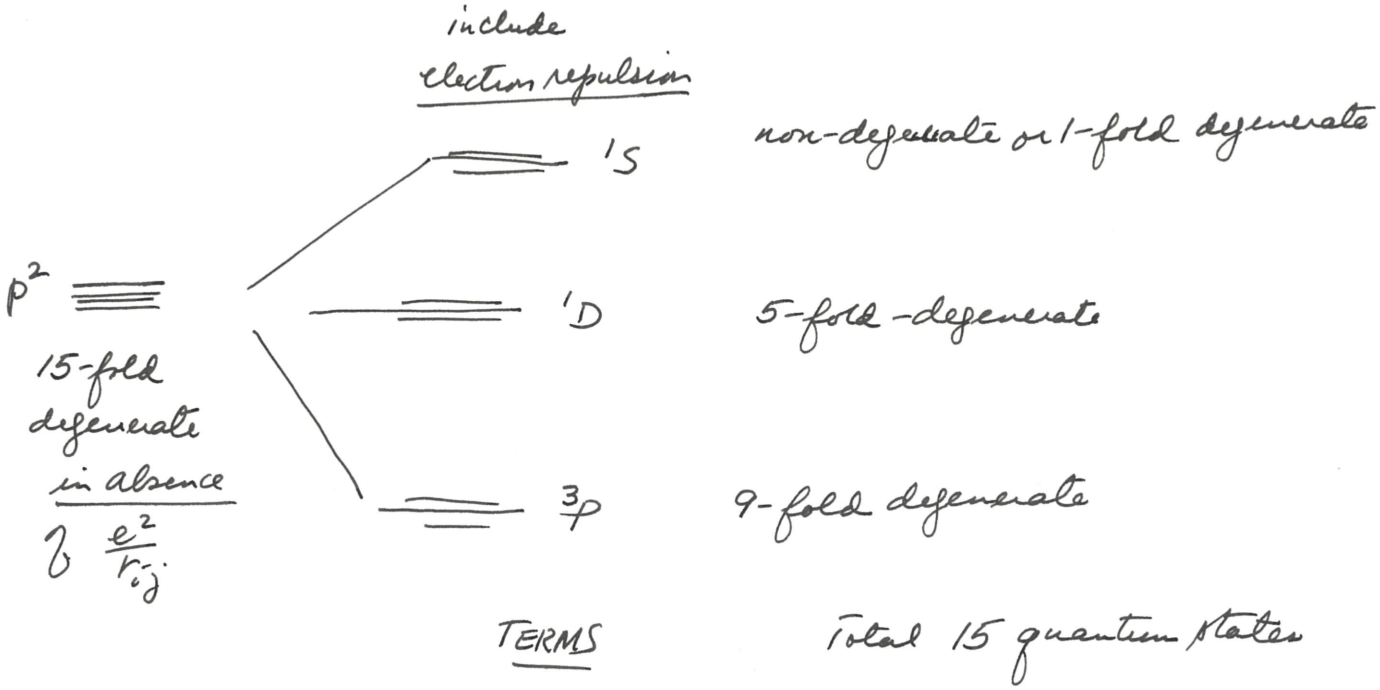
2S+1 refer to as spin multiplicity

There are $(2S+1)(2L+1)$ states associated with term, and they are all degenerate if there is no spin-orbit interaction (magnetic interaction arising from interaction of $\vec{\mu}_s$ with $\vec{H}$ orbital motion of system $(\propto \vec{l}\,)$



Illustrate above result by p^2 configuration

Possible terms are ^1S, ^1D and ^3P



Hund's rules

(1) States with higher S lie lower
(2e⁻ do not like to be in the same orbital and prefer to have spins in the same direction in different orbitals)

(2) States with higher L lie lower
(spread e⁻'s into different orbitals; 2e⁻ do not like to be in same orbital, even with spins paired)

(3) (1) & (2) above in decreasing importance

Introduce spin-orbit interaction

$$\mathcal{H}_{SO} = \sum_i \langle \xi(r_i)\rangle \vec{l}_i \cdot \vec{s}_i$$

where $\langle \xi(r_i)\rangle = -\frac{|e|\hbar^2}{2m_e^2c^2}\left\langle \frac{1}{r_i}\frac{\partial V}{\partial r_i}\right\rangle$

V is the electrostatic potential at electron due to nucleus

For $1e^-$ atom or ion,

$$V = \frac{Z|e|}{r}$$

so that $$\frac{1}{r}\frac{\partial V}{\partial r} = -\frac{Z|e|}{r^3}$$

and $$\langle \xi(r) \rangle = + \frac{|e|\hbar^2}{2m_e^2c^2}\left\langle \frac{Z}{r^3} \right\rangle$$

<u>Two points</u>: 1) $\langle \xi(r) \rangle$ always >0

2) Spin-orbit interaction more important for heavy elements

For hydrogen-like atom orbitals with quantum numbers n, l

$$\xi(n,l) = \langle \xi(r) \rangle = \int_0^\infty R_{nl}^2(r)\, \xi(r)\, dr$$

$$= \frac{e^2\hbar^2}{2m_e^2c^2} \frac{Z^4}{n^3 l(l+\frac{1}{2})(l+1)} \frac{1}{a_0^3}$$ ($a_0 \equiv$ Bohr radius)

For many electron atoms or ions,

$$\mathcal{H}_{SO} = \sum_k \xi(r_k)\, \vec{l}_k \cdot \vec{s}_k$$

$$\xrightarrow[\text{can be shown}]{} \lambda(\alpha, LS) \langle LS M_L M_S | \vec{L}\cdot\vec{S} | LS M_L M_S \rangle$$

independent of M_L & M_S

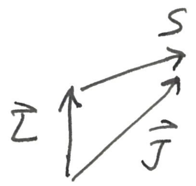
$$\longrightarrow \lambda(\alpha LS)\, \vec{L}\cdot\vec{S}$$

λ >0 for less than half-filled shells

<0 for greater than half-filled shells

(Hund's fine structure rule)

Spin-orbit energies are readily obtained by vector model



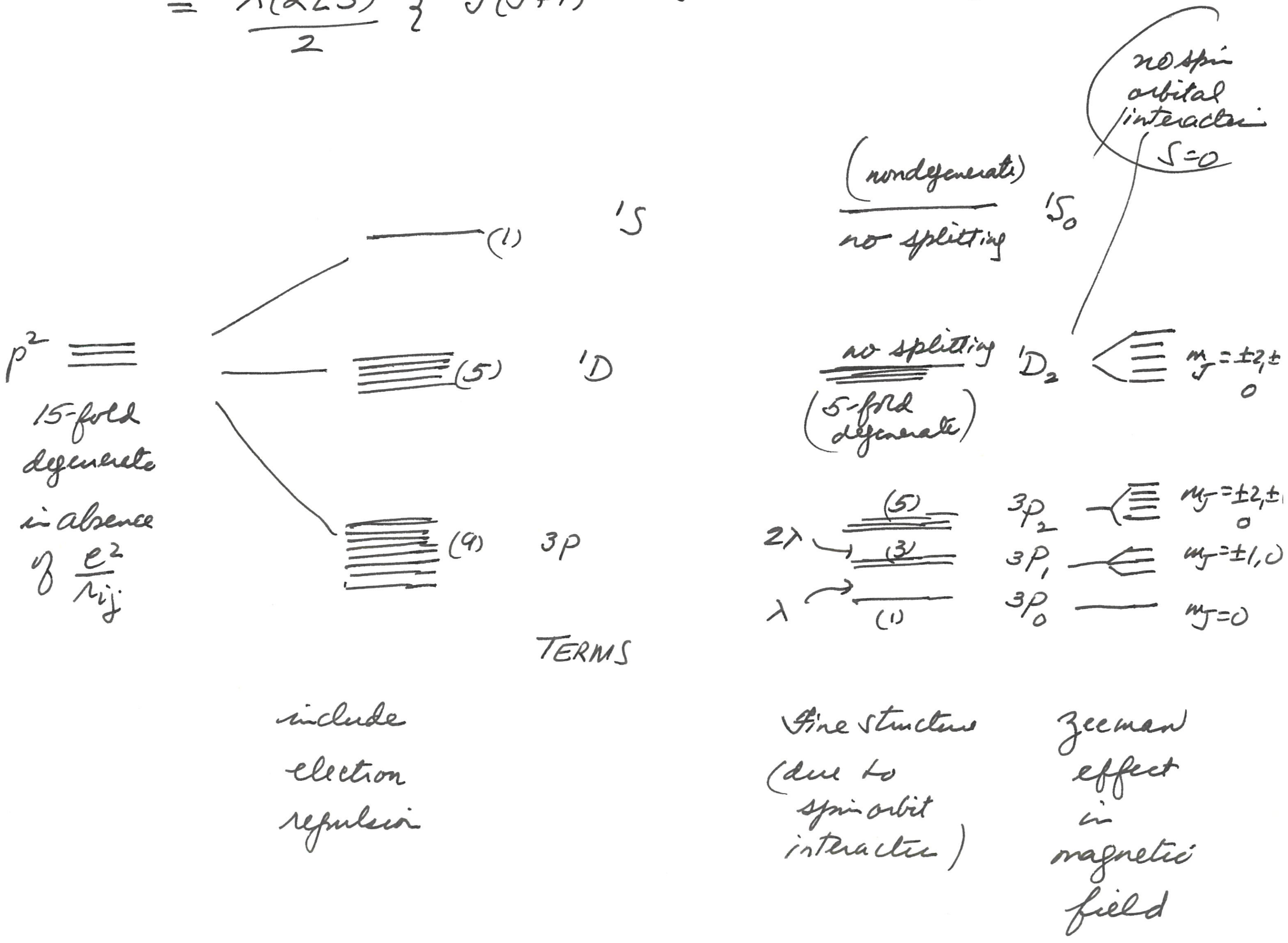
Since $J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$

$$\mathcal{H}_{SO} = \lambda\,\vec{L}\cdot\vec{S}$$

$$W_{SO} = \lambda(\alpha LS)\,\langle \alpha LS|\,\vec{L}\cdot\vec{S}\,|\alpha LS\rangle$$

$$= \lambda(\alpha LS)\,\langle \alpha LS|\,\frac{J^2-L^2-S^2}{2}\,|\alpha LS\rangle$$

$$= \frac{\lambda(\alpha LS)}{2}\left\{ J(J+1) - L(L+1) - S(S+1)\right\}$$



Return to Fine Structure in $3p \rightarrow 3s$ transition of Na

3p level

$L = l = 1$ and $J = 3/2,\ 1/2$

$S = s = 1/2$

^2P Term $\longrightarrow$ ^2P_J or $^2P_{3/2}$ and $^2P_{1/2}$

Spin-orbit energies

$^2P_{3/2}$:

$$\frac{\lambda(3p)}{2}\left[\left(\tfrac{3}{2}\right)\left(\tfrac{3}{2}+1\right) - (1)(1+1) - \tfrac{1}{2}\left(\tfrac{1}{2}+1\right)\right]$$

$$= \frac{\lambda(3p)}{2}\left[\frac{15}{4} - \frac{8}{4} - \frac{3}{4}\right] = \frac{\lambda(^3P)}{2} = \frac{1}{2}\zeta(3p)$$

$^2P_{1/2}$:

$$\frac{\lambda(^3P)}{2}\left[\left(\tfrac{1}{2}\right)\left(\tfrac{1}{2}+1\right) - (1)(1+1) - \tfrac{1}{2}\left(\tfrac{1}{2}+1\right)\right]$$

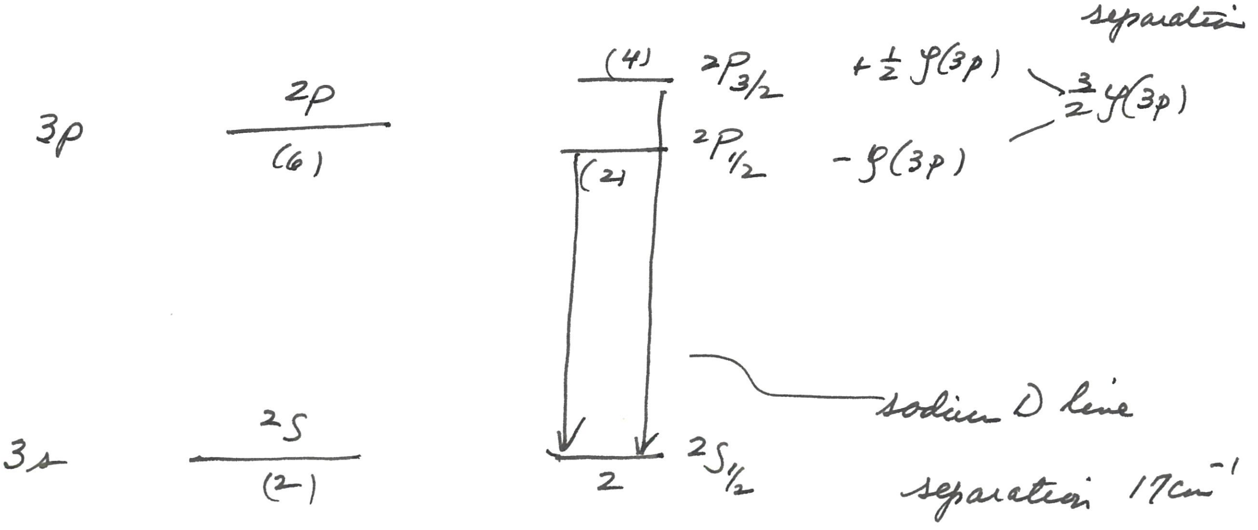
$$= -\lambda(^3P) = -\zeta(3p)$$

3s level

$L = 0$

$S = 1/2$

$^2S_{1/2}$ no spin-orbit interaction



Free Radicals

Molecules or Molecular Species with unpaired electrons

→ 1 unpaired electron in particular

$\therefore S = 1/2$

$L = 0$ because unlike in atoms or ions, coulomb field on electron no longer spherical

Accordingly, angular ^orbital^ momentum no longer conserved

$$\vec{\mu}_J = \vec{\mu}_S + \vec{\mu}_L = -(g_S \beta \vec{S} + g_L \beta \vec{L})$$

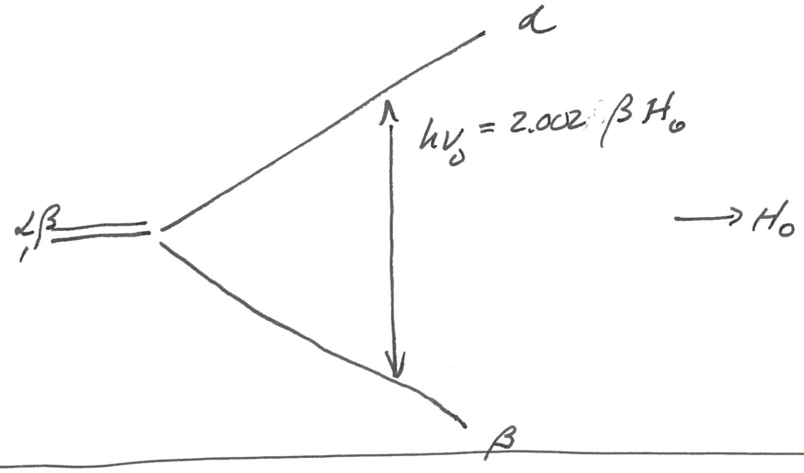
$$\cong -g_S \beta \vec{S} \quad \text{spin only} \quad \langle \vec{L} \rangle = 0$$

and
$$\mathcal{H}_Z = -\vec{\mu}_J \cdot \vec{H} = g_S \beta \vec{S} \cdot \vec{H} + g_L \beta \vec{L} \cdot \vec{H}$$

$$\cong g_S \beta \vec{S} \cdot \vec{H}$$

$$= g_S \beta S_z H_0$$

and
$$W_Z = 2.0023 \beta m_S H_0 \quad \text{with } m_S = \pm 1/2$$



$$\boxed{\text{Orbital angular momentum of unpaired electron is quenched}}$$