

Notes on Using the Faraday Effect to Measure Alkali Metal Vapor Density and Polarization

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Abstract

The Faraday Effect is the rotation of the plane of linearly polarized light propagating parallel to a magnetic field. The angle of rotation is proportional to the density of the medium, the magnitude of the applied magnetic field, and the polarization of the medium. By monitoring the amount of Faraday Rotation in the target cell, the relative populations of all the magnetic substates of the alkali metal vapor can be measured. Using this population distribution and the total amount of Faraday Rotation, the vapor density and polarization can be deduced. This tech note will develop some of the mathematical apparatus, discuss some practical aspects of the experimental procedure, and catalog some useful physical data and constants.

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1 A Brief Mathematical Description of Polarized Light

1.1 Introduction

We will use the Jones convention for defining the polarization state of the light (vectors) and the action of the various optical elements (matrices). This convention uses complex number representation and a linear polarization basis. The electric field component of an electromagnetic wave with propagation vector $\vec{k} = k\hat{z}$ at time t is

$$\vec{E}(z, t) = \vec{E}_0 e^{i(kz - \omega t)} \quad (1)$$

$$\vec{E}_0 = \vec{E}_{0x} + \vec{E}_{0y} \quad (2)$$

$$\vec{E}_{0x} = E_{0x} e^{i\alpha_x} \hat{E}_x \quad (3)$$

$$\vec{E}_{0y} = E_{0y} e^{i\alpha_y} \hat{E}_y \quad (4)$$

$$|E\rangle = \begin{bmatrix} E_{0x} e^{i\alpha_x} \\ E_{0y} e^{i\alpha_y} \end{bmatrix} \quad (5)$$

where the relative phase shift is $\alpha = \alpha_x - \alpha_y$. At a fixed point in space and over one period ($= \frac{2\pi}{\omega}$) in time, \vec{E} sweeps out an ellipse in the E_x - E_y plane given by (from Born and Wolf or Jackson)

$$\left(\frac{E_x}{E_{0x}}\right)^2 + \left(\frac{E_y}{E_{0y}}\right)^2 - 2\left(\frac{E_x}{E_{0x}}\right)\left(\frac{E_y}{E_{0y}}\right)\cos(\alpha) = \sin^2(\alpha) \quad (6)$$

Finally, only the time averaged intensity of the light is measured,

$$\langle I \rangle_{time} = \sqrt{\frac{\epsilon}{\mu}} \vec{E}^* \cdot \vec{E} = \sqrt{\frac{\epsilon}{\mu}} \langle E | E \rangle = \frac{c}{\mu} \langle B | B \rangle \quad (7)$$

1.2 Linear Polarization

For linear polarization, the relative phase shift is an integer multiple of half a wave,

$$\alpha = \pm n\pi \quad (8)$$

or in other words the two components are in phase. Eqn. (6) becomes degenerate,

$$\left(\frac{E_x}{E_{0x}}\right)^2 + \left(\frac{E_y}{E_{0y}}\right)^2 \mp 2\left(\frac{E_x}{E_{0x}}\right)\left(\frac{E_y}{E_{0y}}\right) = 0 \quad (9)$$

with solutions

$$\frac{E_y}{E_{0y}} = \mp \frac{E_x}{E_{0x}} \quad (10)$$

Two specific solutions are the orthogonal axes of the E_x - E_y plane which correspond to horizontal and vertical linearly polarized light. Horizontal linearly polarized light is denoted by

$$|\mathcal{P}\rangle = |x\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (11)$$

Vertical linearly polarized light is denoted by

$$|\mathcal{S}\rangle = |y\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (12)$$

Linear polarization at an angle θ counterclockwise from the E_x -axis is

$$|\theta\rangle = \begin{bmatrix} \cos(\theta) \\ \sin(\theta) \end{bmatrix} \quad (13)$$

1.3 Circular Polarization

When the relative phase shift is a quarter wave,

$$\alpha = \pm(2n + 1)\frac{\pi}{2} \quad (14)$$

and the magnitudes of the two components are identical,

$$E_{0x} = E_{0y} \quad (15)$$

then eqn. (6) reduces to a circle

$$E_x^2 + E_y^2 = 1 \quad (16)$$

The two orthogonal states are labeled by their helicity, namely the sign of the projection of the spin to the propagation vector. Right circularly polarized light,

$$|\mathcal{R}\rangle = |+\rangle = \frac{\sqrt{2}}{2} \begin{bmatrix} 1 \\ +i \end{bmatrix} \quad (17)$$

following the right hand rule such that the spin is parallel to the direction of propagation. Left circularly polarized light,

$$|\mathcal{L}\rangle = |-\rangle = \frac{\sqrt{2}}{2} \begin{bmatrix} 1 \\ -i \end{bmatrix} \quad (18)$$

is antiparallel. Note that the standard optics convention is opposite to the helicity convention. In the helicity convention, for right circularly polarized light, \vec{E} rotates counterclockwise in the E_x - E_y plane at a fixed point in space. In the standard optics convention, for right circularly polarized light, \vec{E} rotates counterclockwise in the E_x - E_y plane at a fixed moment in time as you move forward in the direction of propagation. See fig. (1). Unless otherwise noted, *the helicity convention* will be used.

1.4 Beam Splitting Polarizing Cubes

A beam splitting polarizing cube (BSPC) simply splits an incoming beam into it's two linearly polarized components. Once separated, the two beam paths are orthogonal, see fig. 2. The horizontal component \mathcal{P} is selected by

$$\hat{C}_{\mathcal{P}} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \quad (19)$$

and the vertical component \mathcal{S} is selected by

$$\hat{C}_{\mathcal{S}} = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \quad (20)$$

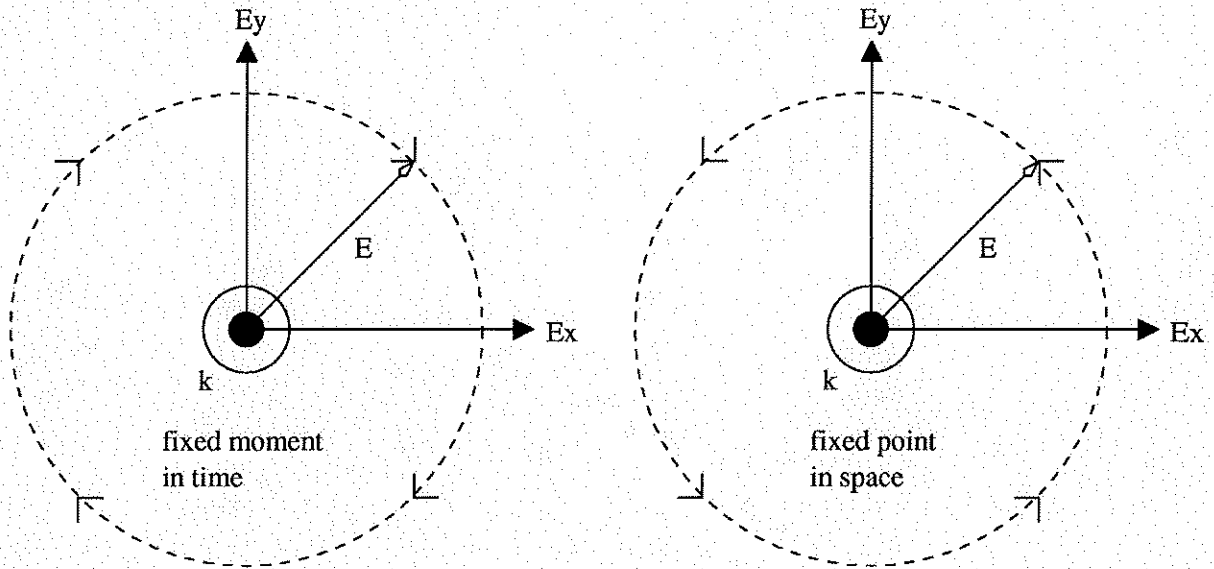


Figure 1: Right (helicity) circularly polarized light. Left: fixed time, forward in space. Right: fixed space, forward in time.

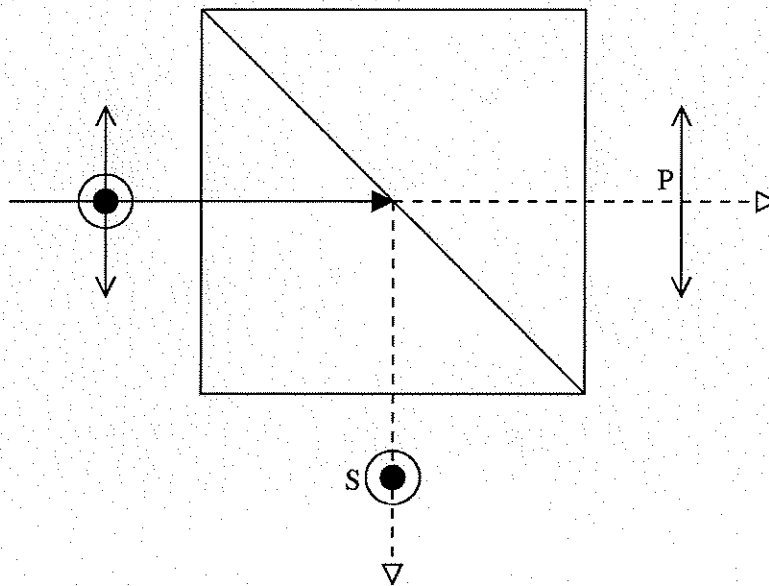


Figure 2: Top view of BSPC

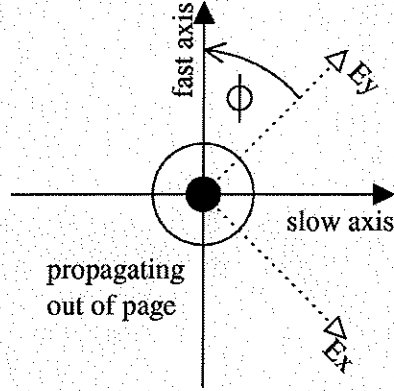


Figure 3: Coordinate System of a Waveplate

1.5 Waveplates

A waveplate is an optical element that has differing indices of refraction along two orthogonal axes, see fig. (3). This results in a net phase shift between the components of the polarization vector. First, the polarization vector has to be expressed in the basis of the waveplate. Therefore, a passive or coordinate system rotation of angle ϕ radians is performed,

$$\hat{R}(\phi) = \begin{bmatrix} \cos(\phi) & \sin(\phi) \\ -\sin(\phi) & \cos(\phi) \end{bmatrix} \quad (21)$$

followed by a relative phase retardation of β ,

$$\hat{W}(\beta) = \begin{bmatrix} \exp(i\beta) & 0 \\ 0 & 1 \end{bmatrix} \quad (22)$$

and finally a rotation back to the original basis, $\hat{R}(-\phi)$. The complete waveplate operator is thus

$$\hat{W}(\phi, \beta) = \hat{R}(-\phi)\hat{W}(\beta)\hat{R}(\phi) \quad (23)$$

(Note that for 1 complete wave, $\beta = 2\pi$.) Typically the fast axis is taken to be vertical. It is easy to show that for a quarter-waveplate at angle of 45°

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right) = \frac{1}{2} \begin{bmatrix} 1+i & -1+i \\ -1+i & 1+i \end{bmatrix} \quad (24)$$

and a half-waveplate at an angle of ϕ is simply a rotation by 2ϕ

$$\hat{W}_{\frac{1}{2}}(\phi) = \begin{bmatrix} \cos(2\phi) & -\sin(2\phi) \\ \sin(2\phi) & \cos(2\phi) \end{bmatrix} \quad (25)$$

To be explicit, a quarter-waveplate with its fast axis rotated counterclockwise by 45° turns horizontal linearly polarized light into right circularly polarized light,

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right)|\mathcal{P}\rangle = e^{i\frac{\pi}{4}}|\mathcal{R}\rangle \quad (26)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right)|\mathcal{R}\rangle = -|\mathcal{S}\rangle \quad (27)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right)|\mathcal{S}\rangle = e^{-i\frac{\pi}{4}}|\mathcal{L}\rangle \quad (28)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right)|\mathcal{L}\rangle = +|\mathcal{P}\rangle \quad (29)$$

and so forth following the simple pattern $\mathcal{P} \rightarrow \mathcal{R} \rightarrow \mathcal{S} \rightarrow \mathcal{L} \rightarrow \mathcal{P}$. An angle of -45° simply reverses the direction of the arrows. A half-waveplate, also at $\pm 45^\circ$, simply flips $\mathcal{P} \leftrightarrow \mathcal{S}$ and $\mathcal{L} \leftrightarrow \mathcal{R}$. Note that on the RHS of the first three equations, there is an overall phase factor which for our purposes is irrelevant.

2 Quantum Mechanical Treatment of an Alkali Metal Atom in a Magnetic Field

2.1 Notation & Conventions

All quantities will be denoted in SI. Angular momentum operators will be unitless:

$$\hat{J}^2 |J, m_J\rangle = J(J+1) |J, m_J\rangle \quad (30)$$

$$\hat{J}_z |J, m_J\rangle = m_J |J, m_J\rangle, m_J = -J..J \quad (31)$$

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \quad (32)$$

$$\hat{J}_\pm |J, m_J\rangle = \sqrt{J(J+1) - m_J(m_J \pm 1)} |J, m_J \pm 1\rangle \quad (33)$$

The statistical weight is denoted by $[J]$ and is defined by $[J] = 2J + 1$. The magnetic moment arising from spin will be written:

$$\vec{\mu}_S = \frac{\mu_S}{S} \vec{S} \quad (34)$$

$$\frac{\mu_S}{S} = g_S \mu_x \quad (35)$$

The magnetic moment arising from the orbital angular momentum will be written:

$$\vec{\mu}_L = \mu_L \vec{L} \quad (36)$$

$$\mu_L = g_L \mu_x \quad (37)$$

g is the unitless Landé factor. Note that the sign of the magnetic moment is carried implicitly in g or alternatively μ_J . For example, $g \approx -2$ for the electron, $g \approx 2(2.79)$ for the proton, and $g \approx 2(-1.91)$ for the neutron. The units are carried in μ_x , which is the Bohr magneton (μ_B) for the electron and the nuclear magneton (μ_N) for nuclei. The different angular momenta will be identified as:

- \vec{S} is the sum of the spins of each electron in the atom,
- \vec{L} is the sum of the orbital angular momenta of each electron in the atom,
- $\vec{J} (= \vec{L} + \vec{S})$ is the total electronic angular momentum of the atom,
- \vec{I} is the spin of the nucleus,
- $\vec{F} (= \vec{I} + \vec{J})$ is the total internal angular momentum of the atom.

Operators and matrices will be denoted by hats \hat{M} . Hamiltonians will be \mathcal{H} , energies will be E , frequencies will be ν (with units of Hz), and angular frequencies ω (with units of rad·Hz).

2.2 Hamiltonian of a Single Free Atom without Nuclear Spin

The basic structure of the atomic hamiltonian is summarized below, more details can be found in Woodgate:

1. The electrostatic interaction within the atom can be expressed as a central force and a non-central force.
2. The central force is a Coulomb interaction between the electrons and an effective nuclear charge.
3. The non-central force is the residual electrostatic repulsion among the electrons.
4. For most atoms, the non-central force dominates over the spin-orbit coupling.
5. Due to the dominance of the non-central forces, the orbital angular momenta of the electrons are correlated.

6. Because of Fermi-Dirac statistics, the total electronic spin and the total electronic orbital angular momentum is 0 for closed shells.
7. Because of spherical symmetry, the non-central force is independant of orbital angular momentum for closed shells. Therefore, the non-central force is important only for interactions between valence electrons.
8. In this limit, the spin-orbit coupling occurs between the total valence electronic spin and the total valence electronic orbital angular momentum.
9. Finally, all higher order interactions, such as those involving quadrapole moments, will be ignored.

Consider \mathcal{H}_0 with \mathcal{H}_{es} , electrostatic interaction, and \mathcal{H}_{so} , spin-orbit coupling:

$$\mathcal{H}_0 = \mathcal{H}_{es} + \mathcal{H}_{so} \quad (38)$$

Under the conditions described before, the form of \mathcal{H}_{so} is

$$\vec{J}^2 = (\vec{L} + \vec{S})^2 = \vec{L}^2 + 2\vec{L} \cdot \vec{S} + \vec{S}^2 \quad (39)$$

$$\mathcal{H}_{so} = A_{so} \vec{L} \cdot \vec{S} \quad (40)$$

$$= \frac{A_{so}}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \quad (41)$$

From the second form of \mathcal{H}_{so} above, it should be clear that the natural eigenbasis is the LS -coupling (Russell-Saunders) scheme $\{|J, m_J\rangle\}$. Each group of degenerate eigenstates is labeled by a Russell-Saunders term of the form

$$n^{2S+1}L_J \quad (42)$$

where n is the principal quantum number which labels the configuration. Usually n refers to the configuration that contains the valence electrons. L labels the valence orbital in the following way,

- $L = 0 \rightarrow L = S$
- $L = 1 \rightarrow L = P$
- $L = 2 \rightarrow L = D$, and so on

All closed shells have

$$\vec{L}_{shell} = \vec{S}_{shell} = 0 \quad (43)$$

Therefore, for an alkali metal atom, \vec{J} , \vec{L} , and \vec{S} all refer to the single valence electron. In the ground state, $J = \frac{1}{2}$ and the RS term is $n^2S_{\frac{1}{2}}$. The first two excited states have $J = \frac{1}{2}$ and $J = \frac{3}{2}$ and are labeled $n^2P_{\frac{1}{2}}$ and $n^2P_{\frac{3}{2}}$. Spin-orbit coupling breaks the degeneracy of these n^2P states and results in *fine structure*. Fine structure also refers to relativistic and other corrections. However, except for Hydrogen, these corrections are much smaller than the spin-orbit coupling. Regardless, these corrections only shift the energies collectively, independant of m_J and they do not mix the eigenstates. The transitions from the ground state to the first two excited states $n^2S_{\frac{1}{2}} \rightarrow n^2P_{\frac{1}{2}}$ and $n^2S_{\frac{1}{2}} \rightarrow n^2P_{\frac{3}{2}}$ are called the D1 and D2 transitions respectively.

2.3 Hamiltonian of a Single Atom without Nuclear Spin in a Magnetic Field

The Hamiltonian describing the atom in a magnetic field \vec{B} is

$$\mathcal{H} = \mathcal{H}_0 - \vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B} \quad (44)$$

$$= \mathcal{H}_{es} + \mathcal{H}_{so} - \vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B} \quad (45)$$

To recap:

- The first term \mathcal{H}_{es} contains all the terms that do not involve the electron spin.

- The second term is the spin-orbit interaction.
- The third and fourth terms are the Zeeman terms for the orbital and spin angular momentum respectively.

Using $\vec{B} = B\hat{z}$ & $J_z = L_z + S_z$:

$$\mathcal{H} = \mathcal{H}_{ee} + \mathcal{H}_{so} - \vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B} \quad (46)$$

$$= \mathcal{H}_{ee} + \frac{A_{so}}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) - g_L \mu_B L_z B - g_S \mu_B S_z B \quad (47)$$

$$= \mathcal{H}_{ee} + \frac{A_{so}}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) - g_L \mu_B (J_z - S_z) B - g_S \mu_B S_z B \quad (48)$$

$$= \mathcal{H}_{ee} + \left(-\frac{A_{so}}{2} (\vec{L}^2 + \vec{S}^2) - g_L \mu_B B J_z \right) + \mathcal{H}' \quad (49)$$

$$\mathcal{H}' = \frac{A_{so}}{2} \vec{J}^2 - (g_S - g_L) \mu_B B S_z \quad (50)$$

$$g_S \simeq -2 \quad (51)$$

$$g_L = \begin{cases} 0 & , L = 0 \\ -1 & , L > 0 \end{cases} \quad (52)$$

The hamiltonian is separated into three terms intentionally. States within a $n^{2S+1}L$ term with the same m_J but different J are mixed by the Zeeman interaction. This means that the first two terms are diagonal simultaneously in the $\{|J, m_J\rangle\}$ basis and the eigenbasis of \mathcal{H} . Therefore, only \mathcal{H}' has to be diagonalized.

2.4 Fine Structure Mixing in Alkali Metal Atoms

2.4.1 Energies

Let's specialize to the case $S = \frac{1}{2}$, since an alkali metal atom is being considered. J can be $L \pm \frac{1}{2}$. Therefore in the $\{|J, m_J\rangle\}$ basis, the S_z term is block diagonal with subblocks no greater than 2 by 2 in size. The 2 by 2 subblocks are made of the states with different J and same m_J . For the special case of $m_J = \pm J_{max} = \pm (L + \frac{1}{2})$, there are no other states to mix with. Thus, they reside in subblocks of size 1 by 1. This is true for the $m_J = \pm \frac{1}{2}$ states of the ground state term $n^2S_{\frac{1}{2}}$ and the $m_J = \pm \frac{3}{2}$ states of the excited state term $n^2P_{\frac{3}{2}}$. On the other hand, the $m_J = \pm \frac{1}{2}$ states of the terms $n^2P_{\frac{1}{2}, \frac{3}{2}}$ mix and therefore need to be diagonalized. To diagonalize \mathcal{H} , we only have to diagonalize each subblock of \mathcal{H}' ,

$$\mathcal{H}' = \frac{A_{so}}{2} \vec{J}^2 - (g_S - g_L) \mu_B B S_z \quad (53)$$

$$\hat{\mathcal{H}}' = \frac{A_{so}}{2} \begin{bmatrix} (L + \frac{1}{2})(L + \frac{3}{2}) & 0 \\ 0 & (L - \frac{1}{2})(L + \frac{1}{2}) \end{bmatrix} - (g_S - g_L) \mu_B B \begin{bmatrix} \alpha_+ & \beta_- \\ \beta_+ & \alpha_- \end{bmatrix} \quad (54)$$

$$\alpha_{\pm} = \left\langle L \pm \frac{1}{2}, m_J \left| \hat{S}_z \right| L \pm \frac{1}{2}, m_J \right\rangle \quad (55)$$

$$\beta_{\pm} = \left\langle L \mp \frac{1}{2}, m_J \left| \hat{S}_z \right| L \pm \frac{1}{2}, m_J \right\rangle \quad (56)$$

The first term can be simplified to give:

$$\frac{A_{so}}{2} \hat{J}^2 = \frac{A_{so}}{2} \left(L + \frac{1}{2} \right) \left(L + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \quad (57)$$

α_{\pm} & β_{\pm} in the second term are most easily calculated in the $\{|L, m_L\rangle |S, m_S\rangle\}$ basis:

$$|L, m_L\rangle |S, m_S\rangle = |m_L, m_S\rangle \quad (58)$$

$$|J, m_J\rangle = \sum |m_L, m_S\rangle \langle m_L, m_S | J, m_J \rangle \quad (59)$$

Using known formulas for Clebsch-Gordon coefficients (Cohen-Tannoudji?):

$$\begin{aligned}\left\langle m_J \mp \frac{1}{2}, \pm \frac{1}{2} \mid L + \frac{1}{2}, m_J \right\rangle &= \frac{1}{\sqrt{2L+1}} \sqrt{L + \frac{1}{2} \pm m_J} \\ \left\langle m_J \mp \frac{1}{2}, \pm \frac{1}{2} \mid L - \frac{1}{2}, m_J \right\rangle &= \frac{\mp 1}{\sqrt{2L+1}} \sqrt{L + \frac{1}{2} \mp m_J}\end{aligned}\quad (60)$$

For α_{\pm} :

$$\alpha_{\pm} = \left\langle L \pm \frac{1}{2}, m_J \mid \hat{S}_z \mid L \pm \frac{1}{2}, m_J \right\rangle \quad (61)$$

$$\begin{aligned}&= \sum_{m_S, m'_S = -\frac{1}{2}}^{\frac{1}{2}} \langle m_J - m'_S, m'_S \mid \hat{S}_z \mid m_J - m_S, m_S \rangle \\ &\quad \times \langle J, m_J \mid m_J - m'_S, m'_S \rangle \langle m_J - m_S, m_S \mid J, m_J \rangle\end{aligned}\quad (62)$$

$$= \sum_{m_S = -\frac{1}{2}}^{\frac{1}{2}} m_S |\langle m_J - m_S, m_S \mid J, m_J \rangle|^2, \quad J = L \pm \frac{1}{2} \quad (63)$$

$$= \frac{1}{2} \left(\frac{L + \frac{1}{2} \pm m_J - L - \frac{1}{2} \pm m_J}{2L+1} \right) \quad (64)$$

$$= \pm \left(\frac{m_J}{2L+1} \right) = \pm(\alpha) \quad (65)$$

For β_{\pm} :

$$\beta_{\pm} = \left\langle L \mp \frac{1}{2}, m_J \mid \hat{S}_z \mid L \pm \frac{1}{2}, m_J \right\rangle \quad (66)$$

$$\begin{aligned}&= \sum_{m_S, m'_S = -\frac{1}{2}}^{\frac{1}{2}} \langle m_J - m'_S, m'_S \mid \hat{S}_z \mid m_J - m_S, m_S \rangle \\ &\quad \times \left\langle L \mp \frac{1}{2}, m_J \mid m_J - m'_S, m'_S \right\rangle \left\langle m_J - m_S, m_S \mid L \pm \frac{1}{2}, m_J \right\rangle\end{aligned}\quad (67)$$

$$\begin{aligned}&= \sum_{m_S = -\frac{1}{2}}^{\frac{1}{2}} m_S \left\langle L \mp \frac{1}{2}, m_J \mid m_J - m_S, m_S \right\rangle \\ &\quad \times \left\langle m_J - m_S, m_S \mid L \pm \frac{1}{2}, m_J \right\rangle\end{aligned}\quad (68)$$

$$\begin{aligned}&= +\frac{1}{2} \left(\frac{-\sqrt{(L + \frac{1}{2} \mp m_J)(L + \frac{1}{2} \pm m_J)}}{2L+1} \right) \\ &\quad - \frac{1}{2} \left(\frac{+\sqrt{(L + \frac{1}{2} \pm m_J)(L + \frac{1}{2} \mp m_J)}}{2L+1} \right)\end{aligned}\quad (69)$$

$$= - \left(\frac{\sqrt{(L + \frac{1}{2})^2 - m_J^2}}{2L+1} \right) = -(\beta) \quad (70)$$

To solve for the energies, we only to diagonalize the last term in \mathcal{H}' :

$$\mathcal{H}' = \frac{A_{so}}{2} \left(L + \frac{1}{2} \right) \left(L + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right)$$

$$\begin{aligned}
& -(g_S - g_L) \mu_B B \begin{bmatrix} \alpha_+ & \beta_- \\ \beta_+ & \alpha_- \end{bmatrix} \\
& = \frac{A_{so}}{2} \left(L + \frac{1}{2}\right) \left(L + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\right)
\end{aligned} \tag{71}$$

$$\begin{aligned}
& + (g_L - g_S) \mu_B B \begin{bmatrix} \alpha & -\beta \\ -\beta & -\alpha \end{bmatrix} \\
& = \frac{A_{so}}{2} \left(L + \frac{1}{2}\right)^2 + \frac{A_{so}}{2} \left(L + \frac{1}{2}\right)
\end{aligned} \tag{72}$$

$$\times \left(\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + 2 \frac{(g_L - g_S) \mu_B B}{A_{so} \left(L + \frac{1}{2}\right)} \begin{bmatrix} \alpha & -\beta \\ -\beta & -\alpha \end{bmatrix} \right) \tag{73}$$

$$= \frac{A_{so}}{2} \left(L + \frac{1}{2}\right)^2 + \frac{A_{so}}{2} \left(L + \frac{1}{2}\right) \begin{bmatrix} 1 + 2\alpha y & -2\beta y \\ -2\beta y & -(1 + 2\alpha y) \end{bmatrix} \tag{74}$$

$$y = (g_L - g_S) \frac{\mu_B B}{A_{so} \left(L + \frac{1}{2}\right)} \tag{75}$$

This is done by solving the secular equation:

$$0 = \det(\hat{M} - \hat{I}\lambda) \tag{76}$$

$$0 = \begin{vmatrix} 1 + 2\alpha y - \lambda & -2\beta y \\ -2\beta y & -(1 + 2\alpha y + \lambda) \end{vmatrix} \tag{77}$$

$$0 = -(1 + 2\alpha y - \lambda)(1 + 2\alpha y + \lambda) - (2\beta y)^2 \tag{78}$$

$$0 = \lambda^2 - (1 + 2\alpha y)^2 - (2\beta y)^2 \tag{79}$$

$$\lambda = \pm \sqrt{(1 + 2\alpha y)^2 + (2\beta y)^2} \tag{80}$$

$$\lambda = \pm \sqrt{1 + 4\alpha y + 4(\alpha^2 + \beta^2)y^2} \tag{81}$$

Using the values 65 and 70, the following useful relations are derived:

$$\alpha^2 + \beta^2 = \frac{m_J^2 + \left(L + \frac{1}{2}\right)^2 - m_J^2}{(2L + 1)^2} \tag{82}$$

$$= \frac{\left(L + \frac{1}{2}\right)^2}{2^2 \left(L + \frac{1}{2}\right)^2} \tag{83}$$

$$= \frac{1}{4} \tag{84}$$

$$4\alpha^2 + 4\beta^2 = 1 \tag{85}$$

We get the eigenvalues:

$$\pm \left(\lambda = \sqrt{1 + 4\alpha y + y^2} \right) \tag{86}$$

The total energy is therefore:

$$E = E_0 - \frac{A_{so}}{2} \left(L(L+1) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right) - g_L \mu_B m_J B + E' \tag{87}$$

$$E' = \frac{A_{so}}{2} \left(L + \frac{1}{2}\right)^2 \pm \frac{A_{so}}{2} \left(L + \frac{1}{2}\right) \lambda \tag{88}$$

The $\pm \lambda$ eigenvalue is used for states evolving from the $J = L \pm \frac{1}{2}$ term. In the zero field case, $B = 0$, we find the spin-orbit (fine structure) splitting between the two terms is:

$$\Delta E = \frac{A_{so}(2L + 1)}{2} = h\nu_{so} \tag{89}$$

Relabeling the energies without spin-orbit coupling and without field as E_0^L and relating A_{so} to the zero field spin-orbit splitting $h\nu_{so}$, we get:

$$E = E_0^L - \frac{h\nu_{so}}{2(2L+1)} - g_L\mu_B m_J B \pm \frac{h\nu_{so}}{2} \sqrt{1 + \frac{4m_J}{2L+1}y + y^2} \quad (90)$$

$$y = (g_L - g_S) \frac{\mu_B B}{h\nu_{so}} \quad (91)$$

When $L = 0$, $g_L = 0$ and *the positive root* of the square root is taken. Note that y is a unitless quantity that gives a relative measure of the Zeeman interaction wrt the spin-orbit interaction. For $y \approx 1$, $B \approx 510T$, the Zeeman interaction is comparable to the spin-orbit interaction!

We'll discuss three special cases now (still with $S = \frac{1}{2}$). If $L = 0$, then the energies for the $n^2S_{\frac{1}{2}}$ term are:

$$L = 0 \rightarrow J = S \rightarrow m_J = m_S = \pm \frac{1}{2} \quad (92)$$

$$y = -\frac{g_S\mu_B B}{h\nu_{so}} \quad (93)$$

$$E_{\pm\frac{1}{2}} = E_0^0 - \frac{h\nu_{so}}{2} + \frac{h\nu_{so}}{2} \sqrt{1 \pm \frac{4}{2}y + y^2} \quad (94)$$

$$= E_0^0 - \frac{h\nu_{so}}{2} + \frac{h\nu_{so}}{2} (1 \pm y) \quad (95)$$

$$= E_0^0 \pm \frac{h\nu_{so}}{2} \left(\frac{-g_S\mu_B B}{h\nu_{so}} \right) \quad (96)$$

$$= E_0^0 \mp \frac{g_S}{2} \mu_B B = E_0^0 - g_S\mu_B m_J \quad (97)$$

If $L > 0$, then the energies of the $m_J = \pm(L + \frac{1}{2})$ states in the $J = L + \frac{1}{2}$ term are:

$$E_{\pm(L+\frac{1}{2})} = E_0^L - \frac{h\nu_{so}}{2(2L+1)} \pm \mu_B \left(L + \frac{1}{2} \right) B + \frac{h\nu_{so}}{2} \sqrt{1 \pm \frac{4(L+\frac{1}{2})}{2L+1}y + y^2} \quad (98)$$

$$= E_0^L - \frac{h\nu_{so}}{2(2L+1)} \pm \mu_B \left(L + \frac{1}{2} \right) B + \frac{h\nu_{so}}{2} \sqrt{1 \pm 2y + y^2} \quad (99)$$

$$= E_0^L - \frac{h\nu_{so}}{2(2L+1)} \pm \mu_B \left(L + \frac{1}{2} \right) B + \frac{h\nu_{so}}{2} (1 \pm y) \quad (100)$$

$$= E_0^L + \left(\frac{L}{2L+1} \right) h\nu_{so} \pm \mu_B \left(L + \frac{1}{2} \right) B \mp \frac{h\nu_{so}}{2} (1 + g_S) \frac{\mu_B B}{h\nu_{so}} \quad (101)$$

$$= E_0^L + \left(\frac{L}{2L+1} \right) h\nu_{so} \pm \mu_B B \left(L + \frac{1}{2} - \frac{1 + g_S}{2} \right) \quad (102)$$

$$= E_0^L + \left(\frac{L}{2L+1} \right) h\nu_{so} \pm \left(L - \frac{g_S}{2} \right) \mu_B B \quad (103)$$

At low field ($B \ll 510T$, for Rubidium), to first order in B , the energies for the $J = L \pm \frac{1}{2}$ terms are:

$$E \simeq E_0^L - \frac{h\nu_{so}}{2(2L+1)} - g_L\mu_B m_J B \pm \frac{h\nu_{so}}{2} \left(1 + \frac{2m_J}{2L+1}y \right) \quad (104)$$

$$\simeq E_0^L + h\nu_{so} \left(-\frac{1}{2(2L+1)} \pm \frac{1}{2} \right) + \left(-g_L \pm \frac{g_L - g_S}{2L+1} \right) \mu_B B m_J \quad (105)$$

$$\simeq E_0^L \pm \left(\frac{L + \frac{1}{2} \mp \frac{1}{2}}{2L+1} \right) h\nu_{so} + \left(-g_L \pm \frac{g_L - g_S}{2L+1} \right) \mu_B B m_J \quad (106)$$

2.4.2 Eigenstates

As noted before, the B -field mixes states with the same L , the same m_J , but different J . Therefore, we represent $\{|m_J^\pm\rangle\}$ in the $\{|J, m_J\rangle\}$ basis:

$$|m_J^\pm\rangle = a_1^\pm \left|L + \frac{1}{2}, m_J\right\rangle + a_2^\pm \left|L - \frac{1}{2}, m_J\right\rangle \quad (107)$$

The values for $a_{1,2}$ come from the diagonalization of eqn 74 where λ_\pm are the eigenvalues given by eqn 86 and α and β are defined by eqns 65 and 70:

$$\hat{M}|a\rangle = \pm\lambda|a\rangle \quad (108)$$

$$1 = a_1^2 + a_2^2 \quad (109)$$

$$a_1^\pm = \frac{2\beta y}{\sqrt{(1 + 2\alpha y \mp \lambda)^2 + 4\beta^2 y^2}} \quad (110)$$

$$a_2^\pm = \frac{1 + 2\alpha y \mp \lambda}{\sqrt{(1 + 2\alpha y \mp \lambda)^2 + 4\beta^2 y^2}} \quad (111)$$

$$a_1^\pm = \pm a_2^\mp \quad (112)$$

The \pm sign is taken for states evolving from the $J = L \pm \frac{1}{2}$ term. Note that eqn (112) is a consequence of orthogonality. Even though J is not a rigorously good quantum number like m_J , at low fields it is still very good. This can be seen by expanding $a_{1,2}$ for low field (to first order in y). The low field expansions are performed using the following useful relations:

$$\sqrt{1+x} \simeq 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \frac{1}{16}x^3 - \frac{5}{128}x^4 + \mathcal{O}(x^5) \quad (113)$$

$$\frac{1}{\sqrt{1+x}} \simeq 1 - \frac{1}{2}x + \frac{3}{8}x^2 - \frac{5}{16}x^3 + \frac{35}{128}x^4 + \mathcal{O}(x^5) \quad (114)$$

$$\begin{aligned} \sqrt{1+ax+bx^2} &\simeq 1 + \left(\frac{a}{2}\right)x + \left(\frac{b}{2} - \frac{a^2}{8}\right)x^2 + \left(\frac{a^3}{16} - \frac{ab}{4}\right)x^3 \\ &\quad + \left(\frac{3a^2b}{16} - \frac{b^2}{8} - \frac{5a^4}{128}\right)x^4 + \mathcal{O}(x^5) \end{aligned} \quad (115)$$

$$\begin{aligned} \frac{1}{\sqrt{1+ax+bx^2}} &\simeq 1 - \left(\frac{a}{2}\right)x + \left(\frac{3a^2}{8} - \frac{b}{2}\right)x^2 + \left(\frac{3ab}{4} - \frac{5a^3}{16}\right)x^3 \\ &\quad + \left(\frac{35a^4}{128} + \frac{3b^2}{8} - \frac{15a^2b}{16}\right)x^4 + \mathcal{O}(x^5) \end{aligned} \quad (116)$$

First we'll expand the eigenvalue to fourth order in field (y):

$$\lambda = \sqrt{1 + 4\alpha y + y^2} \quad (117)$$

$$\begin{aligned} &\simeq 1 + 2\alpha y + \left(\frac{1}{2} - 2\alpha^2\right)y^2 + (4\alpha^3 - \alpha)y^3 \\ &\quad + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right)y^4 + \mathcal{O}(y^5) \end{aligned} \quad (118)$$

$$\simeq 1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right)y^4 + \mathcal{O}(y^5) \quad (119)$$

Now let's consider the denominator of $a_{1,2} = \frac{n_{1,2}}{\sqrt{d}}$:

$$d = (1 + 2\alpha y \mp \lambda)^2 + 4\beta^2 y^2 \quad (120)$$

$$= 1 + 4\alpha^2 y^2 + \lambda^2 + 4\alpha y \mp 2\lambda \mp 4\alpha y \lambda + 4\beta^2 y^2 \quad (121)$$

$$= 1 + 4\alpha^2 y^2 + 1 + 4\alpha y + y^2 + 4\alpha y \mp 2\lambda \mp 4\alpha y \lambda + 4\beta^2 y^2 \quad (122)$$

$$= 2 + 8\alpha y + 2y^2 \mp 2\lambda \mp 4\alpha y \lambda \quad (123)$$

$$= 2 + 8\alpha y + 2y^2 \mp 2(1 + 2\alpha y) \lambda \quad (124)$$

$$\simeq 2 + 8\alpha y + 2y^2 \mp 2(1 + 2\alpha y) \times \left(1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right) y^4\right) \quad (125)$$

$$\simeq 2 + 8\alpha y + 2y^2 \mp 2(2\alpha y + 4\alpha^2 y^2 + 4\alpha\beta^2 y^3 - 8\beta^2 \alpha^2 y^4) \mp 2\left(1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right) y^4\right) \quad (126)$$

$$\simeq 2 + 8\alpha y + 2y^2 \mp 2(1 + 4\alpha y + (4\alpha^2 + 2\beta^2) y^2) \mp 2\left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2 \alpha^2\right) y^4 \quad (127)$$

$$\simeq 2 + 8\alpha y + 2y^2 \mp (2 + 8\alpha y + (2 - 4\beta^2) y^2) \mp 2\left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2 \alpha^2\right) y^4 \quad (128)$$

$$d_+ \simeq 2 + 8\alpha y + 2y^2 - 2 - 8\alpha y - (2 - 4\beta^2) y^2 - 2\left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2 \alpha^2\right) y^4 \quad (129)$$

$$\simeq 4\beta^2 y^2 - 2\left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2 \alpha^2\right) y^4 \quad (130)$$

$$\simeq 4\beta^2 y^2 - 2\left(3\alpha^2 - \frac{1}{8} - 10\left(\frac{1}{16} - \beta^4 - 2\alpha^2 \beta^2\right) - 8\beta^2 \alpha^2\right) y^4 \quad (131)$$

$$\simeq 4\beta^2 y^2 - 2\left(3\alpha^2 - \frac{3}{4} + 10\beta^4 + 12\alpha^2 \beta^2\right) y^4 \quad (132)$$

$$\simeq 4\beta^2 y^2 - (-6\beta^2 + 20\beta^4 + 24\alpha^2 \beta^2) y^4 \quad (133)$$

$$\simeq 4\beta^2 y^2 \left(1 + \frac{6}{4} y^2 - 5\beta^2 y^2 - 6\alpha^2 y^2\right) \quad (134)$$

$$\simeq 4\beta^2 y^2 (1 + 6\alpha^2 y^2 + 6\beta^2 y^2 - 5\beta^2 y^2 - 6\alpha^2 y^2) \quad (135)$$

$$\simeq 4\beta^2 y^2 (1 + \beta^2 y^2) \quad (136)$$

$$d_- \simeq 2 + 8\alpha y + 2y^2 + 2 + 8\alpha y + (2 - 4\beta^2) y^2 + 2\left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2 \alpha^2\right) y^4 \quad (137)$$

$$\simeq 4 + 16\alpha y + 4(1 - \beta^2) y^2 \quad (138)$$

Note that a fourth order expansion of λ was needed for d_+ , but not for d_- . Now let's expand the inverse square root $\frac{1}{\sqrt{d}}$:

$$d_+^{-\frac{1}{2}} \simeq \left(\sqrt{4\beta^2 y^2 (1 + \beta^2 y^2)}\right)^{-1} \quad (139)$$

$$\simeq \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2\right) \quad (140)$$

$$d_-^{-\frac{1}{2}} \simeq (4 + 16\alpha y + 4(1 - \beta^2) y^2)^{-\frac{1}{2}} \quad (141)$$

$$\simeq \frac{1}{2} (1 + 4\alpha y + (1 - \beta^2) y^2)^{-\frac{1}{2}} \quad (142)$$

$$\simeq \frac{1}{2} \left(1 - \left(\frac{4\alpha}{2}\right) y + \left(\frac{3 \cdot 16\alpha^2}{8} - \frac{1 - \beta^2}{2}\right) y^2\right) \quad (143)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(6\alpha^2 - \frac{1}{2} + \frac{\beta^2}{2} \right) y^2 \right) \quad (144)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(\frac{6}{4} - 6\beta^2 - \frac{1}{2} + \frac{\beta^2}{2} \right) y^2 \right) \quad (145)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2 \right) y^2 \right) \quad (146)$$

Note that all of the square roots take the positive root. Now let's consider the numerators:

$$n_1^\pm = 2\beta y \quad (147)$$

$$n_2^\pm = 1 + 2\alpha y \mp \lambda \quad (148)$$

$$\simeq 1 + 2\alpha y \mp (1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3) \quad (149)$$

$$n_2^+ \simeq 1 + 2\alpha y - 1 - 2\alpha y - 2\beta^2 y^2 + 4\beta^2 \alpha y^3 \quad (150)$$

$$\simeq -2\beta^2 y^2 + 4\beta^2 \alpha y^3 \quad (151)$$

$$n_2^- \simeq 1 + 2\alpha y + 1 + 2\alpha y + 2\beta^2 y^2 \quad (152)$$

$$\simeq 2 + 4\alpha y + 2\beta^2 y^2 \quad (153)$$

Finally let's calculate the the mixing coefficients:

$$a_1^+ = \frac{n_1^+}{\sqrt{d_+}} = \frac{2\beta y}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} \quad (154)$$

$$\simeq (2\beta y) \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2 \right) \quad (155)$$

$$\simeq 1 - \frac{\beta^2}{2} y^2 \quad (156)$$

$$a_2^+ = \frac{n_2^+}{\sqrt{d_+}} = \frac{1 + 2\alpha y - \lambda}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} \quad (157)$$

$$\simeq (-2\beta^2 y^2 + 4\beta^2 \alpha y^3) \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2 \right) \quad (158)$$

$$\simeq -(\beta y - 2\alpha \beta y^2) \left(1 - \frac{\beta^2}{2} y^2 \right) \quad (159)$$

$$\simeq -\beta y + 2\alpha \beta y^2 \quad (160)$$

$$a_1^- = \frac{n_1^-}{\sqrt{d_-}} = \frac{2\beta y}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \quad (161)$$

$$\simeq (2\beta y) \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2 \right) y^2 \right) \quad (162)$$

$$\simeq \beta y - 2\alpha \beta y^2 \quad (163)$$

$$a_2^- = \frac{n_2^-}{\sqrt{d_-}} = \frac{1 + 2\alpha y + \lambda}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \quad (164)$$

$$\simeq (2 + 4\alpha y + 2\beta^2 y^2) \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2 \right) y^2 \right) \quad (165)$$

$$\simeq (1 + 2\alpha y + \beta^2 y^2) \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2 \right) y^2 \right) \quad (166)$$

$$\simeq 1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2 \right) y^2 + 2\alpha y - 4\alpha^2 y^2 + \beta^2 y^2 \quad (167)$$

$$\simeq 1 + \left(1 - \frac{11}{2}\beta^2 - 4\alpha^2 + \beta^2 \right) y^2 \quad (168)$$

$$\simeq 1 + \left(1 - \frac{11}{2}\beta^2 + 4\beta^2 - 1 + \beta^2\right) y^2 \quad (169)$$

$$\simeq 1 - \frac{\beta^2}{2} y^2 \quad (170)$$

This gives, for the $\{|m_J^\pm\rangle\}$ states to first order in y :

$$\beta y = \frac{\sqrt{(L + \frac{1}{2})^2 - m_J^2}}{2L + 1} (g_L - g_S) \frac{\mu_B B}{h\nu_{so}} \quad (171)$$

$$|m_J^\pm\rangle = \left|L \pm \frac{1}{2}, m_J\right\rangle \mp \beta y \left|L \mp \frac{1}{2}, m_J\right\rangle \quad (172)$$

2.5 Hamiltonian of a Single Free Atom with Nuclear Spin

Adding nuclear spin \vec{I} to the system introduces the hyperfine interaction:

$$\mathcal{H}_{hfs} = A_{hfs} \vec{I} \cdot \vec{J} \quad (173)$$

A_{hfs} hides all the factors that don't depend on the spins. IJ -coupling causes states with different m_J to mix. Since $m_F (= m_I + m_J)$ is conserved, the $\{|F, m_F\rangle\}$ states form a natural eigenbasis. This is more easily seen with a little arithmetic:

$$\vec{F}^2 = (\vec{I} + \vec{J})^2 = \vec{I}^2 + 2\vec{I} \cdot \vec{J} + \vec{J}^2 \quad (174)$$

$$\mathcal{H}_{hfs} = \frac{A_{hfs}}{2} (\vec{F}^2 - \vec{I}^2 - \vec{J}^2) \quad (175)$$

The hyperfine interaction splits the $^2S_{1/2}$, $^2P_{1/2}$, and $^2P_{3/2}$ terms into 2, 2, and 4 manifolds which are labeled by F . This is called the *hyperfine structure*. Note that many calculations to follow will be identical to those done for the fine structure mixing. The following table depicts the analogy.

<i>Spin-Orbit</i>	<i>Hyperfine</i>
\vec{L}	\vec{I}
\vec{S}	\vec{J}
\vec{J}	\vec{F}
mixes states with different J	mixes states with different F
mixes states with same m_J	mixes states with same m_F
A_{so}	A_{hfs}
$\nu_{so} \approx 10^7$ MHz	$\nu_{hfs} \approx 10^3$ MHz
y	x
$y \approx 1 \rightarrow B \approx 10^7$ gauss	$x \approx 1 \rightarrow B \approx 10^3$ gauss

2.6 Hamiltonian of a Single Atom with Nuclear Spin in a Magnetic Field

The Hamiltonian describing the atom in a magnetic field \vec{B} is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{hfs} - \vec{\mu}_I \cdot \vec{B} - \vec{\mu}_J \cdot \vec{B} \quad (176)$$

To recap:

- The first term H_0 contains all the terms that do not involve the nuclear spin.
- The second term is the hyperfine interaction.
- The third and fourth terms are the Zeeman terms for the nuclear spin and the total electronic angular momentum respectively.

Using $\vec{B} = B\hat{z}$ & $F_z = I_z + J_z$ and some rearrangement results in,

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_0 + \left(-\frac{A_{hfs}}{2} (\vec{I}^2 + \vec{J}^2) - g_I \mu_N B F_z \right) \\ &\quad + \left(\frac{A_{hfs}}{2} \vec{F}^2 + (g_I \mu_N - g_J \mu_B) B J_z \right)\end{aligned}\quad (177)$$

The hamiltonian is separated into three terms intentionally. States within a $n^{2S+1}L_J$ term with the same m_F but on different manifolds F are mixed by the Zeeman interaction. This means that the first two terms are diagonal simultaneously in the $\{|F, m_F\rangle\}$ basis and the eigenbasis of \mathcal{H} . Therefore, the last term has to be diagonalized.

2.7 Derivation of the Breit-Rabi Equation

The Breit-Rabi equation, first derived in 193x give ref., gives the energies of the ground state hyperfine splitting of single valence electron atoms and ions in the presence of a magnetic field. Let's specialize to this case $L = 0, S = \frac{1}{2}, J = \frac{1}{2}$. F can be $I \pm \frac{1}{2}$. Therefore in the $\{|F, m_F\rangle\}$ basis, the J_z term is block diagonal with subblocks no greater than 2 by 2 in size. The 2 by 2 subblocks are made of the states with different F and same m_F . For the special case of $m_F = \pm F_{max} = \pm (I + \frac{1}{2})$, there are no other states to mix with. Thus, they reside in subblocks of size 1 by 1. To diagonalize \mathcal{H} , we only have to diagonalize each subblock of \mathcal{H}' ,

$$\mathcal{H}' = \frac{A_{hfs}}{2} \vec{F}^2 + (g_I \mu_N - g_S \mu_B) B J_z \quad (178)$$

$$\begin{aligned}\hat{\mathcal{H}}' &= \frac{A_{hfs}}{2} \begin{bmatrix} (I + \frac{1}{2})(I + \frac{3}{2}) & 0 \\ 0 & (I - \frac{1}{2})(I + \frac{1}{2}) \end{bmatrix} \\ &\quad + (g_I \mu_N - g_S \mu_B) B \begin{bmatrix} \alpha_+ & \beta_- \\ \beta_+ & \alpha_- \end{bmatrix}\end{aligned}\quad (179)$$

$$\alpha_{\pm} = \left\langle I \pm \frac{1}{2}, m_F \left| \hat{J}_z \right| I \pm \frac{1}{2}, m_F \right\rangle \quad (180)$$

$$\beta_{\pm} = \left\langle I \mp \frac{1}{2}, m_F \left| \hat{J}_z \right| I \pm \frac{1}{2}, m_F \right\rangle \quad (181)$$

The first term can be simplified to give:

$$\frac{A_{hfs}}{2} \hat{F}^2 = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \left(I + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \quad (182)$$

α_{\pm} & β_{\pm} in the second term are most easily calculated in the $\{|I, m_I\rangle |J, m_J\rangle\}$ basis:

$$|I, m_I\rangle |J, m_J\rangle = |m_I, m_J\rangle \quad (183)$$

$$|F, m_F\rangle = \sum |m_I, m_J\rangle \langle m_I, m_J | F, m_F \rangle \quad (184)$$

Using the formulas for Clebsch-Gordon coefficients from before 60:

$$\begin{aligned}\left\langle m_F \mp \frac{1}{2}, \pm \frac{1}{2} \left| I + \frac{1}{2}, m_F \right\rangle &= \frac{1}{\sqrt{2I+1}} \sqrt{I + \frac{1}{2} \pm m_F} \\ \left\langle m_F \mp \frac{1}{2}, \pm \frac{1}{2} \left| I - \frac{1}{2}, m_F \right\rangle &= \frac{\mp 1}{\sqrt{2I+1}} \sqrt{I + \frac{1}{2} \mp m_F}\end{aligned}\quad (185)$$

which gives:

$$\alpha_{\pm} = \pm(\alpha) = \pm \left(\frac{m_F}{2I+1} \right) \quad (186)$$

$$\beta_{\pm} = -(\beta) = - \left(\frac{\sqrt{(I + \frac{1}{2})^2 - m_F^2}}{2I+1} \right) \quad (187)$$

To solve for the energies, we only need to diagonalize the last term in \mathcal{H}' :

$$\mathcal{H}' = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right)^2 + \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \begin{bmatrix} 1 + 2\alpha x & -2\beta x \\ -2\beta x & -(1 + 2\alpha x) \end{bmatrix} \quad (188)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{2B}{A(2I + 1)} \quad (189)$$

This is easily done and, just like fine structure mixing, gives the eigenvalues:

$$\pm \left(\lambda = \sqrt{1 + 4\alpha x + x^2} \right) \quad (190)$$

The total energy is therefore:

$$E = E_0 - \frac{A_{hfs}}{2} \left(I(I + 1) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right) - g_I \mu_N m_F B + E' \quad (191)$$

$$E' = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right)^2 \pm \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \lambda \quad (192)$$

In this case, E_0 is the energy of the (possibly mixed) spin-orbit coupled states. The $\pm \lambda$ eigenvalue is used for states evolving from the $F = I \pm \frac{1}{2}$ manifold. In the zero field case, $B = 0$, we find the hyperfine splitting between the two manifolds is:

$$\Delta E = \frac{A_{hfs}(2I + 1)}{2} = h\nu_{hfs} \quad (193)$$

Dropping E_0 and relating A_{hfs} to the zero field hyperfine splitting $h\nu_{hfs}$, we get the celebrated Breit-Rabi equation:

$$E = -\frac{h\nu_{hfs}}{2(2I + 1)} - g_I \mu_N B m_F \pm \frac{h\nu_{hfs}}{2} \sqrt{1 + \frac{4m_F}{2I + 1} x + x^2} \quad (194)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{B}{h\nu_{hfs}} \quad (195)$$

Note that x is a unitless quantity that gives a relative measure of the Zeeman interaction wrt the hyperfine interaction. For $x \approx 1$, $B \approx 0.2T$, the Zeeman interaction is comparable to the hyperfine interaction.

We'll discuss two special cases now. The energies of the $m_F = \pm(I + \frac{1}{2})$ states in the $F = I + \frac{1}{2}$ manifold are:

$$E_{\pm(I + \frac{1}{2})} = \left(\frac{I}{2I + 1} \right) h\nu_{hfs} \mp \left(g_I \mu_N I + \frac{g_S}{2} \mu_B \right) B \quad (196)$$

At low field ($B \ll 0.2T$ for Rubidium), to second order in B , the energies for the the $F = I \pm \frac{1}{2}$ manifolds are

$$\begin{aligned} E_{\pm} &= \pm \left(\frac{I + \frac{1}{2} \mp \frac{1}{2}}{2I + 1} \right) h\nu_{hfs} - \frac{2m_F}{2I + 1} \left(\left(I + \frac{1}{2} \mp \frac{1}{2} \right) g_I \mu_N \pm \frac{g_S}{2} \mu_B \right) B \\ &\pm \left(1 - \left(\frac{2m_F}{2I + 1} \right)^2 \right) (g_I \mu_N - g_S \mu_B)^2 \frac{B^2}{4h\nu_{hfs}} \end{aligned} \quad (197)$$

2.8 The EPR Spectrum

2.8.1 Frequencies

EPR stands for *Electron Paramagnetic Resonance*. It refers to the transitions between adjacent states within a particular manifold. The frequency corresponding to these transitions within the $F = I \pm \frac{1}{2}$ manifold are:

$$\nu_{\pm} = \mp \frac{g_I \mu_N B}{h} + \frac{\nu_{hfs}}{2} \left(\sqrt{1 + \frac{4m_F}{2I + 1} x + x^2} - \sqrt{1 + \frac{4(m_F - 1)}{2I + 1} x + x^2} \right) \quad (198)$$

We label the transitions with the higher m_F of the two states ($m_F \leftrightarrow m_F - 1$). In the low field limit, to second order in B , this becomes:

$$\begin{aligned} \nu_{\pm} = & \mp \frac{2}{2I+1} \left(\left(I + \frac{1}{2} \mp \frac{1}{2} \right) g_I \mu_N \pm \frac{g_S}{2} \mu_B \right) \frac{B}{h} \\ & + \left(\frac{1-2m_F}{(2I+1)^2} \right) (g_I \mu_N - g_S \mu_B)^2 \frac{B^2}{h^2 \nu_{hf_s}} \end{aligned} \quad (199)$$

The difference in frequencies between two adjacent transitions is just a constant (to second order in B) for both manifolds:

$$\Delta\nu = \frac{2}{(2I+1)^2} (g_I \mu_N - g_S \mu_B)^2 \frac{B^2}{h^2 \nu_{hf_s}} \quad (200)$$

The derivative of the frequency with respect to the field is:

$$\frac{d\nu}{dB} = \mp \frac{g_I \mu_N}{h} + \frac{(g_I \mu_N - g_S \mu_B)}{h} \left(\frac{\frac{m_F}{2I+1} + \frac{x}{2}}{\sqrt{1 + \frac{4m_F}{2I+1} x + x^2}} - \frac{\frac{m_F-1}{2I+1} + \frac{x}{2}}{\sqrt{1 + \frac{4(m_F-1)}{2I+1} x + x^2}} \right) \quad (201)$$

To first order in field, the derivative is:

$$\begin{aligned} \frac{d\nu_{\pm}}{dB} = & \mp \frac{2}{2I+1} \left(\left(I + \frac{1}{2} \mp \frac{1}{2} \right) g_I \mu_N \pm \frac{g_S}{2} \mu_B \right) \frac{1}{h} \\ & + \frac{2-4m_F}{(2I+1)^2} (g_I \mu_N - g_S \mu_B)^2 \frac{B}{h^2 \nu_{hf_s}} \end{aligned} \quad (202)$$

See fig. 4 for a qualitative energy level diagram for ⁸⁵Rubidium.

By applying a weak transverse field \vec{B}_{rf} at the appropriate frequency, the various EPR transitions can be excited. The lineshape of each transition is ideally a Lorentzian. The width is inversely proportional to the lifetimes of the initial and final states. Magnetic field inhomogenities and RF power can broaden the line. However, the area under the peak is a very robust quantity because it is conserved and therefore does not depend on the details of the lineshape. It is proportional to the net transition probability rate which is given by Fermi's Golden Rule:

$$w_{\pm} = \frac{2\pi}{h} \left| \left\langle m_F - \frac{1}{2} \pm \frac{1}{2} \right| \hat{W} \left| m_F - \frac{1}{2} \mp \frac{1}{2} \right\rangle \right|^2 \rho_{\pm}(E) \quad (203)$$

$$\Delta w = w_+ - w_- \quad (204)$$

where \hat{W} is the operator inducing the transition and $\rho_{\pm}(E)$ is the density of available states as a function of the transition energy. Because of the principle of detailed balancing, the absorption rate is identical to the stimulated emission rate ($w_+ = w_-$) for a given transition. Therefore, the net transition probability rate is,

$$\Delta w = \left(\frac{2\pi}{h} \left| \langle m_F - 1 | \hat{W} | m_F \rangle \right|^2 \right) (\rho_+(E) - \rho_-(E)) \quad (205)$$

where $\rho_{\pm}(E)$ is density of the states that are absorbing (emitting). First we will derive the the matrix element in δw and then we will discuss the relative populations $\rho_{\pm}(E)$.

2.8.2 Transition Matrix Element

We can treat the RF field \vec{B}_{rf} as a time dependant perturbation to our original hamiltonian:

$$\mathcal{H}_{EPR} = \mathcal{H} + \mathcal{W} \quad (206)$$

$$\mathcal{W} = -\vec{\mu}_I \cdot \vec{B}_{rf} - \vec{\mu}_J \cdot \vec{B}_{rf} \quad (207)$$

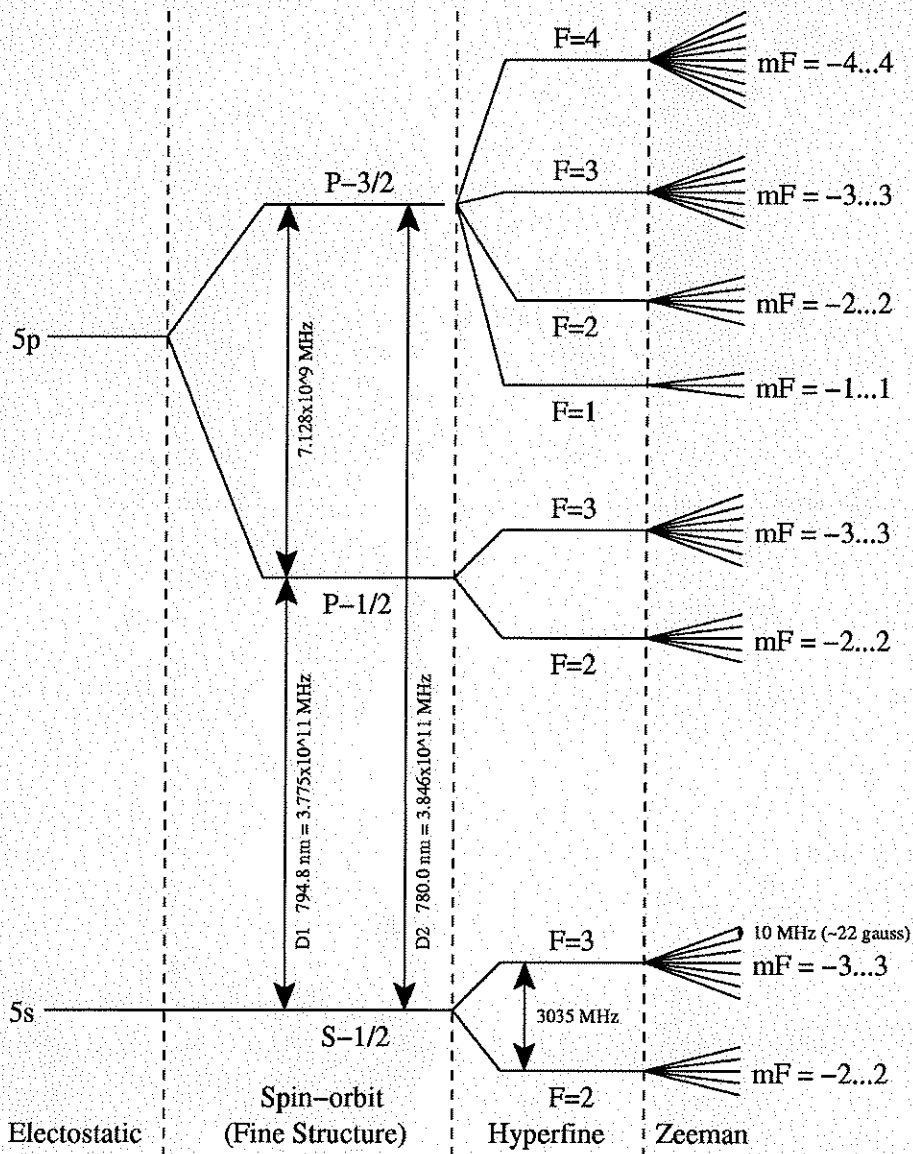


Figure 4: Qualitative Energy Level Diagram for ^{85}Rb ($I = 5/2$) in a Weak Field

We'll choose the rf-field to be in the \hat{x} direction. After expressing the angular momentum operators as ladder operators ($\hat{J}_x = \frac{1}{2}(\hat{J}_+ + \hat{J}_-)$) and treating only the case of stimulated emission ($m_F \rightarrow m_F - 1$), the matrix element of interest becomes:

$$W_{fi} = \frac{\hbar}{2} \langle m_F - 1 | \omega_I \hat{I}_- + \omega_J \hat{J}_- | m_F \rangle \quad (208)$$

$$= \frac{\hbar}{2} \langle m_F - 1 | \omega_I \hat{F}_- + (\omega_J - \omega_I) \hat{J}_- | m_F \rangle \quad (209)$$

$$= \frac{\hbar}{2} \langle f | \omega_I \hat{F}_- + (\omega_J - \omega_I) \hat{J}_- | i \rangle \quad (210)$$

$$\omega_I = \frac{g_I \mu_N B_{RF}}{\hbar} \quad (211)$$

$$\omega_J = \frac{g_S \mu_B B_{RF}}{\hbar} \quad (212)$$

(The following is analogous to fine structure mixing.) This matrix element is most easily evaluated in the $\{|m_I, m_J\rangle\}$ basis. However, we must first represent $\{|m_F^\pm\rangle\}$ in the $\{|F, m_F\rangle\}$ basis. Note that since we are considering the ground state term of an alkali metal atom, there is no fine structure mixing. However the field B does result in hyperfine structure mixing (states with the same m_F but different F):

$$|m_F^\pm\rangle = a_1^\pm \left| I + \frac{1}{2}, m_F \right\rangle + a_2^\pm \left| I - \frac{1}{2}, m_F \right\rangle \quad (213)$$

$$|F, m_F\rangle = \sum_{m_J = -\frac{1}{2}}^{+\frac{1}{2}} |m_F - m_J, m_J\rangle \langle m_F - m_J, m_J | F, m_F \rangle \quad (214)$$

$$b_1^\pm(m_F) = \left\langle m_F - \frac{1}{2}, +\frac{1}{2} \left| I \pm \frac{1}{2}, m_F \right\rangle \right\rangle \quad (215)$$

$$b_2^\pm(m_F) = \left\langle m_F + \frac{1}{2}, -\frac{1}{2} \left| I \pm \frac{1}{2}, m_F \right\rangle \right\rangle \quad (216)$$

$$\left| I \pm \frac{1}{2}, m_F \right\rangle = b_1^\pm \left| m_F - \frac{1}{2}, +\frac{1}{2} \right\rangle + b_2^\pm \left| m_F + \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (217)$$

The values for $a_{1,2}^\pm$ come from the diagonalization of eqn 188 where λ_\pm are the eigenvalues given by eqn 190 and α and β are defined by eqns 186 and 187:

$$a_1^\pm = \frac{2\beta x}{\sqrt{(1 + 2\alpha x \mp \lambda)^2 + 4\beta^2 x^2}} \quad (218)$$

$$a_2^\pm = \frac{1 + 2\alpha x \mp \lambda}{\sqrt{(1 + 2\alpha x \mp \lambda)^2 + 4\beta^2 x^2}} \quad (219)$$

$$a_1^\pm = \pm a_2^\mp \quad (220)$$

The \pm sign is taken for transitions within the $F = I \pm \frac{1}{2}$ manifold. For simplicity (due to orthogonality):

$$a_1 \equiv a_1^+ = a_2^- \quad (221)$$

$$a_2 \equiv a_2^+ = -a_1^- \quad (222)$$

$$b_1 \equiv b_1^+ = b_2^- \quad (223)$$

$$b_2 \equiv b_2^+ = -b_1^- \quad (224)$$

$$\left| I \pm \frac{1}{2}, m_F \right\rangle = b_1 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm b_2 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \quad (225)$$

$$|m_F^\pm\rangle = a_1 \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 \left| I \mp \frac{1}{2}, m_F \right\rangle \quad (226)$$

Putting this altogether gives:

$$|m_F^\pm\rangle = a_1 \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 \left| I \mp \frac{1}{2}, m_F \right\rangle \quad (227)$$

$$= a_1 \left(b_1 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm b_2 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right) \quad (228)$$

$$\pm a_2 \left(b_1 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \mp b_2 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \right) \quad (229)$$

$$= (a_1 b_1 - a_2 b_2) \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm (a_1 b_2 + a_2 b_1) \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \quad (230)$$

To start with, let's calculate the matrix element of \hat{F}_- :

$$\langle \hat{F}_- \rangle = \langle m_F^\pm - 1 | \hat{F}_- | m_F^\pm \rangle \quad (231)$$

$$= \left[a_1 (m_F - 1) \left\langle I \pm \frac{1}{2}, m_F - 1 \right| \pm a_2 (m_F - 1) \left\langle I \mp \frac{1}{2}, m_F - 1 \right| \right] \hat{F}_- \left[a_1 (m_F) \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 (m_F) \left| I \mp \frac{1}{2}, m_F \right\rangle \right] \quad (232)$$

$$= \left[a_1 (m_F - 1) \left\langle I \pm \frac{1}{2}, m_F - 1 \right| \pm a_2 (m_F - 1) \left\langle I \mp \frac{1}{2}, m_F - 1 \right| \right] \left[f_\pm a_1 (m_F) \left| I \pm \frac{1}{2}, m_F - 1 \right\rangle \pm f_\mp a_2 (m_F) \left| I \mp \frac{1}{2}, m_F - 1 \right\rangle \right] \quad (233)$$

$$= f_\pm a_1 (m_F) a_1 (m_F - 1) + f_\mp a_2 (m_F) a_2 (m_F - 1) \quad (234)$$

$$= f_\pm a_1 f a_{1i} + f_\mp a_2 f a_{2i} \quad (235)$$

$$f_\pm = \sqrt{\left(I + \frac{1}{2} \right) \left(I + \frac{1}{2} \pm 1 \right) - m_F (m_F - 1)} \quad (236)$$

Now let's calculate the matrix element of \hat{J}_- :

$$\langle \hat{J}_- \rangle^\pm = \langle m_F^\pm - 1 | \hat{J}_- | m_F^\pm \rangle \quad (237)$$

$$= (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - 1 \mp \frac{1}{2}, \pm \frac{1}{2} \right| \pm (a_{1f} b_{2f} + a_{2f} b_{1f}) \times \left\langle m_F - 1 \pm \frac{1}{2}, \mp \frac{1}{2} \right| \hat{J}_- \left[(a_{1i} b_{1i} - a_{2i} b_{2i}) \times \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm (a_{1i} b_{2i} + a_{2i} b_{1i}) \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right] \quad (238)$$

$$\langle \hat{J}_- \rangle^+ = (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - \frac{3}{2}, +\frac{1}{2} \right| + (a_{1f} b_{2f} + a_{2f} b_{1f}) \times \left\langle m_F - \frac{1}{2}, -\frac{1}{2} \right| \left[\sqrt{\frac{13}{22} + \frac{11}{22}} \left[(a_{1i} b_{1i} - a_{2i} b_{2i}) \left| m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \right] \right] \quad (239)$$

$$= [a_{1f} b_{2f} + a_{2f} b_{1f}] \times [a_{1i} b_{1i} - a_{2i} b_{2i}] \quad (240)$$

$$\langle \hat{J}_- \rangle^- = (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - \frac{1}{2}, -\frac{1}{2} \right| - (a_{1f} b_{2f} + a_{2f} b_{1f}) \times \left\langle m_F - \frac{3}{2}, +\frac{1}{2} \right| \left[\sqrt{\frac{13}{22} + \frac{11}{22}} \left[- (a_{1i} b_{2i} + a_{2i} b_{1i}) \left| m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \right] \right]$$

(241)

$$= [a_{2f}b_{2f} - a_{1f}b_{1f}] \times [a_{1i}b_{2i} + a_{2i}b_{1i}] \quad (242)$$

Note the following relations:

$$b_{2f}b_{1i} = \frac{\sqrt{(I + \frac{1}{2})(I + \frac{3}{2}) - m_F(m_F - 1)}}{2I + 1} = \frac{f_+}{2I + 1} \quad (243)$$

$$b_{1f}b_{2i} = \frac{\sqrt{(I + \frac{1}{2})(I - \frac{1}{2}) - m_F(m_F - 1)}}{2I + 1} = \frac{f_-}{2I + 1} \quad (244)$$

$$b_{1f}b_{1i} = \frac{\sqrt{(I + \frac{1}{2})(I - \frac{1}{2}) + m_F(m_F - 1) + 2m_F(I + \frac{1}{2})}}{2I + 1} = \frac{g_-}{2I + 1} \quad (245)$$

$$b_{2f}b_{2i} = \frac{\sqrt{(I + \frac{1}{2})(I + \frac{3}{2}) + m_F(m_F - 1) - 2m_F(I + \frac{1}{2})}}{2I + 1} = \frac{g_+}{2I + 1} \quad (246)$$

$$g_{\pm} = \sqrt{\left(I + \frac{1}{2}\right) \left(I + \frac{1}{2} \pm 1\right) + m_F(m_F - 1) \mp 2m_F \left(I + \frac{1}{2}\right)} \quad (247)$$

Going back to $\langle \hat{J}_- \rangle^{\pm}$:

$$\langle \hat{J}_- \rangle^+ = [a_{1f}b_{2f} + a_{2f}b_{1f}] \times [a_{1i}b_{1i} - a_{2i}b_{2i}] \quad (248)$$

$$= a_{1f}a_{1i} \frac{f_+}{2I + 1} + a_{2f}a_{1i} \frac{g_-}{2I + 1} - a_{1f}a_{2i} \frac{g_+}{2I + 1} - a_{2f}a_{2i} \frac{f_-}{2I + 1} \quad (249)$$

$$\langle \hat{J}_- \rangle^- = [a_{2f}b_{2f} - a_{1f}b_{1f}] \times [a_{1i}b_{2i} + a_{2i}b_{1i}] \quad (250)$$

$$= a_{2f}a_{1i} \frac{g_+}{2I + 1} - a_{1f}a_{1i} \frac{f_-}{2I + 1} + a_{2f}a_{2i} \frac{f_+}{2I + 1} - a_{1f}a_{2i} \frac{g_-}{2I + 1} \quad (251)$$

$$\langle \hat{J}_- \rangle^{\pm} = \pm a_{1f}a_{1i} \frac{f_{\pm}}{2I + 1} + a_{2f}a_{1i} \frac{g_{\mp}}{2I + 1} - a_{1f}a_{2i} \frac{g_{\pm}}{2I + 1} \mp a_{2f}a_{2i} \frac{f_{\mp}}{2I + 1} \quad (252)$$

(253)

Putting this altogether,

$$W_{fi} = \frac{\hbar}{2} \omega_I (f_{\pm} a_{1f} a_{1i} + f_{\mp} a_{2f} a_{2i}) + \frac{\hbar}{2} (\omega_J - \omega_I) \times \left(\pm a_{1f} a_{1i} \frac{f_{\pm}}{2I + 1} + a_{2f} a_{1i} \frac{g_{\mp}}{2I + 1} - a_{1f} a_{2i} \frac{g_{\pm}}{2I + 1} \mp a_{2f} a_{2i} \frac{f_{\mp}}{2I + 1} \right) \quad (254)$$

$$= \frac{\hbar}{2} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I + 1} \right) f_{\pm} a_{1f} a_{1i} + \frac{\hbar}{2} \left(\frac{2I\omega_I + (1 \pm 1)\omega_I \mp \omega_J}{2I + 1} \right) \times f_{\mp} a_{2f} a_{2i} + \frac{\hbar}{2} \left(\frac{\omega_J - \omega_I}{2I + 1} \right) (g_{\mp} a_{2f} a_{1i} - g_{\pm} a_{1f} a_{2i}) \quad (255)$$

Using the small field approximations from before:

$$a_1 = 1 - \frac{\beta^2}{2} x^2 \quad (256)$$

$$a_2 = -\beta x + 2\alpha\beta x^2 \quad (257)$$

We're interested in the mod square of the matrix element to first order in x :

$$\begin{aligned} |W_{fi}|^2 &\simeq \frac{\hbar^2}{4} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I+1} \right)^2 f_{\pm}^2 - \frac{\hbar^2}{4} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I+1} \right) \\ &\times \left(\frac{\omega_J - \omega_I}{2I+1} \right) f_{\pm} (g_{\mp}\beta_f - g_{\pm}\beta_i) x + \mathcal{O}(x^2) \end{aligned} \quad (258)$$

2.8.3 Spin Temperature Distribution

To discuss the relative population of each state, we must introduce two concepts: the density operator and spin temperature. The density operator is often used to represent a large ensemble of systems in a statistical mixture of pure quantum states. To be explicit, given a statistical probability p_k of being in the pure quantum state $|\psi_k\rangle$, the density operator in the basis $\{|u_n\rangle\}$ is:

$$\begin{aligned} \hat{\rho} &= \sum_k p_k |\psi_k\rangle \langle \psi_k| \\ &= \sum_k p_k \sum_{n,m} \langle \psi_k | u_m \rangle \langle u_n | \psi_k \rangle |u_n\rangle \langle u_m| \end{aligned} \quad (259)$$

The diagonal elements have a simple and straightforward physical interpretation: they are the combined statistical and quantum mechanical probabilities of being in a basis state $|u_n\rangle$:

$$\rho_{nn} = \sum_k p_k |\langle u_n | \psi_k \rangle|^2 \quad (260)$$

which means that $\text{Tr}(\hat{\rho}) = 1$ as one would expect. In quantum statistical mechanics, for a canonical ensemble (fixed number of particles in equilibrium with a heat reservoir at a common temperature T), the diagonal elements of the density operator are:

$$\rho_{nn} = \frac{e^{-\beta E_n}}{Z} \quad (261)$$

$$Z = \sum_n e^{-\beta E_n} \quad (262)$$

$$\beta = \frac{1}{kT} \quad (263)$$

where Z is the partition function. It has been shown that under the optical pumping/spin exchange conditions that exist within the target cells, the diagonal elements of the density operator for both manifolds are:

$$\rho_{m_F} = \frac{e^{\beta m_F}}{Z_F} = \frac{e^{\beta m_J} e^{\beta m_I}}{Z_J Z_I} \quad (264)$$

$$Z_F = \sum_{m_F=-F}^{+F} e^{\beta m_F} \quad (265)$$

$$Z_J = \sum_{m_J=-J}^{+J} e^{\beta m_J} \quad (266)$$

$$Z_I = \sum_{m_I=-I}^{+I} e^{\beta m_I} \quad (267)$$

$$m_F = m_J + m_I \quad (268)$$

Spin temperature is best described by the original reference by Anderson et al.

Direct substitution into these equations shows that in the steady state the solution is given by

$$\begin{aligned} a_{\frac{3}{2}} : a_{\frac{1}{2}} : a_{-\frac{1}{2}} : a_{-\frac{3}{2}} &= \alpha^3 : \alpha^2 : \alpha : 1 \\ b_{\frac{1}{2}} : b_{-\frac{1}{2}} &= \alpha : 1 \end{aligned}$$

This solution suggests the general form of the steady-state solution for all spin-exchange problems. It is the most probable way in which two sets of particles can be arranged so that the number of particles in each set is a constant and so that the total z component of angular momentum is a constant. This implies that the density matrix for a system of Na and N in spin-exchange equilibrium is given by where β is such that the total z component of the angular momentum of the system is given by $Tr[(I_{1z} + S_{1z} + I_{2z} + S_{2z})\rho]$. The parameter β might be called an angular momentum spin temperature.

They were discussing spin-exchange between sodium and nitrogen, but it is perfectly applicable to other spin-exchange systems including "pure" and "hybrid" cells. Putting together all of these results, we get

$$A_{m_F} \propto \Delta w = |W_{fi}|^2 e^{\beta m_F} \left(\frac{1 - e^{-\beta}}{Z} \right) \quad (269)$$

To zeroth order in x , noting $\omega_J \gg \omega_I$, and $g_S \simeq -2.0$, the area under the curve for a particular transition is

$$A_{m_F} \simeq A \frac{\hbar^2}{4} \left(\frac{\omega_J}{2I+1} \right)^2 f_{\pm}^2 e^{\beta m_F} + \mathcal{O}(x) \quad (270)$$

$$\simeq A \left(\frac{B_{RF}}{2I+1} \right)^2 [F(F+1) - m_F(m_F - 1)] e^{\beta m_F} \quad (271)$$

where A is a common factor for all transitions. Note that this β is the spin temperature and not beta-eqn.

3 The Faraday Effect

3.1 Description

The rotation of the plane of vibration of linearly polarized light in a medium within an applied magnetic field is called the Faraday effect. It is caused by the circular birefringence exhibited by the medium due to the applied field. Circular birefringence is the property of having two different indices of refraction for the two orthogonal states of circular polarization. Therefore, the speed at which the two states of circular polarization travel through the medium is different. This can be explained qualitatively by imagining the photons undergoing a series of absorptions and subsequent reemissions by the atoms in the medium. The process of absorption and reemission is called a virtual transition. It is analogous to one-loop diagrams within propagators in QFT. Applying Fermi's Golden Rule again, the rate of virtual transitions is proportional to the probability of virtual transition and the population of initial state. Differences in either the virtual transition probabilities or populations among the possible initial states of the atoms in the medium will give different virtual transition rates. The Zeeman shift resulting from a magnetic field changes the virtual transition probabilities. A non-zero polarization reflects a difference in initial state populations. The speed of a photon in a medium is inversely proportional to the rate at which it undergoes virtual transitions in that medium. In effect, the virtual transitions can be thought of as "slowing" down the photons. Differences in speed of propagation result in a relative phase shift between the components of circularly polarized light that make up the linearly polarized probe light. Therefore, polarized alkali metal vapor in a magnetic field will rotate the plane of vibration of a linearly polarized probe beam by an angle that is proportional to alkali metal vapor density, alkali metal vapor polarization, and the magnitude of the applied magnetic field.

3.2 General Formula for Rotation Angle

A linearly polarized probe beam can be written as

$$|\psi(z, t)\rangle = |\mathcal{P}\rangle e^{i(kz - \omega t)} \quad \text{Propagating along } \hat{z} \quad (272)$$

This can be rewritten in the circular polarization basis:

$$|\psi(z, t)\rangle = (|\mathcal{R}\rangle e^{ik_{\mathcal{R}}z} + |\mathcal{L}\rangle e^{ik_{\mathcal{L}}z}) \frac{e^{-i\omega t}}{\sqrt{2}} \quad (273)$$

where the wavenumber k is explicitly dependant on the circular polarization, but the angular frequency ω is not. Outside the medium $k = k_{\mathcal{R}} = k_{\mathcal{L}}$ but inside the medium $k_{\mathcal{R}} \neq k_{\mathcal{L}}$. At $z = t = 0$, it has horizontal linear polarization and it is just entering the birefringent medium of length l . After leaving the medium, $z = l + z'$ and the explicit dependance of k on the circular polarization is removed once again:

$$|\psi(z', t)\rangle = (|\mathcal{R}\rangle e^{ik_{\mathcal{R}}l} + |\mathcal{L}\rangle e^{ik_{\mathcal{L}}l}) \frac{e^{i(kz' - \omega t)}}{\sqrt{2}} \quad (274)$$

Pulling out a factor of $e^{i(k_{\mathcal{R}} + k_{\mathcal{L}}) \frac{l}{2}}$

$$|\psi\rangle = e^{i((k_{\mathcal{R}} + k_{\mathcal{L}}) \frac{l}{2} + kz' - \omega t)} \left[\frac{e^{i(k_{\mathcal{R}} - k_{\mathcal{L}}) \frac{l}{2}} |\mathcal{R}\rangle + e^{i(-k_{\mathcal{R}} + k_{\mathcal{L}}) \frac{l}{2}} |\mathcal{L}\rangle}{\sqrt{2}} \right] \quad (275)$$

Making the substitution

$$\phi = \frac{l}{2} (k_{\mathcal{L}} - k_{\mathcal{R}}) \quad (276)$$

and using $e^{i\phi} = \cos(\phi) + i \sin(\phi)$, we get:

$$|\psi\rangle = e^{i((k_{\mathcal{R}} + k_{\mathcal{L}}) \frac{l}{2} + kz' - \omega t)} \left[\cos(\phi) \left(\frac{|\mathcal{R}\rangle + |\mathcal{L}\rangle}{\sqrt{2}} \right) + \sin(\phi) \left(\frac{|\mathcal{R}\rangle - |\mathcal{L}\rangle}{\sqrt{2}i} \right) \right] \quad (277)$$

In the linear polarization basis, this is simply:

$$|\psi\rangle = e^{i((k_{\mathcal{R}} + k_{\mathcal{L}}) \frac{l}{2} + kz' - \omega t)} [\cos(\phi) |\mathcal{P}\rangle + \sin(\phi) |\mathcal{S}\rangle] \quad (278)$$

Therefore ϕ is the Faraday rotation angle and it is defined by Eqn. (276). Note that there is a relative phase shift between the two components circular polarization. There is no relative phase shift between the two components of linear polarization.

3.3 General Formula for Atomic Polarizability

The wavenumbers k_{\pm} are written using the helicity sign convention (where right circularly polarized light is positive). They are related to the index of refraction by:

$$k_{\pm} = \frac{\omega}{c} n_{\pm} \quad (279)$$

The real part of the index of refraction yields the dispersion relation which affects the phase of the wave. Differences in the real part give rise to circular birefringence. The imaginary part of the index of refraction yields the attenuation constant which affects the amplitude of the wave. Differences in the imaginary part give rise to circular dichroism which is the selective absorption of light based on the sense of circular polarization. Assuming a linear, isotropic, and rarefied medium, the Ucomplex index of refraction can be written as:

$$n_{\pm} = \sqrt{\frac{\epsilon_{\pm}}{\epsilon_0}} \quad (280)$$

where ϵ_{\pm} is the dielectric constant & ϵ_0 is the permittivity of free space and we've assumed $\mu = \mu_0$. Using Maxwell's eqns:

$$\vec{D} = \epsilon \vec{E} = \epsilon_0 \vec{E} + \vec{P} \quad (281)$$

$$\vec{P} = [A] \langle \vec{d} \rangle \quad (282)$$

The dipole moment is actually the quantum mechanical expectation value of the dipole operator averaged over every atom or molecule in the medium. The Hamiltonian of the system is:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{W} \quad (283)$$

where \mathcal{W} contains the atom-em wave interaction and \mathcal{H}_0 is the hamiltonian of free atom in a magnetic field. The general state of a single atom can be expanded in the eigenbasis of \mathcal{H}_0 :

$$|\Psi\rangle = \sum_n c_n(t) e^{-i\omega_n t} |n\rangle \quad (284)$$

$$\hat{\mathcal{H}}_0 |n\rangle = E_n |n\rangle = \hbar\omega_n |n\rangle \quad (285)$$

If $\mathcal{W} = 0$, then c_n would be independant of time. Inserting this into the Schrodinger eqn:

$$\hat{\mathcal{H}} |\Psi\rangle = i\hbar \frac{\partial |\Psi\rangle}{\partial t} \quad (286)$$

Projecting $e^{-i\omega_k t} |k\rangle$ onto both sides of the previous equation and rearranging gives the exact equation:

$$i\hbar \frac{d}{dt} c_k(t) = \sum_n c_n(t) e^{i\omega_{kn} t} \langle k | \hat{\mathcal{W}} | n \rangle \quad (287)$$

$$\omega_{kn} = \omega_k - \omega_n \quad (288)$$

To treat this system of coupled linear differential equations, the following approximations and assumptions will be made. First we will treat \mathcal{W} as a small perturbation. This means that the eigenstates of \mathcal{H}_0 are the eignstates of \mathcal{H} to first order. This is reasonable because the probe beam (≈ 20 milligauss for a 10 mW beam with 2 mm radius) is very small relative to the applied magnetic field (≈ 20 gauss). Second, \mathcal{W} will be expanded using the dipole approximation ($\vec{k} \cdot \vec{r} = \frac{2\pi(0.25nm)}{795nm} \approx 0.002 \ll 1$):

$$\begin{aligned} \mathcal{W} &= -\vec{d} \cdot \vec{E}(\vec{r}, t) = -q\vec{r} \cdot 2\vec{\mathcal{E}} \cos(\vec{k} \cdot \vec{r} - \omega t) \\ &= e\vec{r} \cdot \vec{\mathcal{E}} \left[e^{i(\vec{k} \cdot \vec{r} - \omega t)} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right] \\ &= e\vec{r} \cdot \vec{\mathcal{E}} \left[\left(1 + i\vec{k} \cdot \vec{r} + \dots\right) e^{-i\omega t} + \left(1 - i\vec{k} \cdot \vec{r} + \dots\right) e^{i\omega t} \right] \\ &\approx e\vec{r} \cdot \vec{\mathcal{E}} (e^{-i\omega t} + e^{i\omega t}) \end{aligned} \quad (289)$$

Third, recall the Wigner-Eckardt Theorem:

$$\langle J_f, m_f | \hat{T}_q^k | J_i, m_i \rangle = \frac{1}{\sqrt{2J_f + 1}} [\langle J_i, m_i | \langle k, q | J_f, m_f \rangle] \langle J_f || T^k || J_i \rangle \quad (290)$$

Note that only circular polarization is being considered so $k = 1$ & $q = \pm 1$. Consequently, because of the Clebsch-Gordon coefficient, $m_f = m_i \pm 1$ & $J_f = |J_i - 1| \dots |J_i + 1|$. Because of the reduced matrix element $\langle J_f || T^k || J_i \rangle$ only those matrix elements of $\hat{\mathcal{W}}$ that connect states with opposite parity will be non-zero. For convenience, the initial or excited states will be labeled b_k and the final or ground states will be labeled a_n . To be explicit, only those matrix elements between appropriate states in $\{a_n\}$ and $\{b_k\}$ will be non-zero. Fourth, we will add a phenomenological damping term γ_{b_k} which takes into account the finite lifetime of the excited states. This is the FWHM of the resonant absorption curve. Under our conditions, γ_{b_k} is dominated by pressure broadening, which we use to extract the 3He density. Putting this all together:

$$i\hbar \frac{d}{dt} b_k(t) = e \sum_n a_n(t) e^{i\omega_{kn} t} [e^{-i\omega t} + e^{i\omega t}] \langle k | \vec{r} \cdot \vec{\mathcal{E}} | n \rangle - i\hbar \gamma_{b_k} b_k \quad (291)$$

Fifth, at equilibrium under optical pumping conditions most alkali metal atoms are either in some ground state a_n or in some excited state b_k for only a short amount of time. Using this assumption along with the fact that the probe beam is weak:

$$\frac{da_n}{dt} \approx 0 \Rightarrow a_n = \text{constant} \quad (292)$$

$$P_n = a_n^* a_n \quad (293)$$

where P_n the relative population of a ground state a_n . Eq. 291 is then directly integrable which gives:

$$b_k(t) = -\frac{e}{\hbar} \sum_n a_n \langle b_k | \vec{r} \cdot \vec{\mathcal{E}} | a_n \rangle e^{i\omega_{b_k a_n} t} \left[\frac{e^{-i\omega t}}{\omega_{b_k a_n} - \omega - \frac{i}{2}\gamma_{b_k}} + \frac{e^{i\omega t}}{\omega_{b_k a_n} + \omega - \frac{i}{2}\gamma_{b_k}} \right] \quad (294)$$

with $\omega_{b_k a_n} = \omega_{b_k} - \omega_{a_n}$. The expectation value of the dipole moment for a single atom $\langle \vec{d} \rangle$ is calculated straightforwardly using eqn 284:

$$\begin{aligned} \langle \vec{d} \rangle &= -e \langle \Psi | \vec{r} | \Psi \rangle \\ &= -e \left[\sum_p a_p^* e^{i\omega_{a_p} t} \langle a_p | + \sum_p b_k^*(t) e^{i\omega_{b_k} t} \langle b_k | \right. \\ &\quad \left. \vec{r} \left[\sum_m a_m e^{-i\omega_{a_m} t} | a_m \rangle + \sum_j b_j(t) e^{-i\omega_{b_j} t} | b_j \rangle \right] \right] \\ &= -e \sum_{p,m,k,j} [a_p^* a_m \langle a_p | \vec{r} | a_m \rangle e^{i\omega_{a_p a_m} t} \\ &\quad + a_p^* b_j(t) \langle a_p | \vec{r} | b_j \rangle e^{i\omega_{a_p b_j} t} \\ &\quad + b_k^*(t) a_m \langle b_k | \vec{r} | a_m \rangle e^{i\omega_{b_k a_m} t} \\ &\quad + b_k^*(t) b_j(t) \langle b_k | \vec{r} | b_j \rangle e^{i\omega_{b_k b_j} t}] \quad (295) \end{aligned}$$

Again, only those matrix elements between appropriate states in $\{a_n\}$ and $\{b_k\}$ will be non-zero. Plugging in 294:

$$\begin{aligned} \langle \vec{d} \rangle &= -e \sum_{m,k} [b_k^*(t) a_m \langle b_k | \vec{r} | a_m \rangle e^{i\omega_{b_k a_m} t} + C.C.] \\ &= \frac{e^2}{\hbar} \sum_{m,k,n} a_n^* a_m \langle a_n | \vec{r} \cdot \vec{\mathcal{E}} | b_k \rangle \langle b_k | \vec{r} | a_m \rangle e^{i\omega_{a_n a_m} t} \\ &\quad \left(\frac{e^{i\omega t}}{\omega_{b_k a_n} - \omega + \frac{i}{2}\gamma_{b_k}} + \frac{e^{-i\omega t}}{\omega_{b_k a_n} + \omega + \frac{i}{2}\gamma_{b_k}} \right) + C.C. \quad (296) \end{aligned}$$

Averaging this single atom expectation value over all atoms in the cell and rearranging a few terms:

$$\langle a_n^* a_m \rangle_{\text{cell}} = \delta_{nm} P_n \quad (297)$$

$$\begin{aligned} \langle \vec{d} \rangle_{\text{cell}} &= \frac{e^2}{\hbar} \sum_{k,n} P_n \langle a_n | \vec{r} \cdot \vec{\mathcal{E}} | b_k \rangle \langle b_k | \vec{r} | a_n \rangle \\ &\quad \left(\frac{e^{i\omega t}}{\omega_{b_k a_n} - \omega + \frac{i}{2}\gamma_{b_k}} + \frac{e^{-i\omega t}}{\omega_{b_k a_n} + \omega + \frac{i}{2}\gamma_{b_k}} \right) + C.C. \\ &= \frac{e^2}{\hbar} \vec{\mathcal{E}} e^{-i\omega t} \cdot \sum_{k,n} P_n \langle a_n | \vec{r} | b_k \rangle \langle b_k | \vec{r} | a_n \rangle \\ &\quad \left(\frac{1}{\omega_{b_k a_n} - \omega - \frac{i}{2}\gamma_{b_k}} + \frac{1}{\omega_{b_k a_n} + \omega + \frac{i}{2}\gamma_{b_k}} \right) + C.C. \quad (298) \end{aligned}$$

The relationship between the induced dipole moment and the applied electric field defines the atomic polarizability tensor:

$$\vec{d} = \vec{\alpha} \vec{E} \quad (299)$$

The radius vector \vec{r} of the electron can be expanded in the spherical basis:

$$\begin{aligned} \vec{r} &= r_0^1 + r_{-1}^1 + r_{+1}^1 \\ &= r_z \hat{z} + r_- \hat{e}_- + r_+ \hat{e}_+ \end{aligned} \quad (300)$$

where \hat{e}_\pm are the unit vectors that define the two states of circular polarization. Using these two relations, the expectation value of the atomic polarizability averaged over all atoms in the cell for a given circular polarization of incident light is:

$$\alpha_\pm = \frac{e^2}{\hbar} \sum_{k,n} P_n \langle a_n | r_\mp | b_k \rangle \langle b_k | r_\pm | a_n \rangle \left[\frac{1}{\omega_{b_k a_n} - \omega - \frac{i}{2} \gamma_{b_k}} + \frac{1}{\omega_{b_k a_n} + \omega + \frac{i}{2} \gamma_{b_k}} \right] \quad (301)$$

3.4 Explicit Calculation of Atomic Polarizability

3.4.1 Transitions and Frequencies

The general formula for atomic polarizability 301 is a sum over all transitions from the ground states to the final states. In principle, the correct states to use are the mixed hyperfine eigenstates. However, this is complicated and tedious. It is much easier and a very good approximation to consider just the mixed fine structure eigenstates. This can be seen by considering the scale of the various splittings for Rubidium. The hyperfine splitting is about 3 GHz. The fine structure splitting is about 7000 GHz. The phenomenological damping term $\frac{\gamma_b}{2\pi}$ is the FWHM of the pressure broadened absorption curve. In a typical target cell, this is about 170 GHz. The pressure broadening renders the the hyperfine structure unresolved. Therefore, it should be sufficient to consider only the mixed fine structure states. Note that we are in a sense implicitly averaging out the hyperfine splitting.

Let's specialize to an alkali metal atom. The two ground states $\{|a_n\rangle\}$ are the ground term states $n^2 S_{\frac{1}{2}}$:

$$\left(S = \frac{1}{2} \right) + (L = 0) \rightarrow \left(J = \frac{1}{2} \right) \quad (302)$$

$$m_J = -\frac{1}{2}, \frac{1}{2} \quad (303)$$

The six excited states $\{|b_k\rangle\}$ are the excited term states $n^2 P_{\frac{1}{2}, \frac{3}{2}}$:

$$\left(S = \frac{1}{2} \right) + (L = 1) \rightarrow \left(J = 1 \pm \frac{1}{2} = \frac{1}{2}, \frac{3}{2} \right) \quad (304)$$

$$m_J = -\frac{1}{2}, +\frac{1}{2} \text{ for } J = \frac{1}{2} \quad (305)$$

$$m_J = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2} \text{ for } J = \frac{3}{2} \quad (306)$$

The B -field mixes the $m_J = \pm \frac{1}{2}$ states of the $n^2 P$ term. The energies for these states in the low field limit and with $g_S = -2.0023193043718 \simeq -2$ are:

$$E_{\frac{1}{2}, -\frac{1}{2}}^S = E_0^S - \mu_B B \quad (307)$$

$$E_{\frac{1}{2}, +\frac{1}{2}}^S = E_0^S + \mu_B B \quad (308)$$

$$E_{\frac{1}{2}, -\frac{1}{2}}^P = E_0^P - \left(\frac{2}{3} \right) h\nu_{so} - \left(\frac{1}{3} \right) \mu_B B \quad (309)$$

$$E_{\frac{1}{2}, +\frac{1}{2}}^P = E_0^P - \left(\frac{2}{3} \right) h\nu_{so} + \left(\frac{1}{3} \right) \mu_B B \quad (310)$$

$$E_{\frac{3}{2},-\frac{3}{2}}^P = E_0^P + \left(\frac{1}{3}\right) h\nu_{so} - 2\mu_B B \quad (311)$$

$$E_{\frac{3}{2},-\frac{1}{2}}^P = E_0^P + \left(\frac{1}{3}\right) h\nu_{so} - \left(\frac{2}{3}\right) \mu_B B \quad (312)$$

$$E_{\frac{3}{2},+\frac{1}{2}}^P = E_0^P + \left(\frac{1}{3}\right) h\nu_{so} + \left(\frac{2}{3}\right) \mu_B B \quad (313)$$

$$E_{\frac{3}{2},+\frac{3}{2}}^P = E_0^P + \left(\frac{1}{3}\right) h\nu_{so} + 2\mu_B B \quad (314)$$

For right circularly polarized light (which has +1 unit of angular momentum), the possible transitions are:

$$\left|S_{\frac{1}{2},-\frac{1}{2}}\right\rangle \leftrightarrow a_1 \left|P_{\frac{3}{2},+\frac{1}{2}}\right\rangle + a_2 \left|P_{\frac{3}{2},+\frac{1}{2}}\right\rangle \quad (315)$$

$$\left|S_{\frac{1}{2},-\frac{1}{2}}\right\rangle \leftrightarrow a_1 \left|P_{\frac{3}{2},+\frac{1}{2}}\right\rangle - a_2 \left|P_{\frac{1}{2},+\frac{1}{2}}\right\rangle \quad (316)$$

$$\left|S_{\frac{1}{2},+\frac{1}{2}}\right\rangle \leftrightarrow \left|P_{\frac{3}{2},+\frac{3}{2}}\right\rangle \quad (317)$$

For left circularly polarized light (which has -1 unit of angular momentum), the possible transitions are:

$$\left|S_{\frac{1}{2},+\frac{1}{2}}\right\rangle \leftrightarrow a_1 \left|P_{\frac{1}{2},-\frac{1}{2}}\right\rangle + a_2 \left|P_{\frac{3}{2},-\frac{1}{2}}\right\rangle \quad (318)$$

$$\left|S_{\frac{1}{2},+\frac{1}{2}}\right\rangle \leftrightarrow a_1 \left|P_{\frac{3}{2},-\frac{1}{2}}\right\rangle - a_2 \left|P_{\frac{1}{2},-\frac{1}{2}}\right\rangle \quad (319)$$

$$\left|S_{\frac{1}{2},-\frac{1}{2}}\right\rangle \leftrightarrow \left|P_{\frac{3}{2},-\frac{3}{2}}\right\rangle \quad (320)$$

Now we will calculate the frequencies for each of these transitions. It will be convenient to express these frequencies with respect to the zero field D1 and D2 transitions frequencies:

$$\omega_{\frac{1}{2}}^0 = \frac{E_0^P - E_0^S}{\hbar} - \left(\frac{2}{3}\right) \omega_{so} = 2\pi\nu_{\frac{1}{2}}^0 \quad (321)$$

$$\omega_{\frac{3}{2}}^0 = \frac{E_0^P - E_0^S}{\hbar} + \left(\frac{1}{3}\right) \omega_{so} = 2\pi\nu_{\frac{3}{2}}^0 \quad (322)$$

$$\omega_{so} = \omega_{\frac{3}{2}} - \omega_{\frac{1}{2}} = \left(\frac{1}{3} - -\frac{2}{3}\right) \omega_{so} = 2\pi\nu_{so} \quad (323)$$

$$\omega_{\frac{1}{2}} = \omega_{\frac{1}{2}}^0 + \delta\omega_{\frac{1}{2}} \quad (324)$$

$$\omega_{\frac{3}{2}} = \omega_{\frac{3}{2}}^0 + \delta\omega_{\frac{3}{2}} \quad (325)$$

$$\delta\omega = \delta\omega_{\frac{3}{2}} - \delta\omega_{\frac{1}{2}} \quad (326)$$

where the $\delta\omega$ terms refer to the pressure shift caused by the buffer gas. The transition frequencies will be labeled as $\omega_i^f = \frac{\Delta E_{f-i}}{\hbar}$:

$$\omega_{\frac{1}{2},-\frac{1}{2}}^{\frac{1}{2},+\frac{1}{2}} = \omega_{\frac{1}{2}} + \left(\frac{4}{3}\right) \frac{\mu_B}{\hbar} B \quad (327)$$

$$\omega_{\frac{3}{2},-\frac{1}{2}}^{\frac{3}{2},+\frac{1}{2}} = \omega_{\frac{3}{2}} + \left(\frac{5}{3}\right) \frac{\mu_B}{\hbar} B \quad (328)$$

$$\omega_{\frac{3}{2},+\frac{3}{2}}^{\frac{3}{2},+\frac{3}{2}} = \omega_{\frac{3}{2}} + \frac{\mu_B}{\hbar} B \quad (329)$$

$$\omega_{\frac{1}{2},+\frac{1}{2}}^{\frac{1}{2},-\frac{1}{2}} = \omega_{\frac{1}{2}} - \left(\frac{4}{3}\right) \frac{\mu_B}{\hbar} B \quad (330)$$

$$\omega_{\frac{3}{2}, +\frac{1}{2}}^{\frac{3}{2}, -\frac{1}{2}} = \omega_{\frac{3}{2}} - \left(\frac{5}{3}\right) \frac{\mu_B}{\hbar} B \quad (331)$$

$$\omega_{\frac{3}{2}, -\frac{1}{2}}^{\frac{3}{2}, -\frac{1}{2}} = \omega_{\frac{3}{2}} - \frac{\mu_B}{\hbar} B \quad (332)$$

3.4.2 Oscillator Strengths and Radial Matrix Elements

Evaluation of the matrix elements will be briefly described and then explicitly calculated. Each matrix element is composed of an angular part and a radial part. The two parts can be separated using the Wigner-Eckhart Theorem. The angular part is simply the squareroot of the statistical weight of the final state and a Clebsch-Gordon coefficient. The radial part is obtained by making a connection to the oscillator strength of the transition. We are making the approximation that a small B -field makes a negligible difference to the radial wavefunctions of the atom. (*Need to justify this assertion*).

Suppose that a uniform spectrum of light ranging over all frequencies is illuminating an alkali metal atom in its ground state. The probability that the valence electron will undergo some transition is unity. However, only certain discrete frequencies of light will be absorbed and result in a transition. The probability for a particular transition to occur is given by the oscillator strength. The reduced oscillator strength is the sum over final states and average over initial states for a transition between two terms:

$$f_{i \rightarrow f} = \frac{2m\omega_f^2}{3\hbar} \frac{\sum_{m_i} \left[\sum_{m_f} |\langle J_f, m_f | \vec{r} | J_i, m_i \rangle|^2 \right]}{2J_i + 1} \quad (333)$$

Recall the Wigner-Eckardt Theorem:

$$\langle J_f, m_f | \hat{T}_q^k | J_i, m_i \rangle = \frac{1}{\sqrt{2J_f + 1}} [\langle J_i, m_i | \langle k, q | J_f, m_f \rangle] \langle J_f || T^k || J_i \rangle \quad (334)$$

Note that the operator $\vec{r} = \sum_q r_q^1$ itself is complex: $r_q^1 = r_{-q}$ and $r_{\pm} = r_{\pm 1} = r_x \pm ir_y$. Applying this theorem, we get in general:

$$\left| \langle L'_{J_f}, m_f | r_q^1 | L_{J_i}, m_i \rangle \right|^2 = \langle L_{J_i}, m_i | r_{-q}^1 | L'_{J_f}, m_f \rangle \langle L'_{J_f}, m_f | r_q^1 | L_{J_i}, m_i \rangle \quad (335)$$

$$= \frac{1}{\sqrt{2J_i + 1}} [\langle J_f, m_f | \langle 1, -q | J_i, m_i \rangle] \langle L_{J_i} || r^1 || L'_{J_f} \rangle \\ \times \frac{1}{\sqrt{2J_f + 1}} [\langle J_i, m_i | \langle 1, q | J_f, m_f \rangle] \langle L'_{J_f} || r^1 || L_{J_i} \rangle \quad (336)$$

$$= \frac{1}{\sqrt{2J_i + 1}} \langle (J_f, 1) m_f, -q | J_i, m_i \rangle \\ \times \frac{1}{\sqrt{2J_f + 1}} \langle (J_i, 1) m_i, q | J_f, m_f \rangle \left| \langle L'_{J_f} || r^1 || L_{J_i} \rangle \right|^2 \quad (337)$$

The last term in the product is just the modulus square radial matrix element, which we are going to relate to the reduced oscillator strength. The other terms are square roots of statistical weights and and Clebsch-Gordon coefficients. Wigner $3j$ symbols can be used to relate these quantities. The $3j$ symbol $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ stands for the addition of angular momenta of j_1 and j_2 to give j_3 :

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{2j_3 + 1}} \langle (j_1, j_2) m_1, m_2 | j_3, m_3 \rangle \delta_{m_1 + m_2 + m_3}^0 \quad (338)$$

$$= (-1)^{-j_1 - j_2 - j_3} \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix} \quad (339)$$

Using these relationships:

$$\frac{(-1)^{J_f - 1 - m_i}}{\sqrt{2J_i + 1}} \langle (J_f, 1) m_f, -q | J_i, m_i \rangle = (-1)^{-J_i - J_f - 1} \frac{(-1)^{J_i - 1 - m_f}}{\sqrt{2J_f + 1}} \langle (J_i, 1) m_i, q | J_f, m_f \rangle \quad (340)$$

where $m_f = m_i + q$, we find:

$$\langle (J_f, 1) m_f, -q | J_i, m_i \rangle = (-1)^{2J_f+q+1} \frac{\sqrt{2J_i+1}}{\sqrt{2J_f+1}} \langle (J_i, 1) m_i, q | J_f, m_f \rangle \quad (341)$$

Therefore we can write the modulus squared matrix elements in general:

$$\left| \langle L'_{J_f}, m_f | r_q | L_{J_i}, m_i \rangle \right|^2 = \frac{(-1)^{2J_f+q+1}}{2J_f+1} \langle (J_i, 1) m_i, q | J_f, m_f \rangle^2 \left| \langle L'_{J_f} || r^1 || L_{J_i} \rangle \right|^2 \quad (342)$$

For simplicity, the Clebsch-Gordon coefficient in brackets will be relabeled $\langle m_i, q | J_f, m_f \rangle$ such that $m_i + q = m_f$. Note that the convention is that $f < 0$ for emission and $f > 0$ for absorption. In other words, the physical process under consideration determines the sign for f and *not* the $(-1)^{2J_f+q+1}$ factor. The oscillator strengths for the D1 and D2 transitions will be labeled $f_{\frac{1}{2}}$ and $f_{\frac{3}{2}}$ respectively. Using this notation, $J_i = \frac{1}{2}, S_{\frac{1}{2}}, J_f = J, P_J$, and the zero-field frequencies for the transitions:

$$f_J = \frac{m\omega_J}{3\hbar} \sum_{m_f=-J}^{+J} \left| \langle P_J, m_f | r_{-1}^1 | S_{\frac{1}{2}}, -\frac{1}{2} \rangle \right|^2 + \left| \langle P_J, m_f | r_0^1 | S_{\frac{1}{2}}, -\frac{1}{2} \rangle \right|^2 + \left| \langle P_J, m_f | r_{+1}^1 | S_{\frac{1}{2}}, -\frac{1}{2} \rangle \right|^2 \\ + \left| \langle P_J, m_f | r_{-1}^1 | S_{\frac{1}{2}}, +\frac{1}{2} \rangle \right|^2 + \left| \langle P_J, m_f | r_0^1 | S_{\frac{1}{2}}, +\frac{1}{2} \rangle \right|^2 + \left| \langle P_J, m_f | r_{+1}^1 | S_{\frac{1}{2}}, +\frac{1}{2} \rangle \right|^2 \quad (343)$$

$$= \frac{m\omega_J}{3\hbar} \frac{\left| \langle P_J || r^1 || S_{\frac{1}{2}} \rangle \right|^2}{2J+1} \sum_{m_f=-J}^{+J} \left\langle -\frac{1}{2}, -1 | P_J, m_f \right\rangle^2 + \left\langle -\frac{1}{2}, 0 | P_J, m_f \right\rangle^2 + \left\langle -\frac{1}{2}, +1 | P_J, m_f \right\rangle^2 \\ + \left\langle +\frac{1}{2}, -1 | P_J, m_f \right\rangle^2 + \left\langle +\frac{1}{2}, 0 | P_J, m_f \right\rangle^2 + \left\langle +\frac{1}{2}, +1 | P_J, m_f \right\rangle^2 \quad (344)$$

Note that each matrix element was chosen to be positive since we are considering absorption. The Clebsch-Gordon coefficients for adding angular momenta of $\frac{1}{2}$ and 1 are:

$$\left\langle \pm\frac{1}{2}, m_f \mp \frac{1}{2} | \frac{3}{2}, m_f \right\rangle = \frac{1}{\sqrt{3}} \sqrt{\frac{3}{2} \pm m_f} \quad (345)$$

$$\left\langle \pm\frac{1}{2}, m_f \mp \frac{1}{2} | \frac{1}{2}, m_f \right\rangle = \frac{\mp 1}{\sqrt{3}} \sqrt{\frac{3}{2} \mp m_f} \quad (346)$$

Putting in these values, we get:

$$f_{\frac{1}{2}} = \frac{m\omega_{\frac{1}{2}}}{6\hbar} \left| \langle P_{\frac{1}{2}} || r^1 || S_{\frac{1}{2}} \rangle \right|^2 \\ \times \left(\left\langle -\frac{1}{2}, 0 | P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle^2 + \left\langle -\frac{1}{2}, +1 | P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle^2 + \left\langle +\frac{1}{2}, -1 | P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle^2 + \left\langle +\frac{1}{2}, 0 | P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle^2 \right) \quad (347) \\ = \frac{m\omega_{\frac{1}{2}}}{18\hbar} \left| \langle P_{\frac{1}{2}} || r^1 || S_{\frac{1}{2}} \rangle \right|^2 \left(\frac{3}{2} + \frac{-1}{2} + \frac{3}{2} + \frac{+1}{2} + \frac{3}{2} - \frac{-1}{2} + \frac{3}{2} - \frac{+1}{2} \right) \quad (348)$$

$$f_{\frac{1}{2}} = \frac{m\omega_{\frac{1}{2}}}{3\hbar} \left| \langle P_{\frac{1}{2}} || r^1 || S_{\frac{1}{2}} \rangle \right|^2 \quad (349)$$

$$f_{\frac{3}{2}} = \frac{m\omega_{\frac{3}{2}}}{12\hbar} \left| \langle P_{\frac{3}{2}} || r^1 || S_{\frac{1}{2}} \rangle \right|^2 \left\langle -\frac{1}{2}, -1 | P_{\frac{3}{2}}, -\frac{3}{2} \right\rangle^2 + \left\langle -\frac{1}{2}, 0 | P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle^2 + \left\langle -\frac{1}{2}, +1 | P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle^2 \\ + \left\langle +\frac{1}{2}, -1 | P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle^2 + \left\langle +\frac{1}{2}, 0 | P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle^2 + \left\langle +\frac{1}{2}, +1 | P_{\frac{3}{2}}, +\frac{3}{2} \right\rangle^2 \quad (350)$$

$$= \frac{m\omega_{\frac{3}{2}}}{36\hbar} \left| \langle P_{\frac{3}{2}} || r^1 || S_{\frac{1}{2}} \rangle \right|^2 \left(\frac{3}{2} - \frac{-3}{2} + \frac{3}{2} - \frac{-1}{2} + \frac{3}{2} - \frac{+1}{2} + \frac{3}{2} + \frac{-1}{2} + \frac{3}{2} + \frac{+1}{2} + \frac{3}{2} + \frac{+3}{2} \right) \quad (351)$$

$$f_{\frac{3}{2}} = \frac{m\omega_{\frac{3}{2}}}{3\hbar} \left| \langle P_{\frac{3}{2}} || r^1 || S_{\frac{1}{2}} \rangle \right|^2 \quad (352)$$

In summary, the zero-field modulus squared radial matrix elements are:

$$\left| \left\langle P_{\frac{1}{2}, \frac{3}{2}} \left\| r^1 \left\| S_{\frac{1}{2}} \right\rangle \right\rangle \right|^2 = \frac{3\hbar}{m\omega_{\frac{1}{2}, \frac{3}{2}}} f_{\frac{1}{2}, \frac{3}{2}} \quad (353)$$

The modulus squared matrix elements for transitions involving the absorption of photon with helicity +1 are calculated below. Note that since we are considering absorption, the positive sign is taken.

$$\left| \left\langle P_{\frac{1}{2}, +\frac{1}{2}} \left\| r_+ \left\| S_{\frac{1}{2}, -\frac{1}{2}} \right\rangle \right\rangle \right|^2 = \frac{1}{2} \left\langle -\frac{1}{2}, +1 \left| P_{\frac{1}{2}, +\frac{1}{2}} \right\rangle \right|^2 \left| \left\langle P_{\frac{1}{2}} \left\| r^1 \left\| S_{\frac{1}{2}} \right\rangle \right\rangle \right|^2 \quad (354)$$

$$= \frac{1}{2 \cdot 3} \left(+\frac{3}{2} + \frac{+1}{2} \right) \frac{3\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} = \frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \quad (355)$$

$$\left| \left\langle P_{\frac{3}{2}, +\frac{1}{2}} \left\| r_+ \left\| S_{\frac{1}{2}, -\frac{1}{2}} \right\rangle \right\rangle \right|^2 = \frac{1}{4} \left\langle -\frac{1}{2}, +1 \left| P_{\frac{3}{2}, +\frac{1}{2}} \right\rangle \right|^2 \left| \left\langle P_{\frac{3}{2}} \left\| r^1 \left\| S_{\frac{1}{2}} \right\rangle \right\rangle \right|^2 \quad (356)$$

$$= \frac{1}{4 \cdot 3} \left(+\frac{3}{2} - \frac{+1}{2} \right) \frac{3\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} = \frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \quad (357)$$

$$\left| \left\langle P_{\frac{3}{2}, +\frac{3}{2}} \left\| r_+ \left\| S_{\frac{1}{2}, +\frac{1}{2}} \right\rangle \right\rangle \right|^2 = \frac{1}{4} \left\langle +\frac{1}{2}, +1 \left| P_{\frac{3}{2}, +\frac{3}{2}} \right\rangle \right|^2 \left| \left\langle P_{\frac{3}{2}} \left\| r^1 \left\| S_{\frac{1}{2}} \right\rangle \right\rangle \right|^2 \quad (358)$$

$$= \frac{1}{4 \cdot 3} \left(+\frac{3}{2} + \frac{+3}{2} \right) \frac{3\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} = \frac{3\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \quad (359)$$

$$(360)$$

The modulus squared matrix elements for transitions involving the absorption of photon with helicity -1:

$$\left| \left\langle P_{\frac{1}{2}, -\frac{1}{2}} \left\| r_- \left\| S_{\frac{1}{2}, +\frac{1}{2}} \right\rangle \right\rangle \right|^2 = \frac{1}{2} \left\langle +\frac{1}{2}, -1 \left| P_{\frac{1}{2}, -\frac{1}{2}} \right\rangle \right|^2 \left| \left\langle P_{\frac{1}{2}} \left\| r^1 \left\| S_{\frac{1}{2}} \right\rangle \right\rangle \right|^2 \quad (361)$$

$$= \frac{1}{2 \cdot 3} \left(+\frac{3}{2} - \frac{-1}{2} \right) \frac{3\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} = \frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \quad (362)$$

$$\left| \left\langle P_{\frac{3}{2}, -\frac{1}{2}} \left\| r_- \left\| S_{\frac{1}{2}, +\frac{1}{2}} \right\rangle \right\rangle \right|^2 = \frac{1}{4} \left\langle +\frac{1}{2}, -1 \left| P_{\frac{3}{2}, -\frac{1}{2}} \right\rangle \right|^2 \left| \left\langle P_{\frac{3}{2}} \left\| r^1 \left\| S_{\frac{1}{2}} \right\rangle \right\rangle \right|^2 \quad (363)$$

$$= \frac{1}{4 \cdot 3} \left(+\frac{3}{2} + \frac{-1}{2} \right) \frac{3\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} = \frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \quad (364)$$

$$\left| \left\langle P_{\frac{3}{2}, -\frac{3}{2}} \left\| r_- \left\| S_{\frac{1}{2}, -\frac{1}{2}} \right\rangle \right\rangle \right|^2 = \frac{1}{4} \left\langle -\frac{1}{2}, -1 \left| P_{\frac{3}{2}, -\frac{3}{2}} \right\rangle \right|^2 \left| \left\langle P_{\frac{3}{2}} \left\| r^1 \left\| S_{\frac{1}{2}} \right\rangle \right\rangle \right|^2 \quad (365)$$

$$= \frac{1}{4 \cdot 3} \left(+\frac{3}{2} - \frac{-3}{2} \right) \frac{3\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} = \frac{3\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \quad (366)$$

$$(367)$$

Some of the excited eigenstates $\{|b_k\rangle\}$ are mixed states. These matrix elements are evaluated in the following way. Note that special care needs to be taken for the sign convention of this matrix element. The absorption sign convention dictates that the whole matrix element must be positive. A negative sign is needed to make the whole matrix element positive. Note that since the first two terms are from the previous eqns, they already implicitly take the negative sign into account to yield positive values. However, the crossterms need an explicit negative sign for consistency.

$$\begin{aligned} \left| \left(c_1^* \left\langle P_{\frac{3}{2}, \pm\frac{1}{2}} \left\| + c_2^* \left\langle P_{\frac{1}{2}, \pm\frac{1}{2}} \right\rangle \right\| r_{\pm} \left\| S_{\frac{1}{2}, \mp\frac{1}{2}} \right\rangle \right) \right|^2 &= c_1^2 \left| \left\langle P_{\frac{3}{2}, \pm\frac{1}{2}} \left\| r_{\pm} \left\| S_{\frac{1}{2}, \mp\frac{1}{2}} \right\rangle \right\rangle \right|^2 + c_2^2 \left| \left\langle P_{\frac{1}{2}, \pm\frac{1}{2}} \left\| r_{\pm} \left\| S_{\frac{1}{2}, \mp\frac{1}{2}} \right\rangle \right\rangle \right|^2 \\ &\quad - c_1^* c_2 \left\langle P_{\frac{3}{2}, \pm\frac{1}{2}} \left\| r_{\pm} \left\| S_{\frac{1}{2}, \mp\frac{1}{2}} \right\rangle \right\rangle^\dagger \left\langle P_{\frac{1}{2}, \pm\frac{1}{2}} \left\| r_{\pm} \left\| S_{\frac{1}{2}, \mp\frac{1}{2}} \right\rangle \right\rangle \end{aligned}$$

$$\begin{aligned}
& -c_1 c_2^* \left\langle P_{\frac{3}{2}}, \pm \frac{1}{2} \left| r_{\pm} \right| S_{\frac{1}{2}}, \mp \frac{1}{2} \right\rangle \left\langle P_{\frac{3}{2}}, \pm \frac{1}{2} \left| r_{\pm} \right| S_{\frac{1}{2}}, \mp \frac{1}{2} \right\rangle^\dagger \quad (368) \\
& = c_1^2 \left| \left\langle P_{\frac{3}{2}}, \pm \frac{1}{2} \left| r_{\pm} \right| S_{\frac{1}{2}}, \mp \frac{1}{2} \right\rangle \right|^2 + c_2^2 \left| \left\langle P_{\frac{3}{2}}, \pm \frac{1}{2} \left| r_{\pm} \right| S_{\frac{1}{2}}, \mp \frac{1}{2} \right\rangle \right|^2 \\
& -c_1 c_2 \left\langle S_{\frac{1}{2}}, \mp \frac{1}{2} \left| r_{\mp} \right| P_{\frac{3}{2}}, \pm \frac{1}{2} \right\rangle \left\langle P_{\frac{3}{2}}, \pm \frac{1}{2} \left| r_{\pm} \right| S_{\frac{1}{2}}, \mp \frac{1}{2} \right\rangle \\
& -c_1 c_2 \left\langle P_{\frac{3}{2}}, \pm \frac{1}{2} \left| r_{\pm} \right| S_{\frac{1}{2}}, \mp \frac{1}{2} \right\rangle \left\langle S_{\frac{1}{2}}, \mp \frac{1}{2} \left| r_{\mp} \right| P_{\frac{3}{2}}, \pm \frac{1}{2} \right\rangle \quad (369)
\end{aligned}$$

The cross terms will be expanded using WE thm:

$$\left\langle S_{\frac{1}{2}}, \mp \frac{1}{2} \left| r_{\mp} \right| P_{\frac{3}{2}}, \pm \frac{1}{2} \right\rangle = \frac{1}{\sqrt{2(\frac{1}{2})+1}} \left\langle \left(\frac{3}{2}, 1 \right) \pm \frac{1}{2}, \mp 1 \left| \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right\rangle \langle S_{\frac{1}{2}} \| r^1 \| P_{\frac{3}{2}} \rangle \quad (370)$$

$$= \frac{1}{\sqrt{2}} \left\langle \left(\frac{3}{2}, 1 \right) \pm \frac{1}{2}, \mp 1 \left| \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right\rangle \sqrt{\frac{3\hbar f_{\frac{3}{2}}}{m\omega_{\frac{3}{2}}}} \quad (371)$$

$$= \frac{1}{\sqrt{2}} \frac{1}{\sqrt{6}} \sqrt{\frac{3\hbar f_{\frac{3}{2}}}{m\omega_{\frac{3}{2}}}} = \frac{1}{2} \sqrt{\frac{\hbar f_{\frac{3}{2}}}{m\omega_{\frac{3}{2}}}} \quad (372)$$

$$\left\langle P_{\frac{3}{2}}, \pm \frac{1}{2} \left| r_{\pm} \right| S_{\frac{1}{2}}, \mp \frac{1}{2} \right\rangle = \frac{1}{\sqrt{2(\frac{1}{2})+1}} \left\langle \left(\frac{1}{2}, 1 \right) \mp \frac{1}{2}, \pm 1 \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle \right\rangle \langle P_{\frac{3}{2}} \| r^1 \| S_{\frac{1}{2}} \rangle \quad (373)$$

$$= \frac{-1}{\sqrt{2}} \left\langle \left(1, \frac{1}{2} \right) \pm 1, \mp \frac{1}{2} \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle \right\rangle \sqrt{\frac{3\hbar f_{\frac{1}{2}}}{m\omega_{\frac{1}{2}}}} \quad (374)$$

$$= \frac{-1 \pm \sqrt{2}}{\sqrt{2} \sqrt{3}} \sqrt{\frac{3\hbar f_{\frac{1}{2}}}{m\omega_{\frac{1}{2}}}} = \mp \sqrt{\frac{\hbar f_{\frac{1}{2}}}{m\omega_{\frac{1}{2}}}} \quad (375)$$

$$\left\langle P_{\frac{3}{2}}, \pm \frac{1}{2} \left| r_{\pm} \right| S_{\frac{1}{2}}, \mp \frac{1}{2} \right\rangle = \frac{1}{\sqrt{2(\frac{3}{2})+1}} \left\langle \left(\frac{1}{2}, 1 \right) \mp \frac{1}{2}, \pm 1 \left| \frac{3}{2}, \pm \frac{1}{2} \right\rangle \right\rangle \langle P_{\frac{3}{2}} \| r^1 \| S_{\frac{1}{2}} \rangle \quad (376)$$

$$= \frac{-1}{2} \left\langle \left(1, \frac{1}{2} \right) \pm 1, \mp \frac{1}{2} \left| \frac{3}{2}, \pm \frac{1}{2} \right\rangle \right\rangle \sqrt{\frac{3\hbar f_{\frac{3}{2}}}{m\omega_{\frac{3}{2}}}} \quad (377)$$

$$= \frac{-1}{2} \frac{1}{\sqrt{3}} \sqrt{\frac{3\hbar f_{\frac{3}{2}}}{m\omega_{\frac{3}{2}}}} = \frac{-1}{2} \sqrt{\frac{\hbar f_{\frac{3}{2}}}{m\omega_{\frac{3}{2}}}} \quad (378)$$

$$\left\langle S_{\frac{1}{2}}, \mp \frac{1}{2} \left| r_{\mp} \right| P_{\frac{1}{2}}, \pm \frac{1}{2} \right\rangle = \frac{1}{\sqrt{2(\frac{1}{2})+1}} \left\langle \left(\frac{1}{2}, 1 \right) \pm \frac{1}{2}, \mp 1 \left| \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right\rangle \langle S_{\frac{1}{2}} \| r^1 \| P_{\frac{1}{2}} \rangle \quad (379)$$

$$= \frac{-1}{\sqrt{2}} \left\langle \left(1, \frac{1}{2} \right) \mp 1, \pm \frac{1}{2} \left| \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right\rangle \sqrt{\frac{3\hbar f_{\frac{1}{2}}}{m\omega_{\frac{1}{2}}}} \quad (380)$$

$$= \frac{-1 \mp \sqrt{2}}{\sqrt{2} \sqrt{3}} \sqrt{\frac{3\hbar f_{\frac{1}{2}}}{m\omega_{\frac{1}{2}}}} = \pm \sqrt{\frac{\hbar f_{\frac{1}{2}}}{m\omega_{\frac{1}{2}}}} \quad (381)$$

Note that when swithing the order of the two angular momenta (j_1, j_2) being added together in the Clebsch-Gordon coefficient, a minus sign can be picked up:

$$\langle (j_1, j_2) m_1, m_2 | j_3, m_3 \rangle = (-1)^{j_3 - j_1 - j_2} \langle (j_2, j_1) m_2, m_1 | j_3, m_3 \rangle \quad (382)$$

Note also the following relation between radial matrix element and oscillator strength used above:

$$\langle P_{\frac{1}{2}, \frac{3}{2}} \| r^1 \| S_{\frac{1}{2}} \rangle = \langle S_{\frac{1}{2}} \| r^1 \| P_{\frac{1}{2}, \frac{3}{2}} \rangle = \sqrt{\frac{3\hbar}{m\omega_{\frac{1}{2}, \frac{3}{2}}}} f_{\frac{1}{2}, \frac{3}{2}} \quad (383)$$

This is the case for the last three terms calculated above. Putting this together, we get:

$$\left| \left(c_1^* \left\langle P_{\frac{3}{2}, \pm \frac{1}{2}} \right| + c_2^* \left\langle P_{\frac{1}{2}, \pm \frac{1}{2}} \right| \right) r_{\pm} \left| S_{\frac{1}{2}, \mp \frac{1}{2}} \right. \right|^2 = c_1^2 \frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} + c_2^2 \frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \pm c_1 c_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{m\omega_{\frac{3}{2}}}} \sqrt{\frac{\hbar f_{\frac{1}{2}}}{m\omega_{\frac{1}{2}}}} \quad (384)$$

3.4.3 Atomic Polarizability for Circularly Polarized Light

Putting this altogether, the atomic polarizability for right circularly polarized light is:

$$\begin{aligned} \frac{\hbar}{e^2} \alpha_{+} &= P_{-} \left[a_1^2 \left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) + a_2^2 \left(\frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right) \pm a_1 a_2 \sqrt{\left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) \left(\frac{\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{1}{2}} + \left(\frac{4}{3} \right) \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} + \left(\omega_{\frac{1}{2}} + \left(\frac{4}{3} \right) \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} \right] \\ &+ P_{-} \left[a_2^2 \left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) + a_1^2 \left(\frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right) \mp a_1 a_2 \sqrt{\left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) \left(\frac{\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{3}{2}} + \left(\frac{5}{3} \right) \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} + \left(\frac{5}{3} \right) \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \\ &+ P_{+} \left[\frac{3\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right] \times \left[\left(\omega_{\frac{3}{2}} + \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} + \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \quad (385) \end{aligned}$$

The atomic polarizability for left circularly polarized light is:

$$\begin{aligned} \frac{\hbar}{e^2} \alpha_{-} &= P_{+} \left[a_1^2 \left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) + a_2^2 \left(\frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right) \pm a_1 a_2 \sqrt{\left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) \left(\frac{\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{1}{2}} - \left(\frac{4}{3} \right) \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} + \left(\omega_{\frac{1}{2}} - \left(\frac{4}{3} \right) \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} \right] \\ &+ P_{+} \left[a_2^2 \left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) + a_1^2 \left(\frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right) \mp 2a_1 a_2 \sqrt{\left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) \left(\frac{\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{3}{2}} - \left(\frac{5}{3} \right) \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} - \left(\frac{5}{3} \right) \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \\ &+ P_{-} \left[\frac{3\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right] \times \left[\left(\omega_{\frac{3}{2}} - \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} - \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \quad (386) \end{aligned}$$

Rearranging a few things:

$$\begin{aligned} \frac{m}{e^2} \alpha_{\pm} &= P_{\mp} \left[a_1^2 \left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) + a_2^2 \left(\frac{f_{\frac{3}{2}}}{4\omega_{\frac{3}{2}}} \right) \pm a_1 a_2 \sqrt{\left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left(\frac{f_{\frac{3}{2}}}{\omega_{\frac{3}{2}}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{1}{2}} \pm \left(\frac{4}{3} \right) \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} + \left(\omega_{\frac{1}{2}} \pm \left(\frac{4}{3} \right) \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} \right] \\ &+ P_{\mp} \left[a_2^2 \left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) + a_1^2 \left(\frac{f_{\frac{3}{2}}}{4\omega_{\frac{3}{2}}} \right) \mp a_1 a_2 \sqrt{\left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left(\frac{f_{\frac{3}{2}}}{\omega_{\frac{3}{2}}} \right)} \right] \end{aligned}$$

$$\begin{aligned}
& \times \left[\left(\omega_{\frac{3}{2}} \pm \left(\frac{5}{3} \right) \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} \pm \left(\frac{5}{3} \right) \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \\
& + P_{\pm} \left[\frac{3f_{\frac{3}{2}}}{4\omega_{\frac{3}{2}}} \right] \times \left[\left(\omega_{\frac{3}{2}} \pm \frac{\mu_B}{\hbar} B - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} \pm \frac{\mu_B}{\hbar} B + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \quad (387)
\end{aligned}$$

There are quite a few items to note about this equation,

1. The energies of the $\pm\frac{1}{2}$ states in the P terms used low field energies approximations. They could have very well have been the exact values if necessary.
2. The mixing coefficients a_1 & a_2 are only relevant for the $m_J = \pm\frac{1}{2}$ states in the P terms. The exact values of these coefficients depend on the sign of m_J . However, the low field approximations of a_1 & a_2 , which we will use, do not depend on the sign of m_J .
3. P_{\pm} is the fraction of atoms in the $m_J = \pm\frac{1}{2}$ ground state. Therefore, $P_+ + P_- = 1$ and $P_+ - P_- = P$.
4. The electron mass is m and the absolute value of the electron charge is e .
5. In principle, the oscillator strengths $f_{\frac{1}{2},\frac{3}{2}}$ are affected by the temperature and the density of the buffer gas. We will make the approximation that for both Rb and K that $f_{\frac{1}{2}} \approx \frac{1}{3}$ and that $f_{\frac{3}{2}} \approx \frac{2}{3}$. Most book values are quoted with an uncertainty of about 10%. Therefore, using these approximate values for the oscillator strengths under most conditions is good enough.
6. For measurements with near resonant light $\omega \approx \omega_{\frac{1}{2},\frac{3}{2}}$, the $(\omega_0 + \omega + \dots)^{-1}$ term is dominated by the $(\omega_0 - \omega + \dots)^{-1}$ term. Therefore, we will keep only the dominant term.
7. For Rb, we will be scanning about the D2 transition. For K, we will be scanning close to both the D1 and D2 transitions because they happen to be close together. Therefore it is safe to replace the $\omega_{\frac{1}{2},\frac{3}{2}}$'s located under the oscillator strengths with the probe beam frequency ω . This will prove to be a convenient approximation.

Applying all of these approximations and making substitutions to be consistent with the literature:

$$P_{\pm} = \frac{1 \pm P}{2} \quad (388)$$

$$\Delta_{\frac{1}{2},\frac{3}{2}} = \omega - \omega_{\frac{1}{2},\frac{3}{2}} \quad (389)$$

$$\Omega = \frac{\mu_B}{\hbar} B \quad (390)$$

$$\begin{aligned}
\frac{m}{e^2} \alpha_{\pm} &= P_{\mp} \left[1 \cdot \left(\frac{1}{3} \right) + 0 \cdot \left(\frac{2}{4\omega} \right) \pm \beta y \sqrt{\left(\frac{1}{3} \right) \left(\frac{2}{\omega} \right)} \right] \times \left[\left(-\Delta_{\frac{1}{2}} \pm \left(\frac{4}{3} \right) \Omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} \right] \\
&+ P_{\mp} \left[0 \cdot \left(\frac{1}{\omega} \right) + 1 \cdot \left(\frac{2}{4\omega} \right) \mp \beta y \sqrt{\left(\frac{1}{3} \right) \left(\frac{2}{\omega} \right)} \right] \times \left[\left(-\Delta_{\frac{3}{2}} \pm \left(\frac{5}{3} \right) \Omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \\
&+ P_{\pm} \left[\frac{3\frac{2}{3}}{4\omega} \right] \times \left[\left(-\Delta_{\frac{3}{2}} \pm \Omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \quad (391)
\end{aligned}$$

$$\beta y = \frac{\sqrt{\left(1 + \frac{1}{2}\right)^2 - \frac{1}{4}}}{3} (-1 - -2) \frac{\mu_B B}{\hbar \omega_{80}} = \frac{\sqrt{2}}{3} \frac{\Omega}{\omega_{80}} \quad (392)$$

$$(393)$$

Finally, the explicit and specific formula for the atomic polarizability taking into account fine structure mixing valid for K and Rb is:

$$\left(\frac{m\omega}{e^2} \right) \alpha_{\pm} = \frac{1 \mp P}{2} \left[\frac{1}{3} \pm \frac{\Omega}{\omega_{80}} \frac{2}{9} \right] \left(-\Delta_{\frac{1}{2}} \pm \left(\frac{4}{3} \right) \Omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} + \frac{1 \mp P}{2} \left[\frac{1}{6} \mp \frac{\Omega}{\omega_{80}} \frac{2}{9} \right] \left(-\Delta_{\frac{3}{2}} \pm \left(\frac{5}{3} \right) \Omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1}$$

$$+\frac{1 \pm P}{4} \left(-\Delta_{\frac{3}{2}} \pm \Omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \quad (394)$$

3.5 Explicit Calculation of Rotation Angle

Recall the following relations in SI units:

$$k_{\pm} = \mathcal{R}e \frac{\omega}{c} n_{\pm} \quad (395)$$

$$= \mathcal{R}e \frac{\omega}{c} \sqrt{\frac{\epsilon}{\epsilon_0}} \quad (396)$$

$$= \mathcal{R}e \frac{\omega}{c} \sqrt{\frac{\epsilon_0 + [\mathcal{A}] \alpha_{\pm}}{\epsilon_0}} \quad (397)$$

$$= \mathcal{R}e \frac{\omega}{c} \sqrt{1 + \frac{[\mathcal{A}] \alpha_{\pm}}{\epsilon_0}} \quad (398)$$

$$\simeq \mathcal{R}e \frac{\omega}{c} \left(1 + \frac{[\mathcal{A}] \alpha_{\pm}}{2\epsilon_0} \right) \quad (399)$$

where $[\mathcal{A}]$ is the density of the medium, which in our case is the alkali metal vapor. The formula for the Faraday Rotation angle is:

$$\phi = \frac{l}{2} (k_{\mathcal{L}} - k_{\mathcal{R}}) \quad (400)$$

$$= \frac{l}{2} (k_{-} - k_{+}) \quad (401)$$

$$= \frac{l}{2} \left(\mathcal{R}e \frac{\omega}{c} \left(1 + \frac{[\mathcal{A}] \alpha_{-}}{2\epsilon_0} \right) - \mathcal{R}e \frac{\omega}{c} \left(1 + \frac{[\mathcal{A}] \alpha_{+}}{2\epsilon_0} \right) \right) \quad (402)$$

$$= \frac{l\omega[\mathcal{A}]}{4c\epsilon_0} \mathcal{R}e (\alpha_{-} - \alpha_{+}) \quad (403)$$

$$(404)$$

A useful small field expansion, lowest order in Ω for the real part:

$$\mathcal{R}e \left(-\Delta \pm g\Omega + \frac{i}{2} \gamma \right)^{-1} = \frac{-\Delta \pm g\Omega}{(-\Delta \pm g\Omega)^2 + \frac{\gamma^2}{4}} \quad (405)$$

$$= (-\Delta \pm g\Omega) \left[\Delta^2 + g^2\Omega^2 \mp 2g\Delta\Omega + \frac{\gamma^2}{4} \right]^{-1} \quad (406)$$

$$= \left(\frac{-\Delta \pm g\Omega}{\Delta^2 + \frac{\gamma^2}{4}} \right) \left[1 + \frac{g^2\Omega^2 \mp 2g\Delta\Omega}{\Delta^2 + \frac{\gamma^2}{4}} \right]^{-1} \quad (407)$$

$$\simeq \left(\frac{-\Delta \pm g\Omega}{\Delta^2 + \frac{\gamma^2}{4}} \right) \left[1 - \frac{g^2\Omega^2 \mp 2g\Delta\Omega}{\Delta^2 + \frac{\gamma^2}{4}} \right] \quad (408)$$

$$\simeq \frac{-\Delta \pm g\Omega \mp \frac{2\Delta^2 g\Omega}{\Delta^2 + \frac{\gamma^2}{4}}}{\Delta^2 + \frac{\gamma^2}{4}} \quad (409)$$

$$\simeq \frac{-\Delta \pm g\Omega \left(1 - \frac{2\Delta^2}{\Delta^2 + \frac{\gamma^2}{4}} \right)}{\Delta^2 + \frac{\gamma^2}{4}} \quad (410)$$

$$\simeq \frac{-\Delta \mp g\Omega \left(\frac{\Delta^2 - \frac{\gamma^2}{4}}{\Delta^2 + \frac{\gamma^2}{4}} \right)}{\Delta^2 + \frac{\gamma^2}{4}} \quad (411)$$

$$\approx \frac{-\frac{1}{\Delta} \mp g \frac{\Omega}{\Delta^2} \left(\frac{1 - \frac{\gamma^2}{4\Delta^2}}{1 + \frac{\gamma^2}{4\Delta^2}} \right)}{1 + \frac{\gamma^2}{4\Delta^2}} \quad (412)$$

Putting this in:

$$\begin{aligned} \left(\frac{m\omega}{e^2} \right) \alpha_{\pm} = & \frac{1 \mp P}{2} \left[\frac{1}{3} \pm \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{1}{2}}} \mp \frac{4\Omega}{3\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right] + \frac{1 \mp P}{2} \left[\frac{1}{6} \mp \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} \mp \frac{5\Omega}{3\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \\ & + \frac{1 \pm P}{4} \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} \mp \frac{\Omega}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \end{aligned} \quad (413)$$

$$\begin{aligned} \frac{m\omega}{e^2} (\alpha_- - \alpha_+) = & \frac{1+P}{2} \left[\frac{1}{3} - \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{1}{2}}} + \frac{4\Omega}{3\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right] - \frac{1-P}{2} \left[\frac{1}{3} + \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{1}{2}}} - \frac{4\Omega}{3\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right] \\ & + \frac{1+P}{2} \left[\frac{1}{6} + \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} + \frac{5\Omega}{3\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] - \frac{1-P}{2} \left[\frac{1}{6} - \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} - \frac{5\Omega}{3\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \\ & + \frac{1-P}{4} \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} + \frac{\Omega}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] - \frac{1+P}{4} \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} - \frac{\Omega}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \end{aligned} \quad (414)$$

$$\begin{aligned}
&= \left[\frac{\frac{1}{3}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right] \left[-\frac{P}{\Delta_{\frac{1}{2}}} + \frac{4\Omega}{3\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) \right] + \frac{\Omega}{9} \frac{2}{\omega_{80}\Delta_{\frac{1}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) - \frac{8P\Omega^2}{27\omega_{80}^2\Delta_{\frac{1}{2}}^2} \left[\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{\left(1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}\right)^2} \right] \\
&+ \left[\frac{\frac{1}{6} \mp \frac{\Omega}{\omega_{80}} \frac{2}{9}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \left[-\frac{P}{\Delta_{\frac{3}{2}}} + \frac{5\Omega}{3\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) \right] - \frac{\Omega}{9} \frac{2}{\omega_{80}\Delta_{\frac{3}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) + \frac{10P\Omega^2}{27\omega_{80}^2\Delta_{\frac{3}{2}}^2} \left[\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{\left(1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}\right)^2} \right] \\
&+ \left[\frac{\frac{P}{2\Delta_{\frac{3}{2}}} + \frac{\Omega}{2\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \tag{415}
\end{aligned}$$

$$\begin{aligned}
&= \frac{P}{3} \left[\frac{1}{\Delta_{\frac{3}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) - \frac{1}{\Delta_{\frac{1}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) \right] \\
&+ \frac{\Omega}{9} \left[\frac{4}{\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) + \frac{7}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) + \frac{2}{\omega_{80}\Delta_{\frac{1}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) - \frac{2}{\omega_{80}\Delta_{\frac{3}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) \right] \tag{416}
\end{aligned}$$

$$\begin{aligned}
&= \frac{P}{3} \left[\frac{\Delta_{\frac{3}{2}}}{\Delta_{\frac{3}{2}}^2 + \frac{1}{4}\gamma_{\frac{3}{2}}^2} - \frac{\Delta_{\frac{1}{2}}}{\Delta_{\frac{1}{2}}^2 + \frac{1}{4}\gamma_{\frac{1}{2}}^2} \right] \\
&+ \frac{\Omega}{9} \left[\frac{4}{\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) + \frac{7}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) - \frac{2}{\Delta_{\frac{3}{2}}\Delta_{\frac{1}{2}}} \left(\frac{1 + \frac{\Delta_{\frac{1}{2}}\gamma_{\frac{3}{2}}^2 - \Delta_{\frac{3}{2}}\gamma_{\frac{1}{2}}^2}{4\omega_{80}\Delta_{\frac{3}{2}}\Delta_{\frac{1}{2}}}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2\gamma_{\frac{1}{2}}^2}{16\Delta_{\frac{3}{2}}^2\Delta_{\frac{1}{2}}^2}} \right) \right] \tag{417}
\end{aligned}$$

Note the use of the relation $\omega_{80} = \Delta_{\frac{1}{2}} - \Delta_{\frac{3}{2}}$. Only terms to first order in field (Ω) have been kept. The fine structure mixing plays a significant role in the rotation due to the field, but a very small role (2nd order in field) in the rotation due to the polarization. Putting this into the angle formula, we get:

$$\phi = \frac{l\omega[A]}{4c\epsilon_0} \text{Re}(\alpha_- - \alpha_+) \tag{418}$$

$$\begin{aligned}
&= \frac{l\omega[A]P}{12c\epsilon_0} \frac{e^2}{m\omega} \left[\frac{\Delta_{\frac{3}{2}}}{\Delta_{\frac{3}{2}}^2 + \frac{1}{4}\gamma_{\frac{3}{2}}^2} - \frac{\Delta_{\frac{1}{2}}}{\Delta_{\frac{1}{2}}^2 + \frac{1}{4}\gamma_{\frac{1}{2}}^2} \right] \\
&+ \frac{l\omega[A]\Omega}{36c\epsilon_0} \frac{e^2}{m\omega} \left[\frac{4}{\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) + \frac{7}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) - \frac{2}{\Delta_{\frac{3}{2}}\Delta_{\frac{1}{2}}} \left(\frac{1 + \frac{\Delta_{\frac{1}{2}}\gamma_{\frac{3}{2}}^2 - \Delta_{\frac{3}{2}}\gamma_{\frac{1}{2}}^2}{4\omega_{80}\Delta_{\frac{3}{2}}\Delta_{\frac{1}{2}}}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2\gamma_{\frac{1}{2}}^2}{16\Delta_{\frac{3}{2}}^2\Delta_{\frac{1}{2}}^2}} \right) \right] \tag{419}
\end{aligned}$$

Note that the ω 's cancel. This is an approximation as noted before. The rotation angle can be written as a sum of the parts due to the polarization and the field:)★

$$\phi = \phi_P + \phi_B \quad (420)$$

$$\phi_P = I[A]P_A \left(\frac{e^2}{12mce_0} \right) \left[\frac{\Delta_{\frac{3}{2}}}{\Delta_{\frac{3}{2}}^2 + \frac{1}{4}\gamma_{\frac{3}{2}}^2} - \frac{\Delta_{\frac{1}{2}}}{\Delta_{\frac{1}{2}}^2 + \frac{1}{4}\gamma_{\frac{1}{2}}^2} \right] \quad (421)$$

$$\phi_B = I[A]B \left(\frac{e^2 \mu_B}{36mce_0 \hbar} \right) \left[\frac{4}{\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) + \frac{7}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) - \frac{2}{\Delta_{\frac{3}{2}} \Delta_{\frac{1}{2}}} \left(\frac{1 + \frac{\Delta_{\frac{1}{2}} \gamma_{\frac{3}{2}}^2 - \Delta_{\frac{3}{2}} \gamma_{\frac{1}{2}}^2}{4\omega_{\text{sc}} \Delta_{\frac{3}{2}} \Delta_{\frac{1}{2}}}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2} + \frac{\gamma_{\frac{3}{2}} \gamma_{\frac{1}{2}}^2}{16\Delta_{\frac{3}{2}} \Delta_{\frac{1}{2}}^2}} \right) \right] \quad (422)$$

$$\Delta_{\frac{1}{2}, \frac{3}{2}} = \omega - \omega_{\frac{1}{2}, \frac{3}{2}} = 2\pi \left(\nu - \nu_{\frac{1}{2}, \frac{3}{2}} \right) \quad (423)$$

$$\gamma_{\frac{1}{2}, \frac{3}{2}} = 2\pi \times \text{FWHM}_{\text{PB}}^{\frac{1}{2}, \frac{3}{2}} \quad (424)$$

If the detuning is large ($\Delta \gg \gamma$), then the rotation angle formulas can be simplified:

$$\phi_P = I[A]P_A \left(\frac{e^2}{12mce_0} \right) \left[\frac{1}{\Delta_{\frac{3}{2}}} - \frac{1}{\Delta_{\frac{1}{2}}} \right] \quad (425)$$

$$\phi_B = I[A]B \left(\frac{e^2 \mu_B}{36mce_0 \hbar} \right) \left[\frac{4}{\Delta_{\frac{1}{2}}^2} + \frac{7}{\Delta_{\frac{3}{2}}^2} - \frac{2}{\Delta_{\frac{3}{2}} \Delta_{\frac{1}{2}}} \right] \quad (426)$$

3.6 Comments on Circular Dichroism

4 Experimental Applications

All this will be a part of version 2.0 which is underway!

4.1 General Considerations to Measure Faraday Rotation

4.2 Measuring Alkali Number Density with Alkali Polarization = 0

4.3 Measuring Alkali Number Density with Alkali Polarization $\neq 0$

4.4 Measuring ^3He Density

4.5 Measuring ^3He Polarization using EPR

A Physical Constants

This is a list of physical constants used in this note. All units are in SI. These numbers are quoted from the NIST website <http://physics.nist.gov/cuu/Constants/>. They quote the 2002 CODATA recommended values.

Symbol	Value	Units	Description
c	299 792 458	m s ⁻¹	definition of the speed of light
h	6.626 068 76 × 10 ⁻³⁴	J s	Planck constant
e	1.602 176 462 × 10 ⁻¹⁹	C	electron charge magnitude
m	9.109 381 88 × 10 ⁻³¹	kg	electron mass
ϵ_0	8.854 187 817 × 10 ⁻¹²	C ² N ⁻¹ m ⁻²	permittivity of free space
μ_0	4 π × 10 ⁻⁷	N A ⁻²	permeability of free space
μ_B	9.274 000 949 × 10 ⁻²⁴	J T ⁻¹	Bohr magneton
μ_N	5.050 783 43 × 10 ⁻²⁷	J T ⁻¹	Nuclear magneton
g_S	-2.002 319 304 3718	unitless	electron g -factor

B Physical Data of the Alkali Metals

This is a list of physical data relevant to various alkali metals. All units are in SI unless otherwise noted. Sources are NIST website <http://physics.nist.gov/PhysRefData/Handbook/intro.htm> and *Reference Data on Atoms, Molecules, and Ions* by A.A. Radzig and B.M. Smirnov published by Springer-Verlag (Berlin) 1985.

Isotope	Mass amu	Abundance fraction	Spin	Mag. Moment μ_N	g -factor	$\Delta\nu_{hf}$ MHz
${}^6\text{Li}$	6.015 121	0.075 000	1	+0.822 056	+0.822 056	228.205 26
${}^7\text{Li}$	7.016 003	0.925 000	$\frac{3}{2}$	+3.256 44	+2.170 960	803.504 09
${}^{23}\text{Na}$	22.989 767	1.000 000	$\frac{3}{2}$	+2.217 52	+1.478 347	1 771.626 13
${}^{39}\text{K}$	38.963 707	0.932 581	$\frac{3}{2}$	+0.391 46	+0.260 973	461.719 72
${}^{40}\text{K}$	39.963 999	0.000 120	4	-1.298	-0.324 5	?
${}^{41}\text{K}$	40.961 835	0.067 302	$\frac{3}{2}$	+0.214 87	+0.143 247	254.013 87
${}^{85}\text{Rb}$	84.911 794	0.721 700	$\frac{5}{2}$	+1.353 02	+0.541 208	3 035.732 00
${}^{87}\text{Rb}$	86.909 187	0.278 300	$\frac{5}{2}$	+2.751 2	+1.834 133	6 834.682 60
${}^{133}\text{Cs}$	132.905 429	1.000 000	$\frac{7}{2}$	+2.579	+0.736 857	9 192.631 77

Element	Mass amu	Ground State	D_1 nm	$f_{\frac{1}{2}}$ frac	D_2 nm	$f_{\frac{3}{2}}$ frac	$\Delta\nu_{so}$ GHz
Lithium	6.941	2	670.791	0.247	670.776	0.494	9.994 181
Sodium	22.990	3	589.592	0.318	588.995	0.637	515.385 083
Potassium	39.098	4	769.896	0.35	766.490	0.73	1 730.321 444
Rubidium	85.468	5	794.760	0.32	780.027	0.67	7 124.694 632
Cesium	132.905	6	894.346	0.39	852.112	0.81	16 614.247 210