

A Primer on Using Atom-Light Interactions to Study
Spin-Exchange Optical Pumping Polarized ^3He Target Cells

Jaideep Singh
University of Virginia
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Abstract

The two basic quantities that must be known about a ^3He target cell are its helium density & polarization. To better understand & fully optimize the performance of these cells, it is essential to know the alkali vapor density & polarization as well. The atomic polarizability determines how light is modified after traversing a sample of alkali atoms. The imaginary part of the polarizability is responsible for absorption. The width of the absorption line is pressure broadened and consequently linearly proportional to the helium density. The real part of the atomic polarizability causes Faraday rotation of the the plane of polarization of a linearly polarized probe beam. The amount of rotation is proportional to the alkali density. We probe the Zeeman levels of the alkali atom via EPR RF spectroscopy. Slightly exciting one of the transitions lowers the alkali polarization by a small amount. By sweeping the holding field while keeping the RF frequency fixed, we map out the EPR RF spectrum of the alkali atoms. Ratios of areas under the peaks in this spectrum are related to the alkali polarization and alkali density ratio. Finally the locations of these peaks are shifted due interactions with the polarized helium gas. The size of these frequency shifts are proportional to the He polarization. The goal of this note is to present all of the theoretical derivations needed to understand “where the formulas come from.”

First, we’ll derive the fine & hyperfine structure of the alkali atoms. Then we’ll show how to describe polarized light using the Jones calculus. Using standard semi-classical arguments, we’ll study how the matrix elements of the density operator changes under a harmonic perturbation. As a consequence, we’ll calculate the transition matrix elements due to electric & magnetic dipole interactions. The coherences of the density matrix also depend on the populations of the density matrix, which are at a spin temperature equilibrium. To interpret pressure broadening & Faraday rotation, we’ll calculate the atomic polarizability. Finally we’ll provide an overview of the experimental techniques and summarize how to extract information from the experimental observables associated with the wavelength tunable probe beam. This note is meant to be detailed, explicit, and self-contained.

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Chapter 1

The Structure of Alkali Atoms in a Magnetic Field

1.1 Notation & Conventions

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

$$\hat{J}^2 |J, m_J\rangle = J(J+1) |J, m_J\rangle \quad (1.1)$$

$$\hat{J}_z |J, m_J\rangle = m_J |J, m_J\rangle, m_J = -J..J \quad (1.2)$$

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \quad (1.3)$$

$$\hat{J}_\pm |J, m_J\rangle = \sqrt{J(J+1) - m_J(m_J \pm 1)} |J, m_J \pm 1\rangle \quad (1.4)$$

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

$$\vec{\mu}_S = \frac{\mu_S}{S} \vec{S} \quad (1.5)$$

$$\frac{\mu_S}{S} = g_S \mu_x \quad (1.6)$$

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

$$\vec{\mu}_L = \mu_L \vec{L} \quad (1.7)$$

$$\mu_L = g_L \mu_x \quad (1.8)$$

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. In all cases, the g -factor will be left unevaluated in the equations. However, equations will be written such that approximations can be made without loss of accuracy, for example:

$$-\frac{3}{2}g_S = 3 \underbrace{\left[\frac{g_S}{-2} \right]}_{\approx 1.00116} \approx 3 \quad (1.9)$$

For the electron spin, g_S does not equal -2 exactly due to radiative corrections. There is no reason why g_L must equal exactly -1 . This point is discussed at great length in section IX.5.1 of *Molecular Beams* [1]. Based on experimental results from alkali atoms, $|g_L|$ differs from unity on order of parts per million. Therefore, for $L \geq 1$, we'll take $g_L = -1.0$.

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 usually 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).

1.2 Fine Structure (Ignoring Nuclear Spin)

1.2.1 Zero Field Eigenbasis

The basic structure of the atomic Hamiltonian is summarized below, more details can be found in any good atomic physics book such as Woodgate [2] or Foot [3]:

1. The electrostatic interaction within an atom can be expressed as a central 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. Because the non-central forces are larger, 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 zero for closed shells.
7. Because of spherical symmetry, the non-central force is independent of orbital angular momentum for closed shells. Therefore, the non-central force is relevant only between the 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 quadrupole interactions, will usually be ignored.

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

$$\mathcal{H}_0 = \mathcal{H}_{es} + \mathcal{H}_{so} \quad (1.10)$$

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

$$\vec{J}^2 = (\vec{L} + \vec{S})^2 = \vec{L}^2 + 2\vec{L} \cdot \vec{S} + \vec{S}^2 \quad (1.11)$$

$$\mathcal{H}_{so} = A_{so} \vec{L} \cdot \vec{S} = \frac{A_{so}}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \quad (1.12)$$

From the second form of \mathcal{H}_{so} above, it should be clear that J , L , and S are good quantum numbers, i.e., they commute with the Hamiltonian. A useful eigenbasis with those quantum number is the LS -coupling scheme $\{|J, m_J\rangle\}$. Each group of degenerate eigenstates is labeled by a Russell-Saunders term [3, 4] of the form

$$n^{2S+1}L_J \quad (1.13)$$

where n is the principal quantum number which labels the valence configuration. 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

$$\vec{L}_{shell} = \vec{S}_{shell} = 0 \quad (1.14)$$

For a neutral 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 $n^2P_{\frac{3}{2}}$. Appendix C.5 contains an expansion of the LS -coupling basis $\{|J, m_J\rangle\}$ in the uncoupled L, S basis $\{|L, m_L\rangle |S, m_S\rangle\}$.

Spin-orbit coupling breaks the degeneracy of these n^2P states and results in *fine structure*. Fine structure also refers to other corrections, including relativistic ones, that are of the same order of magnitude. However, except for Hydrogen, these corrections are much smaller than the spin-orbit coupling. (where did i read that?) Regardless, these corrections only shift the energies collectively, independent 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.

1.2.2 Hamiltonian

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

$$\mathcal{H} = \mathcal{H}_0 - \vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B} = \mathcal{H}_{es} + \mathcal{H}_{so} - \vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B} \quad (1.15)$$

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

$$\mathcal{H} = \mathcal{H}_{es} + \mathcal{H}_{so} - \vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B} \quad (1.16)$$

$$= \mathcal{H}_{es} + \frac{A_{so}}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) - g_L \mu_B L_z B - g_S \mu_B S_z B \quad (1.17)$$

$$= \mathcal{H}_{es} + \frac{A_{so}}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) - g_L \mu_B (J_z - S_z) B - g_S \mu_B S_z B \quad (1.18)$$

$$= \mathcal{H}_{es} + \left(-\frac{A_{so}}{2} (\vec{L}^2 + \vec{S}^2) - g_L \mu_B B J_z \right) + \mathcal{H}' \quad (1.19)$$

$$\mathcal{H}' = \frac{A_{so}}{2} \vec{J}^2 - (g_S - g_L) \mu_B B S_z \quad (1.20)$$

$$g_S \simeq -2 \quad (1.21)$$

$$g_L = \begin{cases} 0 & , L = 0 \\ -1 & , L > 0 \end{cases} \quad (1.22)$$

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.

1.2.3 Energies

Matrix Subblocks

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 $m_J = \pm(L + \frac{1}{2})$, 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}' ,

$$\mathcal{H}' = \frac{A_{so}}{2} \vec{J}^2 - (g_S - g_L) \mu_B B S_z \quad (1.23)$$

$$\hat{\mathcal{H}}' = \frac{A_{so}}{2} \begin{bmatrix} (L + \frac{1}{2})(L + \frac{3}{2}) & 0 \\ 0 & (L - \frac{1}{2})(L + \frac{1}{2}) \end{bmatrix} - (g_S - g_L) \mu_B B \begin{bmatrix} \alpha_+ & \beta_- \\ \beta_+ & \alpha_- \end{bmatrix} \quad (1.24)$$

$$\alpha_{\pm} = \left\langle L \pm \frac{1}{2}, m_J \left| \hat{S}_z \right| L \pm \frac{1}{2}, m_J \right\rangle \quad (1.25)$$

$$\beta_{\pm} = \left\langle L \mp \frac{1}{2}, m_J \left| \hat{S}_z \right| L \pm \frac{1}{2}, m_J \right\rangle \quad (1.26)$$

The first term can be simplified to give:

$$\frac{A_{so}}{2} \hat{J}^2 = \frac{A_{so}}{2} \left(L + \frac{1}{2} \right) \left(L + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \quad (1.27)$$

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

$$|L, m_L\rangle |S, m_S\rangle = |m_L, m_S\rangle = |m_L\rangle_L |m_S\rangle_S \quad (1.28)$$

$$|J, m_J\rangle = \sum |m_L, m_S\rangle \underbrace{\langle m_L, m_S | J, m_J \rangle}_{\text{Clebsch-Gordon}} \quad (1.29)$$

Using formulas for Clebsch-Gordon coefficients from the appendix (C.2):

$$\left\langle m_J \mp \frac{1}{2}, \pm \frac{1}{2} \left| L + \frac{1}{2}, m_J \right\rangle = \frac{1}{\sqrt{[L]}} \sqrt{L + \frac{1}{2} \pm m_J} \quad (1.30)$$

$$\left\langle m_J \mp \frac{1}{2}, \pm \frac{1}{2} \left| L - \frac{1}{2}, m_J \right\rangle = \frac{\mp 1}{\sqrt{[L]}} \sqrt{L + \frac{1}{2} \mp m_J}$$

For α_{\pm} :

$$\alpha_{\pm} = \left\langle L \pm \frac{1}{2}, m_J \left| \hat{S}_z \right| L \pm \frac{1}{2}, m_J \right\rangle \quad (1.31)$$

$$\begin{aligned} &= \sum_{m_S, m'_S = -\frac{1}{2}}^{\frac{1}{2}} \langle m_J - m'_S, m'_S | \hat{S}_z | m_J - m_S, m_S \rangle \\ &\quad \times \langle J, m_J | m_J - m'_S, m'_S \rangle \langle m_J - m_S, m_S | J, m_J \rangle \end{aligned} \quad (1.32)$$

$$= \sum_{m_S = -\frac{1}{2}}^{\frac{1}{2}} m_S |\langle m_J - m_S, m_S | J, m_J \rangle|^2, J = L \pm \frac{1}{2} \quad (1.33)$$

$$= \frac{1}{2} \left(\frac{L + \frac{1}{2} \pm m_J - L - \frac{1}{2} \pm m_J}{[L]} \right) \quad (1.34)$$

$$= \pm \left(\frac{m_J}{[L]} \right) = \pm(\alpha) \quad (1.35)$$

For β_{\pm} :

$$\beta_{\pm} = \left\langle L \mp \frac{1}{2}, m_J \left| \hat{S}_z \right| L \pm \frac{1}{2}, m_J \right\rangle \quad (1.36)$$

$$= \sum_{m_S, m'_S = -\frac{1}{2}}^{\frac{1}{2}} \langle m_J - m'_S, m'_S | \hat{S}_z | m_J - m_S, m_S \rangle \times \left\langle L \mp \frac{1}{2}, m_J | m_J - m'_S, m'_S \right\rangle \left\langle m_J - m_S, m_S | L \pm \frac{1}{2}, m_J \right\rangle \quad (1.37)$$

$$= \sum_{m_S = -\frac{1}{2}}^{\frac{1}{2}} m_S \left\langle L \mp \frac{1}{2}, m_J | m_J - m_S, m_S \right\rangle \left\langle m_J - m_S, m_S | L \pm \frac{1}{2}, m_J \right\rangle \quad (1.38)$$

$$= +\frac{1}{2} \left(\frac{-\sqrt{(L + \frac{1}{2} \mp m_J)(L + \frac{1}{2} \pm m_J)}}{[L]} \right) - \frac{1}{2} \left(\frac{+\sqrt{(L + \frac{1}{2} \pm m_J)(L + \frac{1}{2} \mp m_J)}}{[L]} \right) \quad (1.39)$$

$$= - \left(\frac{\sqrt{(L + \frac{1}{2})^2 - m_J^2}}{[L]} \right) = -(\beta) \quad (1.40)$$

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

$$\mathcal{H}' = \frac{A_{so}}{2} \left(L + \frac{1}{2} \right) \left(L + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) - (g_S - g_L) \mu_B B \begin{bmatrix} \alpha_+ & \beta_- \\ \beta_+ & \alpha_- \end{bmatrix} \quad (1.41)$$

$$= \frac{A_{so}}{2} \left(L + \frac{1}{2} \right) \left(L + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) + (g_L - g_S) \mu_B B \begin{bmatrix} \alpha & -\beta \\ -\beta & -\alpha \end{bmatrix} \quad (1.42)$$

$$= \frac{A_{so}}{2} \left(L + \frac{1}{2} \right)^2 + \frac{A_{so}}{2} \left(L + \frac{1}{2} \right) \left(\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + 2 \frac{(g_L - g_S) \mu_B B}{A_{so} (L + \frac{1}{2})} \begin{bmatrix} \alpha & -\beta \\ -\beta & -\alpha \end{bmatrix} \right) \quad (1.43)$$

$$= \frac{A_{so}}{2} \left(L + \frac{1}{2} \right)^2 + \frac{A_{so}}{2} \left(L + \frac{1}{2} \right) \underbrace{\begin{bmatrix} 1 + 2\alpha y & -2\beta y \\ -2\beta y & -(1 + 2\alpha y) \end{bmatrix}}_{\hat{M}} \quad (1.44)$$

$$y = (g_L - g_S) \frac{\mu_B B}{A_{so} (L + \frac{1}{2})} \quad (1.45)$$

Diagonalization

This is done by solving the secular equation:

$$0 = \det(\hat{M} - \hat{I}\lambda) \quad (1.46)$$

$$0 = \begin{vmatrix} 1 + 2\alpha y - \lambda & -2\beta y \\ -2\beta y & -(1 + 2\alpha y + \lambda) \end{vmatrix} \quad (1.47)$$

$$0 = -(1 + 2\alpha y - \lambda)(1 + 2\alpha y + \lambda) - (2\beta y)^2 \quad (1.48)$$

$$0 = \lambda^2 - (1 + 2\alpha y)^2 - (2\beta y)^2 \quad (1.49)$$

$$\lambda = \pm \sqrt{(1 + 2\alpha y)^2 + (2\beta y)^2} \quad (1.50)$$

$$= \pm \sqrt{1 + 4\alpha y + 4(\alpha^2 + \beta^2)y^2} \quad (1.51)$$

Using the eqns. (1.35) and (1.40), the following useful relations are derived:

$$\alpha^2 + \beta^2 = \frac{m_J^2 + (L + \frac{1}{2})^2 - m_J^2}{[L]^2} = \frac{(L + \frac{1}{2})^2}{2^2 (L + \frac{1}{2})^2} = \frac{1}{4} \quad (1.52)$$

$$4\alpha^2 + 4\beta^2 = 1 \quad (1.53)$$

We get the eigenvalues:

$$\pm \left(\lambda = \sqrt{1 + 4\alpha y + y^2} \right) \quad (1.54)$$

The total energy is therefore:

$$E = E_0 - \frac{A_{so}}{2} \left(L(L+1) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right) - g_L \mu_B m_J B + E' \quad (1.55)$$

$$E' = \frac{A_{so}}{2} \left(L + \frac{1}{2} \right)^2 \pm \frac{A_{so}}{2} \left(L + \frac{1}{2} \right) \lambda \quad (1.56)$$

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:

$$\Delta E = \frac{A_{so}[L]}{2} = h\nu_{so} \quad (1.57)$$

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 $h\nu_{so}$, for $L > 0$, we get:

$$E = E_0^L - \frac{h\nu_{so}}{2[L]} + \mu_B m_J B \pm \frac{h\nu_{so}}{2} \sqrt{1 + \frac{4m_J}{[L]} y + y^2} \quad (1.58)$$

$$y = \left(2 \left[\frac{g_S}{-2} \right] - 1 \right) \frac{\mu_B B}{h\nu_{so}} \quad (1.59)$$

where \pm refers to the states with $J = L \pm \frac{1}{2}$. When $L = 0$, $g_L = 0$ and *the positive root* of the square root is taken, which gives the energies for the $n^2 S_{\frac{1}{2}}$ term:

$$L = 0 \rightarrow J = S \rightarrow m_J = m_S = \pm \frac{1}{2} \quad (1.60)$$

$$y = \left[\frac{g_S}{-2} \right] \frac{2\mu_B B}{h\nu_{so}} \quad (1.61)$$

$$E_{\pm\frac{1}{2}} = E_0^S - \frac{h\nu_{so}}{2} + \frac{h\nu_{so}}{2} \sqrt{1 \pm \frac{4}{2} y + y^2} \quad (1.62)$$

$$= E_0^S - \frac{h\nu_{so}}{2} + \frac{h\nu_{so}}{2} (1 \pm y) \quad (1.63)$$

$$= E_0^S \pm \frac{h\nu_{so}}{2} \left(\left[\frac{g_S}{-2} \right] \frac{2\mu_B B}{h\nu_{so}} \right) \quad (1.64)$$

$$= E_0^S \pm \left[\frac{g_S}{-2} \right] \mu_B B \quad (1.65)$$

$$= E_0^S - g_S \mu_B B m_S \quad (1.66)$$

where \pm refers to the sign of $m_S = \pm \frac{1}{2}$. Note that y is a unitless quantity that gives the relative measure of the size of the Zeeman interaction with respect to the spin-orbit interaction. For example the Zeeman interaction is comparable to the spin-orbit interaction ($y \approx 1$) for potassium and rubidium when $B \approx 124$ T & 510 T respectively, see table (A.4). Because of the strength of the spin-orbit interaction, J is almost always a very good quantum number for most alkali metals.

The energies of the $m_J = \pm(L + \frac{1}{2})$ states in the $J = L + \frac{1}{2}$ term are:

$$y = \left(2 \left[\frac{g_S}{-2} \right] - 1 \right) \frac{\mu_B B}{h\nu_{so}} \quad (1.67)$$

$$E_{\pm(L+\frac{1}{2})} = E_0^L - \frac{h\nu_{so}}{2[L]} \pm \mu_B \left(L + \frac{1}{2}\right) B + \frac{h\nu_{so}}{2} \sqrt{1 \pm \frac{4(L+\frac{1}{2})}{[L]}y + y^2} \quad (1.68)$$

$$= E_0^L - \frac{h\nu_{so}}{2[L]} \pm \mu_B \left(L + \frac{1}{2}\right) B + \frac{h\nu_{so}}{2} \sqrt{1 \pm 2y + y^2} \quad (1.69)$$

$$= E_0^L - \frac{h\nu_{so}}{2[L]} \pm \mu_B \left(L + \frac{1}{2}\right) B + \frac{h\nu_{so}}{2} (1 \pm y) \quad (1.70)$$

$$= E_0^L + \frac{L}{[L]} h\nu_{so} \pm \mu_B \left(L + \frac{1}{2}\right) B \mp \frac{h\nu_{so}}{2} (1 + g_S) \frac{\mu_B B}{h\nu_{so}} \quad (1.71)$$

$$= E_0^L + \frac{L}{[L]} h\nu_{so} \pm \mu_B B \left(L + \frac{1}{2} - \frac{1+g_S}{2}\right) \quad (1.72)$$

$$= E_0^L + \frac{L}{[L]} h\nu_{so} \pm \left(L + \left[\frac{g_S}{-2}\right]\right) \mu_B B \quad (1.73)$$

Low Field Energies

At low field, see table (A.4), to second order in B , the energies for the $J = L \pm \frac{1}{2}$ terms with $L > 0$ are:

$$E = E_0^L - \frac{h\nu_{so}}{2[L]} + \mu_B m_J B \pm \frac{h\nu_{so}}{2} \left(1 + \frac{2m_J}{[L]}y + \frac{1}{2} \left(1 - \frac{4m_J^2}{[L]^2}\right) y^2 + \mathcal{O}(y^3)\right) \quad (1.74)$$

$$\pm \left(\frac{E - E_0^L}{h\nu_{so}}\right) = \mp \frac{1}{2[L]} + \pm m_J \frac{\mu_B B}{h\nu_{so}} + \frac{1}{2} + \frac{m_J}{[L]}y + \frac{1}{4} \left(1 - \frac{4m_J^2}{[L]^2}\right) y^2 + \mathcal{O}(y^3) \quad (1.75)$$

$$= \frac{1}{2} \left(1 \mp \frac{1}{[L]}\right) \pm m_J \frac{\mu_B B}{h\nu_{so}} + \frac{m_J}{[L]} \left(2 \left[\frac{g_S}{-2}\right] - 1\right) \frac{\mu_B B}{h\nu_{so}} + \frac{1}{4} \left(1 - \frac{4m_J^2}{[L]^2}\right) y^2 \quad (1.76)$$

$$= \frac{L + \frac{1}{2} \mp \frac{1}{2}}{[L]} + \frac{m_J}{[L]} \left(2 \left[\frac{g_S}{-2}\right] - 1 \pm [L]\right) \frac{\mu_B B}{h\nu_{so}} + \frac{1}{4} \left(1 - \frac{4m_J^2}{[L]^2}\right) y^2 \quad (1.77)$$

The energies for the three lowest RS terms of alkali metals to second order in B are:

$$E_{\frac{1}{2}, -\frac{1}{2}}^S = E_0^S - \left[\frac{g_S}{-2}\right] \mu_B B \quad (1.78)$$

$$E_{\frac{1}{2}, +\frac{1}{2}}^S = E_0^S + \left[\frac{g_S}{-2}\right] \mu_B B \quad (1.79)$$

$$E_{\frac{1}{2}, -\frac{1}{2}}^P = E_0^P - \left(\frac{2}{3}\right) h\nu_{so} - \left[2 + \frac{g_S}{2}\right] \left(\frac{1}{3}\right) \mu_B B - \left(\frac{2}{9}y^2\right) h\nu_{so} \quad (1.80)$$

$$E_{\frac{1}{2}, +\frac{1}{2}}^P = E_0^P - \left(\frac{2}{3}\right) h\nu_{so} + \left[2 + \frac{g_S}{2}\right] \left(\frac{1}{3}\right) \mu_B B - \left(\frac{2}{9}y^2\right) h\nu_{so} \quad (1.81)$$

$$E_{\frac{3}{2}, -\frac{3}{2}}^P = E_0^P + \left(\frac{1}{3}\right) h\nu_{so} - \left[\frac{1}{2} - \frac{g_S}{4}\right] 2\mu_B B \quad (1.82)$$

$$E_{\frac{3}{2}, -\frac{1}{2}}^P = E_0^P + \left(\frac{1}{3}\right) h\nu_{so} - \left[\frac{1}{2} - \frac{g_S}{4}\right] \left(\frac{2}{3}\right) \mu_B B + \left(\frac{2}{9}y^2\right) h\nu_{so} \quad (1.83)$$

$$E_{\frac{3}{2}, +\frac{1}{2}}^P = E_0^P + \left(\frac{1}{3}\right) h\nu_{so} + \left[\frac{1}{2} - \frac{g_S}{4}\right] \left(\frac{2}{3}\right) \mu_B B + \left(\frac{2}{9}y^2\right) h\nu_{so} \quad (1.84)$$

$$E_{\frac{3}{2}, +\frac{3}{2}}^P = E_0^P + \left(\frac{1}{3}\right) h\nu_{so} + \left[\frac{1}{2} - \frac{g_S}{4}\right] 2\mu_B B \quad (1.85)$$

where the bracketed terms evaluate to 1 when the approximation $g_S \approx -2$ is made.

1.2.4 Eigenstates: Fine Structure Mixing

Orthonormality of the Mixing Coefficients

At zero field, with $S = \frac{1}{2}$, and for a given $L > 0$, there are in general two states with the same m_J , but with different J . Note however that when $|m_J| = L + \frac{1}{2}$, there is only one state with the quantum numbers m_J , J , and L . As noted before, the B -field mixes states with the same L , the same m_J , but different J . The result of the mixing are two states with the same m_J but with different J . At low field, the mixed states are, to a very good approximation, the zero field eigenstates with a small admixture of the other eigenstate. The mixed states, labeled by \pm , approach the the zero field states with $J = L \pm \frac{1}{2}$ as the field approaches zero. Because J is still a very good quantum number, we will represent $\{|L_{\pm}, m_J\rangle\}$ in the $\{|J, m_J\rangle\}$ basis:

$$|L_{\pm}, m_J\rangle = a_1^{\pm} \left| L + \frac{1}{2}, m_J \right\rangle + a_2^{\pm} \left| L - \frac{1}{2}, m_J \right\rangle \quad (1.86)$$

where a_1^{\pm}, a_2^{\pm} are the fine structure mixing coefficients, which we choose to be real. To repeat, at a zero field, $L_{\pm} = P_{L \pm \frac{1}{2}}$. The mixed eigenstates must be orthonormal:

$$\langle m_J^{\pm} | m_J^{\pm} \rangle = (a_1^{\pm})^2 + (a_2^{\pm})^2 = 1 \quad (1.87)$$

$$\langle m_J^{-} | m_J^{+} \rangle = a_1^{-} a_1^{+} + a_2^{-} a_2^{+} = 0 \quad (1.88)$$

Some algebra gives:

$$(a_2^{\pm})^2 = 1 - (a_1^{\pm})^2 \quad (1.89)$$

$$(a_1^{-} a_1^{+})^2 = (a_2^{-} a_2^{+})^2$$

$$(a_1^{-} a_1^{+})^2 = 1 + (a_1^{-} a_1^{+})^2 - (a_1^{-})^2 - (a_1^{+})^2$$

$$1 = (a_1^{-})^2 + (a_1^{+})^2 \quad (1.90)$$

$$(a_1^{-})^2 = (a_2^{+})^2 \quad (1.91)$$

$$(a_2^{-})^2 = (a_1^{+})^2 \quad (1.92)$$

$$\frac{a_1^{-}}{a_2^{+}} = -\frac{a_2^{-}}{a_1^{+}} \quad (1.93)$$

$$a_1^{\pm} = \pm a_2^{\mp} \quad (1.94)$$

To recap, orthonormality implies equation (1.94).

Solving for the Mixing Coefficients

The values for $a_{1,2}^{\pm}$ come from the diagonalization of eqn. (1.44) where λ_{\pm} are the eigenvalues given by eqn. (1.54) and α and β are defined by eqns. (1.35) and (1.40):

$$\hat{M} |a\rangle = \pm \lambda |a\rangle \quad (1.95)$$

$$\begin{bmatrix} 1 + 2\alpha y & -2\beta y \\ -2\beta y & -(1 + 2\alpha y) \end{bmatrix} \begin{bmatrix} a_1^{\pm} \\ a_2^{\pm} \end{bmatrix} = \pm \lambda \begin{bmatrix} a_1^{\pm} \\ a_2^{\pm} \end{bmatrix} \quad (1.96)$$

$$(1 + 2\alpha y) a_1^{\pm} - 2\beta y a_2^{\pm} = \pm \lambda a_1^{\pm} \quad (1.97)$$

$$-2\beta y a_2^{\pm} - (1 + 2\alpha y) a_1^{\pm} = \pm \lambda a_2^{\pm} \quad (1.98)$$

These last two equations are redundant. Taking the former, using the normalization condition, and some algebra gives:

$$(1 + 2\alpha y \mp \lambda) a_1^{\pm} = 2\beta y a_2^{\pm} \quad (1.99)$$

$$(1 + 2\alpha y \mp \lambda)^2 (a_1^{\pm})^2 = 4\beta^2 y^2 (1 - (a_1^{\pm})^2) \quad (1.100)$$

$$a_1^\pm = \frac{2\beta y}{\sqrt{(1+2\alpha y \mp \lambda)^2 + 4\beta^2 y^2}} \quad (1.101)$$

$$a_2^\pm = \frac{1+2\alpha y \mp \lambda}{\sqrt{(1+2\alpha y \mp \lambda)^2 + 4\beta^2 y^2}} \quad (1.102)$$

The \pm sign is taken for states evolving from the $J = L \pm \frac{1}{2}$ term. Again even though J is not a rigorously good quantum number like m_J , at low fields it is still very good. This can be more easily seen by expanding $a_{1,2}^\pm$ at low field to second order in $y(B)$.

Low Field Expansion

The low field expansions are performed using the following useful relations (from equations 20.10 and 20.11 of the *Mathematical Handbook* [5]):

$$\sqrt{1+x} \simeq 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \frac{1}{16}x^3 - \frac{5}{128}x^4 + \mathcal{O}(x^5) \quad (1.103)$$

$$\frac{1}{\sqrt{1+x}} \simeq 1 - \frac{1}{2}x + \frac{3}{8}x^2 - \frac{5}{16}x^3 + \frac{35}{128}x^4 + \mathcal{O}(x^5) \quad (1.104)$$

$$\sqrt{1+ax+bx^2} \simeq 1 + \frac{a}{2}x + \left(\frac{b}{2} - \frac{a^2}{8}\right)x^2 + \left(\frac{a^3}{16} - \frac{ab}{4}\right)x^3 + \left(\frac{3a^2b}{16} - \frac{b^2}{8} - \frac{5a^4}{128}\right)x^4 + \mathcal{O}(x^5) \quad (1.105)$$

$$\begin{aligned} \frac{1}{\sqrt{1+ax+bx^2}} &\simeq 1 - \frac{a}{2}x + \left(\frac{3a^2}{8} - \frac{b}{2}\right)x^2 + \left(\frac{3ab}{4} - \frac{5a^3}{16}\right)x^3 \\ &+ \left(\frac{35a^4}{128} + \frac{3b^2}{8} - \frac{15a^2b}{16}\right)x^4 + \mathcal{O}(x^5) \end{aligned} \quad (1.106)$$

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

$$\lambda = \sqrt{1+4\alpha y + y^2} \quad (1.107)$$

$$\simeq 1 + 2\alpha y + \left(\frac{1}{2} - 2\alpha^2\right)y^2 + (4\alpha^3 - \alpha)y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right)y^4 + \mathcal{O}(y^5) \quad (1.108)$$

$$\simeq 1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right)y^4 + \mathcal{O}(y^5) \quad (1.109)$$

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

$$d = (1+2\alpha y \mp \lambda)^2 + 4\beta^2 y^2 \quad (1.110)$$

$$= 1 + 4\alpha^2 y^2 + \lambda^2 + 4\alpha y \mp 2\lambda \mp 4\alpha y \lambda + 4\beta^2 y^2 \quad (1.111)$$

$$= 1 + 4\alpha^2 y^2 + 1 + 4\alpha y + y^2 + 4\alpha y \mp 2\lambda \mp 4\alpha y \lambda + 4\beta^2 y^2 \quad (1.112)$$

$$= 2 + 8\alpha y + 2y^2 \mp 2\lambda \mp 4\alpha y \lambda \quad (1.113)$$

$$= 2 + 8\alpha y + 2y^2 \mp 2(1+2\alpha y)\lambda \quad (1.114)$$

$$\simeq 2 + 8\alpha y + 2y^2 \mp 2(1+2\alpha y)\left(1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right)y^4\right) \quad (1.115)$$

$$\begin{aligned} &\simeq 2 + 8\alpha y + 2y^2 \mp 2(2\alpha y + 4\alpha^2 y^2 + 4\alpha\beta^2 y^3 - 8\beta^2 \alpha^2 y^4) \\ &\mp 2\left(1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right)y^4\right) \end{aligned} \quad (1.116)$$

$$\simeq 2 + 8\alpha y + 2y^2 \mp 2(1 + 4\alpha y + (4\alpha^2 + 2\beta^2)y^2) \mp 2\left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2 \alpha^2\right)y^4 \quad (1.117)$$

$$\simeq 2 + 8\alpha y + 2y^2 \mp (2 + 8\alpha y + (2 - 4\beta^2)y^2) \mp 2\left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2 \alpha^2\right)y^4 \quad (1.118)$$

$$d_+ \simeq 2 + 8\alpha y + 2y^2 - 2 - 8\alpha y - (2 - 4\beta^2) y^2 - 2 \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2\alpha^2 \right) y^4 \quad (1.119)$$

$$\simeq 4\beta^2 y^2 - 2 \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2\alpha^2 \right) y^4 \quad (1.120)$$

$$\simeq 4\beta^2 y^2 - 2 \left(3\alpha^2 - \frac{1}{8} - 10 \left(\frac{1}{16} - \beta^4 - 2\alpha^2\beta^2 \right) - 8\beta^2\alpha^2 \right) y^4 \quad (1.121)$$

$$\simeq 4\beta^2 y^2 - 2 \left(3\alpha^2 - \frac{3}{4} + 10\beta^4 + 12\alpha^2\beta^2 \right) y^4 \quad (1.122)$$

$$\simeq 4\beta^2 y^2 - (-6\beta^2 + 20\beta^4 + 24\alpha^2\beta^2) y^4 \quad (1.123)$$

$$\simeq 4\beta^2 y^2 \left(1 + \frac{6}{4}y^2 - 5\beta^2 y^2 - 6\alpha^2 y^2 \right) \quad (1.124)$$

$$\simeq 4\beta^2 y^2 (1 + 6\alpha^2 y^2 + 6\beta^2 y^2 - 5\beta^2 y^2 - 6\alpha^2 y^2) \quad (1.125)$$

$$\simeq 4\beta^2 y^2 (1 + \beta^2 y^2) \quad (1.126)$$

$$d_- \simeq 2 + 8\alpha y + 2y^2 + 2 + 8\alpha y + (2 - 4\beta^2) y^2 + 2 \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2\alpha^2 \right) y^4 \quad (1.127)$$

$$\simeq 4 + 16\alpha y + 4(1 - \beta^2) y^2 \quad (1.128)$$

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

$$d_+^{-\frac{1}{2}} \simeq \left(\sqrt{4\beta^2 y^2 (1 + \beta^2 y^2)} \right)^{-1} \simeq \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2 \right) \quad (1.129)$$

$$d_-^{-\frac{1}{2}} \simeq (4 + 16\alpha y + 4(1 - \beta^2) y^2)^{-\frac{1}{2}} \quad (1.130)$$

$$\simeq \frac{1}{2} (1 + 4\alpha y + (1 - \beta^2) y^2)^{-\frac{1}{2}} \quad (1.131)$$

$$\simeq \frac{1}{2} \left(1 - \left(\frac{4\alpha}{2} \right) y + \left(\frac{3 \cdot 16\alpha^2}{8} - \frac{1 - \beta^2}{2} \right) y^2 \right) \quad (1.132)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(6\alpha^2 - \frac{1}{2} + \frac{\beta^2}{2} \right) y^2 \right) \quad (1.133)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(\frac{6}{4} - 6\beta^2 - \frac{1}{2} + \frac{\beta^2}{2} \right) y^2 \right) \quad (1.134)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2 \right) y^2 \right) \quad (1.135)$$

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

$$n_1^\pm = 2\beta y \quad (1.136)$$

$$n_2^\pm = 1 + 2\alpha y \mp \lambda \quad (1.137)$$

$$\simeq 1 + 2\alpha y \mp (1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3) \quad (1.138)$$

$$n_2^+ \simeq 1 + 2\alpha y - 1 - 2\alpha y - 2\beta^2 y^2 + 4\beta^2 \alpha y^3 \quad (1.139)$$

$$\simeq -2\beta^2 y^2 + 4\beta^2 \alpha y^3 \quad (1.140)$$

$$n_2^- \simeq 1 + 2\alpha y + 1 + 2\alpha y + 2\beta^2 y^2 \quad (1.141)$$

$$\simeq 2 + 4\alpha y + 2\beta^2 y^2 \quad (1.142)$$

Finally let's calculate the the mixing coefficients:

$$a_1^+ = \frac{n_1^+}{\sqrt{d_+}} = \frac{2\beta y}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} \quad (1.143)$$

$$= (2\beta y) \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2\right) \quad (1.144)$$

$$\simeq 1 - \frac{\beta^2}{2} y^2 \quad (1.145)$$

$$a_2^+ = \frac{n_2^+}{\sqrt{d_+}} = \frac{1 + 2\alpha y - \lambda}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} \quad (1.146)$$

$$= (-2\beta^2 y^2 + 4\beta^2 \alpha y^3) \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2\right) \quad (1.147)$$

$$\simeq -(\beta y - 2\alpha \beta y^2) \left(1 - \frac{\beta^2}{2} y^2\right) \quad (1.148)$$

$$\simeq -\beta y + 2\alpha \beta y^2 \quad (1.149)$$

$$a_1^- = \frac{n_1^-}{\sqrt{d_-}} = \frac{2\beta y}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \quad (1.150)$$

$$\simeq (2\beta y) \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2\right) y^2\right) \quad (1.151)$$

$$\simeq \beta y - 2\alpha \beta y^2 \quad (1.152)$$

$$a_2^- = \frac{n_2^-}{\sqrt{d_-}} = \frac{1 + 2\alpha y + \lambda}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \quad (1.153)$$

$$\simeq (2 + 4\alpha y + 2\beta^2 y^2) \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2\right) y^2\right) \quad (1.154)$$

$$\simeq (1 + 2\alpha y + \beta^2 y^2) \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2\right) y^2\right) \quad (1.155)$$

$$\simeq 1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2\right) y^2 + 2\alpha y - 4\alpha^2 y^2 + \beta^2 y^2 \quad (1.156)$$

$$\simeq 1 + \left(1 - \frac{11}{2}\beta^2 - 4\alpha^2 + \beta^2\right) y^2 \quad (1.157)$$

$$\simeq 1 + \left(1 - \frac{11}{2}\beta^2 + 4\beta^2 - 1 + \beta^2\right) y^2 \quad (1.158)$$

$$\simeq 1 - \frac{\beta^2}{2} y^2 \quad (1.159)$$

As expected $a_1^\pm = \pm a_2^\mp$. For notational convenience, we'll drop the \pm on the mixing coefficients. This gives, for the $\{|m_J^\pm\rangle\}$ states to second order in y (field):

$$a_1 = \frac{2\beta y}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} = \frac{1 + 2\alpha y + \lambda}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \simeq 1 - \frac{\beta^2}{2} y^2 \quad (1.160)$$

$$a_2 = \frac{1 + 2\alpha y - \lambda}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} = \frac{-2\beta y}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \simeq -\beta y + 2\alpha \beta y^2 \quad (1.161)$$

$$\frac{\beta^2}{2} = \frac{1}{8} \left(1 - \frac{4m_J^2}{[L]^2}\right) \quad (1.162)$$

$$2\alpha\beta = \frac{m_J}{[L]} \sqrt{1 - \frac{4m_J^2}{[L]^2}} \quad (1.163)$$

$$|L_+, m_J\rangle = a_1 \left|L \pm \frac{1}{2}, m_J\right\rangle + a_2 \left|L \mp \frac{1}{2}, m_J\right\rangle \quad (1.164)$$

$$|L_-, m_J\rangle = a_1 \left| L \mp \frac{1}{2}, m_J \right\rangle - a_2 \left| L \pm \frac{1}{2}, m_J \right\rangle \quad (1.165)$$

where \pm refers to the value of $J = L \pm \frac{1}{2}$ for the zero field eigenstate that $|m_J^\pm\rangle$ approaches as the field approaches zero.

In the lowest three RS terms for alkali metals, only the $m_J = \pm\frac{1}{2}$ of the $P_{\frac{1}{2}}$ and $P_{\frac{3}{2}}$ terms mix:

$$a_1 \simeq 1 - \frac{y^2}{9} \quad (1.166)$$

$$a_2^\pm \simeq -\frac{\sqrt{2}}{3}y \left(1 \mp \frac{y}{3}\right) \quad (1.167)$$

$$\left| P_-, -\frac{1}{2} \right\rangle = a_1 \left| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle - a_2^- \left| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle \quad (1.168)$$

$$\left| P_+, -\frac{1}{2} \right\rangle = a_1 \left| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle + a_2^- \left| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \quad (1.169)$$

$$\left| P_-, +\frac{1}{2} \right\rangle = a_1 \left| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle - a_2^+ \left| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle \quad (1.170)$$

$$\left| P_+, +\frac{1}{2} \right\rangle = a_1 \left| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle + a_2^+ \left| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \quad (1.171)$$

where \pm now refers to $m_J = \pm\frac{1}{2}$.

1.2.5 Transition Frequencies: Optical Spectrum

Transitions that occur between RS terms are electric dipole transitions. As will be discussed in more detail in the next section, these transitions have to conserve angular momentum and must result in a change of parity. All the possible transitions will be listed in groups labeled by the polarization of the incident light. D1 transitions refer to ones between the $S_{\frac{1}{2}}$ states and the $P_{\frac{1}{2}}$ states; whereas, D2 transitions refer to ones between the $S_{\frac{1}{2}}$ states and the $P_{\frac{3}{2}}$ states. Most of the energy difference between these states is due to electrostatic interactions. It will be convenient to express these frequencies with respect to the zero field D1 and D2 transition frequencies:

$$\omega_{\frac{1}{2}}^0 = \frac{E_0^P - E_0^S}{\hbar} - \left(\frac{2}{3}\right) \omega_{so} = 2\pi\nu_{\frac{1}{2}}^0 \quad (1.172)$$

$$\omega_{\frac{3}{2}}^0 = \frac{E_0^P - E_0^S}{\hbar} + \left(\frac{1}{3}\right) \omega_{so} = 2\pi\nu_{\frac{3}{2}}^0 \quad (1.173)$$

$$\omega_{so} = \omega_{\frac{3}{2}}^0 - \omega_{\frac{1}{2}}^0 = \left(\frac{1}{3} - -\frac{2}{3}\right) \omega_{so} = 2\pi\nu_{so} \quad (1.174)$$

$$\omega_{\frac{1}{2}} = \omega_{\frac{1}{2}}^0 + \delta\omega_{\frac{1}{2}} \quad (1.175)$$

$$\omega_{\frac{3}{2}} = \omega_{\frac{3}{2}}^0 + \delta\omega_{\frac{3}{2}} \quad (1.176)$$

$$\delta\omega = \delta\omega_{\frac{3}{2}} - \delta\omega_{\frac{1}{2}} \quad (1.177)$$

where the $\delta\omega$ terms are “added by hand” to account for the shift in the lines due to the presence of a buffer gas such as ^3He & N_2 . Note that in the following, bracketed $[\dots]$ terms evaluate to 1 when the approximation $g_S = -2$ is made. For light left circularly polarized perpendicular to the B -field (which has -1 unit of angular momentum), the possible transitions are:

$$\left| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \leftrightarrow \left| P_{\frac{3}{2}}, -\frac{3}{2} \right\rangle \implies \omega = \omega_{\frac{3}{2}} - \frac{y\omega_{so}}{[-1 - g_S]} \quad (1.178)$$

$$\left| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \leftrightarrow a_1 \left| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle - a_2^- \left| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle \implies \omega = \omega_{\frac{1}{2}} - \frac{4y}{3} \left(\left[\frac{\frac{1}{2} - \frac{g_S}{4}}{-1 - g_S} \right] + \frac{y}{6} \right) \omega_{so} \quad (1.179)$$

$$\left|S_{\frac{1}{2}}, +\frac{1}{2}\right\rangle \leftrightarrow a_1 \left|P_{\frac{3}{2}}, -\frac{1}{2}\right\rangle + a_2^- \left|P_{\frac{1}{2}}, -\frac{1}{2}\right\rangle \implies \omega = \omega_{\frac{3}{2}} - \frac{5y}{3} \left(\left[\frac{\frac{1}{5} - \frac{2gs}{5}}{-1 - gs} \right] - \frac{2y}{15} \right) \omega_{so} \quad (1.180)$$

For light linearly polarized parallel to the B -field (which has 0 units of angular momentum), the transition frequencies are:

$$\left|S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle \leftrightarrow a_1 \left|P_{\frac{1}{2}}, -\frac{1}{2}\right\rangle - a_2^- \left|P_{\frac{3}{2}}, -\frac{1}{2}\right\rangle \implies \omega = \omega_{\frac{1}{2}} + \frac{2y}{3} \left(1 - \frac{y}{3}\right) \omega_{so} \quad (1.181)$$

$$\left|S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle \leftrightarrow a_1 \left|P_{\frac{3}{2}}, -\frac{1}{2}\right\rangle + a_2^- \left|P_{\frac{1}{2}}, -\frac{1}{2}\right\rangle \implies \omega = \omega_{\frac{3}{2}} + \frac{y}{3} \left(1 + \frac{2y}{3}\right) \omega_{so} \quad (1.182)$$

$$\left|S_{\frac{1}{2}}, +\frac{1}{2}\right\rangle \leftrightarrow a_1 \left|P_{\frac{1}{2}}, +\frac{1}{2}\right\rangle - a_2^+ \left|P_{\frac{3}{2}}, +\frac{1}{2}\right\rangle \implies \omega = \omega_{\frac{1}{2}} - \frac{2y}{3} \left(1 + \frac{y}{3}\right) \omega_{so} \quad (1.183)$$

$$\left|S_{\frac{1}{2}}, +\frac{1}{2}\right\rangle \leftrightarrow a_1 \left|P_{\frac{3}{2}}, +\frac{1}{2}\right\rangle + a_2^+ \left|P_{\frac{1}{2}}, +\frac{1}{2}\right\rangle \implies \omega = \omega_{\frac{3}{2}} - \frac{y}{3} \left(1 - \frac{2y}{3}\right) \omega_{so} \quad (1.184)$$

For light right circularly polarized perpendicular to the B -field (which has +1 unit of angular momentum), the transition frequencies are:

$$\left|S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle \leftrightarrow a_1 \left|P_{\frac{1}{2}}, +\frac{1}{2}\right\rangle - a_2^+ \left|P_{\frac{3}{2}}, +\frac{1}{2}\right\rangle \implies \omega = \omega_{\frac{1}{2}} + \frac{4y}{3} \left(\left[\frac{\frac{1}{2} - \frac{gs}{4}}{-1 - gs} \right] - \frac{y}{6} \right) \omega_{so} \quad (1.185)$$

$$\left|S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle \leftrightarrow a_1 \left|P_{\frac{3}{2}}, +\frac{1}{2}\right\rangle + a_2^+ \left|P_{\frac{1}{2}}, +\frac{1}{2}\right\rangle \implies \omega = \omega_{\frac{3}{2}} + \frac{5y}{3} \left(\left[\frac{\frac{1}{5} - \frac{2gs}{5}}{-1 - gs} \right] + \frac{2y}{15} \right) \omega_{so} \quad (1.186)$$

$$\left|S_{\frac{1}{2}}, +\frac{1}{2}\right\rangle \leftrightarrow \left|P_{\frac{3}{2}}, +\frac{3}{2}\right\rangle \implies \omega = \omega_{\frac{3}{2}} + \frac{y\omega_{so}}{[-1 - gs]} \quad (1.187)$$

1.3 Hyperfine Structure (Including Nuclear Spin)

1.3.1 Zero Field Eigenbasis

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

$$\mathcal{H}_{hfs} = A_{hfs} \vec{I} \cdot \vec{J} \quad (1.188)$$

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:

$$\vec{F}^2 = (\vec{I} + \vec{J})^2 = \vec{I}^2 + 2\vec{I} \cdot \vec{J} + \vec{J}^2 \quad (1.189)$$

$$\mathcal{H}_{hfs} = \frac{A_{hfs}}{2} (\vec{F}^2 - \vec{I}^2 - \vec{J}^2) \quad (1.190)$$

The hyperfine interaction splits the ${}^2S_{\frac{1}{2}}$, ${}^2P_{\frac{1}{2}}$, and ${}^2P_{\frac{3}{2}}$ 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. Table (1.1) depicts the analogy.

1.3.2 Hamiltonian

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

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{hfs} - \vec{\mu}_I \cdot \vec{B} - \vec{\mu}_J \cdot \vec{B} \quad (1.191)$$

To recap:

- The first term H_0 contains all the terms that do not involve the nuclear spin.

Spin-Orbit	Hyperfine
\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

Table 1.1: Analogy between spin-orbit and hyperfine coupling.

- 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,

$$\mathcal{H} = \mathcal{H}_0 + \left(-\frac{A_{hfs}}{2} (\vec{I}^2 + \vec{J}^2) - g_I \mu_N B F_z \right) + \left(\frac{A_{hfs}}{2} \vec{F}^2 + (g_I \mu_N - g_J \mu_B) B J_z \right) \quad (1.192)$$

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. (make some comment about how fine structure mixing effects this stuff)

1.3.3 Energies: Derivation of the Breit-Rabi Equation

Diagonalization

The Breit-Rabi equation, first derived in 1931 [6, 7], gives the energies of the ground state hyperfine levels of atoms and ions with a single valence electron 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}' ,

$$\mathcal{H}' = \frac{A_{hfs}}{2} \vec{F}^2 + (g_I \mu_N - g_S \mu_B) B J_z \quad (1.193)$$

$$\hat{\mathcal{H}}' = \frac{A_{hfs}}{2} \begin{bmatrix} (I + \frac{1}{2})(I + \frac{3}{2}) & 0 \\ 0 & (I - \frac{1}{2})(I + \frac{1}{2}) \end{bmatrix} + (g_I \mu_N - g_S \mu_S) B \begin{bmatrix} \alpha_+ & \beta_- \\ \beta_+ & \alpha_- \end{bmatrix} \quad (1.194)$$

$$\alpha_{\pm} = \left\langle I \pm \frac{1}{2}, m_F \left| \hat{J}_z \right| I \pm \frac{1}{2}, m_F \right\rangle \quad (1.195)$$

$$\beta_{\pm} = \left\langle I \mp \frac{1}{2}, m_F \left| \hat{J}_z \right| I \pm \frac{1}{2}, m_F \right\rangle \quad (1.196)$$

The first term can be simplified to give:

$$\frac{A_{hfs}}{2} \hat{F}^2 = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \left(I + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \quad (1.197)$$

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

$$|I, m_I\rangle |J, m_J\rangle = |m_I, m_J\rangle \quad (1.198)$$

$$|F, m_F\rangle = \sum |m_I, m_J\rangle \underbrace{\langle m_I, m_J | F, m_F \rangle}_{\text{Clebsch-Gordon}} \quad (1.199)$$

Using the formulas for Clebsch-Gordon coefficients (1.31):

$$\left\langle m_F \mp \frac{1}{2}, \pm \frac{1}{2} \middle| I + \frac{1}{2}, m_F \right\rangle = \frac{1}{\sqrt{[I]}} \sqrt{I + \frac{1}{2} \pm m_F} \quad (1.200)$$

$$\left\langle m_F \mp \frac{1}{2}, \pm \frac{1}{2} \middle| I - \frac{1}{2}, m_F \right\rangle = \frac{\mp 1}{\sqrt{[I]}} \sqrt{I + \frac{1}{2} \mp m_F}$$

which gives:

$$\alpha_{\pm} = \pm(\alpha) = \pm \left(\frac{m_F}{[I]} \right) \quad (1.201)$$

$$\beta_{\pm} = -(\beta) = - \left(\frac{\sqrt{(I + \frac{1}{2})^2 - m_F^2}}{[I]} \right) \quad (1.202)$$

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

$$\mathcal{H}' = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right)^2 + \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \begin{bmatrix} 1 + 2\alpha x & -2\beta x \\ -2\beta x & -(1 + 2\alpha x) \end{bmatrix} \quad (1.203)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{2B}{A[I]} \quad (1.204)$$

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

$$\pm \left(\lambda = \sqrt{1 + 4\alpha x + x^2} \right) \quad (1.205)$$

The total energy is therefore:

$$E = E_0 - \frac{A_{hfs}}{2} \left(I(I+1) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right) - g_I \mu_N m_F B + E' \quad (1.206)$$

$$E' = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right)^2 \pm \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \lambda \quad (1.207)$$

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:

$$\Delta E = \frac{A_{hfs}[I]}{2} = h\nu_{hfs} \quad (1.208)$$

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

$$E = -\frac{h\nu_{hfs}}{2[I]} - g_I \mu_N B m_F \pm \frac{h\nu_{hfs}}{2} \sqrt{1 + \frac{4m_F}{[I]} x + x^2} \quad (1.209)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{B}{h\nu_{hfs}} \quad (1.210)$$

where \pm refers to states in the $F = I \pm \frac{1}{2}$ manifold. Note that x is a unitless quantity that gives a relative measure of the size of the Zeeman interaction with respect to the hyperfine interaction. For example, the Zeeman interaction is comparable to the hyperfine interaction ($x \approx 1$) for potassium-39 and rubidium-85 when $B \approx 165$ gauss & 1080 gauss respectively.

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

$$E_{\pm(I+\frac{1}{2})} = \frac{I}{[I]} h\nu_{hfs} \pm \left(\left[\frac{g_S}{-2} \right] \mu_B - g_I \mu_N I \right) B \quad (1.211)$$

where \pm now refers to m_F . A low field ($B < 165$ gauss & 1080 gauss for potassium-39 and rubidium-85 respectively) expansion of the energies for the the $F = I \pm \frac{1}{2}$ manifolds can be performed using:

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + \frac{1}{2}x(2a + x) - \frac{1}{2 \cdot 4}x^2(2a + x)^2 + \frac{1 \cdot 3}{2 \cdot 4 \cdot 6}x^3(2a + x)^3 - \frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6 \cdot 8}x^4(2a + x)^4 \\ &\quad + \frac{1 \cdot 3 \cdot 5 \cdot 7}{2 \cdot 4 \cdot 6 \cdot 8 \cdot 10}x^5(2a + x)^5 - \frac{1 \cdot 3 \cdot 5 \cdot 7 \cdot 9}{2 \cdot 4 \cdot 6 \cdot 8 \cdot 10 \cdot 12}x^6(2a + x)^6 + \dots \end{aligned} \quad (1.212)$$

Expanding each factor of $(2a + x)^n$ and reducing the coefficients in front of each term:

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + \frac{1}{2}x(2a + x) - \frac{1}{8}x^2(4a^2 + x^2 + 4ax) + \frac{1}{16}x^3(8a^3 + 12a^2x + 6ax^2 + x^3) \\ &\quad - \frac{5}{128}x^4(16a^4 + 32a^3x + 24a^2x^2 + 8ax^3 + x^4) \\ &\quad + \frac{7}{256}x^5(32a^5 + 80a^4x + 80a^3x^2 + 40a^2x^3 + 10ax^4 + x^5) \\ &\quad - \frac{21}{1024}x^6(64a^6 + 192a^5x + 240a^4x^2 + 160a^3x^3 + 60a^2x^4 + 12ax^5 + x^6) \dots \end{aligned} \quad (1.213)$$

Keeping only the terms up to sixth order in the dimensionless field parameter x :

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + \frac{1}{2}x(2a + x) - \frac{1}{8}x^2(4a^2 + x^2 + 4ax) + \frac{1}{16}x^3(8a^3 + 12a^2x + 6ax^2 + x^3) \\ &\quad - \frac{5}{16}x^4(2a^4 + 4a^3x + 3a^2x^2) + \frac{7}{16}x^5(2a^5 + 5a^4x) - \frac{21}{16}x^6a^6 + \mathcal{O}(x^7) \end{aligned} \quad (1.214)$$

Collecting all the terms order by order:

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + (a)x + \left(\frac{1}{2} - \frac{a^2}{2} \right) x^2 + \left(-\frac{a}{2} + \frac{a^3}{2} \right) x^3 + \left(-\frac{1}{8} + \frac{3a^2}{4} - \frac{5a^4}{8} \right) x^4 \\ &\quad + \left(\frac{3a}{8} - \frac{5a^3}{4} + \frac{7a^5}{8} \right) x^5 + \left(\frac{1}{16} - \frac{15a^2}{16} + \frac{35a^4}{16} - \frac{21a^6}{16} \right) x^6 + \mathcal{O}(x^7) \end{aligned} \quad (1.215)$$

Pulling out common factors:

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + ax + \frac{1}{2}(1 - a^2)x^2 - \frac{a}{2}(1 - a^2)x^3 - \frac{1}{8}(1 - 6a^2 + 5a^4)x^4 \\ &\quad + \frac{3a}{8} \left(1 - \frac{10a^2}{3} + \frac{7a^4}{3} \right) x^5 + \frac{1}{16}(1 - 15a^2 + 35a^4 - 21a^6)x^6 + \mathcal{O}(x^7) \end{aligned} \quad (1.216)$$

Note that when $a = \pm 1$, the stuff under the square root is a perfect square:

$$\sqrt{1 + 2ax + x^2} = \sqrt{1 \pm 2x + x^2} = \sqrt{(1 \pm x)^2} = 1 \pm x \quad (1.217)$$

In this case ($a = \pm 1$), all terms second order or higher in x have to disappear order by order. Using this insight, a factor $(1 - a^2)$ is pulled out of each higher order term:

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + ax + \frac{1}{2}(1 - a^2)x^2 - \frac{a}{2}(1 - a^2)x^3 - \frac{1}{8}(1 - 5a^2)(1 - a^2)x^4 \\ &\quad + \frac{3a}{8} \left(1 - \frac{7a^2}{3} \right) (1 - a^2)x^5 + \frac{1}{16}(1 - 14a^2 + 21a^4)(1 - a^2)x^6 + \mathcal{O}(x^7) \end{aligned} \quad (1.218)$$

Making the substitution $a = 2m_F/[I]$, dividing both sides of the Breit-Rabi equation (1.209) by $h\nu_{hfs}$, and using the sixth order expansion that was just calculated gives:

$$\pm \frac{E_{\pm}}{h\nu_{hfs}} = a_0 + a_1x + \left[1 - \left(\frac{2m_F}{[I]}\right)^2\right] \left[\sum_{n=2}^6 a_n x^n\right] \quad (1.219)$$

$$x = (g_I\mu_N - g_S\mu_B) \frac{B}{h\nu_{hfs}} \quad (1.220)$$

$$[I] = 2I + 1 \quad (1.221)$$

$$a_0 = \left(\frac{I + \frac{1}{2} \mp \frac{1}{2}}{[I]}\right) \quad (1.222)$$

$$a_1 = \frac{m_F}{[I]} \left(\frac{1 \pm \frac{g_I\mu_N}{g_S\mu_B} ([I] \mp 1)}{1 - \frac{g_I\mu_N}{g_S\mu_B}}\right) \approx \frac{m_F}{[I]} + \mathcal{O}(10^{-3}) \quad (1.223)$$

$$a_2 = +\frac{1}{4} \quad (1.224)$$

$$a_3 = -\frac{m_F}{2[I]} \quad (1.225)$$

$$a_4 = -\frac{1}{16} \left[1 - 5 \left(\frac{2m_F}{[I]}\right)^2\right] \quad (1.226)$$

$$a_5 = +\frac{3m_F}{8[I]} \left[1 - \frac{7}{3} \left(\frac{2m_F}{[I]}\right)^2\right] \quad (1.227)$$

$$a_6 = +\frac{1}{32} \left[1 - 14 \left(\frac{2m_F}{[I]}\right)^2 + 21 \left(\frac{2m_F}{[I]}\right)^4\right] \quad (1.228)$$

where \pm refers to the $F = I \pm \frac{1}{2}$ manifold. Note that eqn. (1.211) shows that the energy for the edge states in the upper manifold ($F = I + \frac{1}{2}$ & $|m_F| = I + \frac{1}{2}$) is linear in field. Therefore, for the edge states, $(2m_F/[I])^2 = 1$ and all terms of order two or higher in field in eqn. (1.219) must disappear order by order. Consequently eqn. (1.219) is written such that the disappearance of higher order terms is evident. Finally, we'll note that the order of the states from highest energy to lowest energy are $F = I + 1/2, m_F = I + 1/2$ down to $-(I + 1/2)$ and then $F = I - 1/2, m_F = -(I + 1/2)$ up to $+(I + 1/2)$.

1.3.4 Eigenstates: Hyperfine Mixing

At low field, it is useful to label states by F and m_F because F is almost a good quantum number. Therefore, at low field, we'll refer to two groups of states as "manifolds" which are labeled by F . Within each manifold, states are distinguished by their m_F . At high field, the nuclear spin and total electronic angular momentum decouple. This is because the Zeeman interaction becomes much larger than the hyperfine interaction. Because the electron magnetic moment is much larger than the nuclear magnetic moment, it is useful to group states by their m_J , which at high field is almost a good quantum number. These groupings are called Zeeman multiplets. Each state within a multiplet is distinguished by its m_I , which at high field is also almost a good quantum number. Note that regardless of the magnitude of the field, m_F is always a good quantum number. For most of this document, we'll be working in the low field limit where the most appropriate quantum numbers are F and m_F . Figure (1.1) depicts a qualitative energy level diagram for the most abundant isotope of Rubidium.

(The following is analogous to fine structure mixing with $y \rightarrow x$) 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):

$$|m_F^{\pm}\rangle = a_1^{\pm} \left|I + \frac{1}{2}, m_F\right\rangle + a_2^{\pm} \left|I - \frac{1}{2}, m_F\right\rangle \quad (1.229)$$

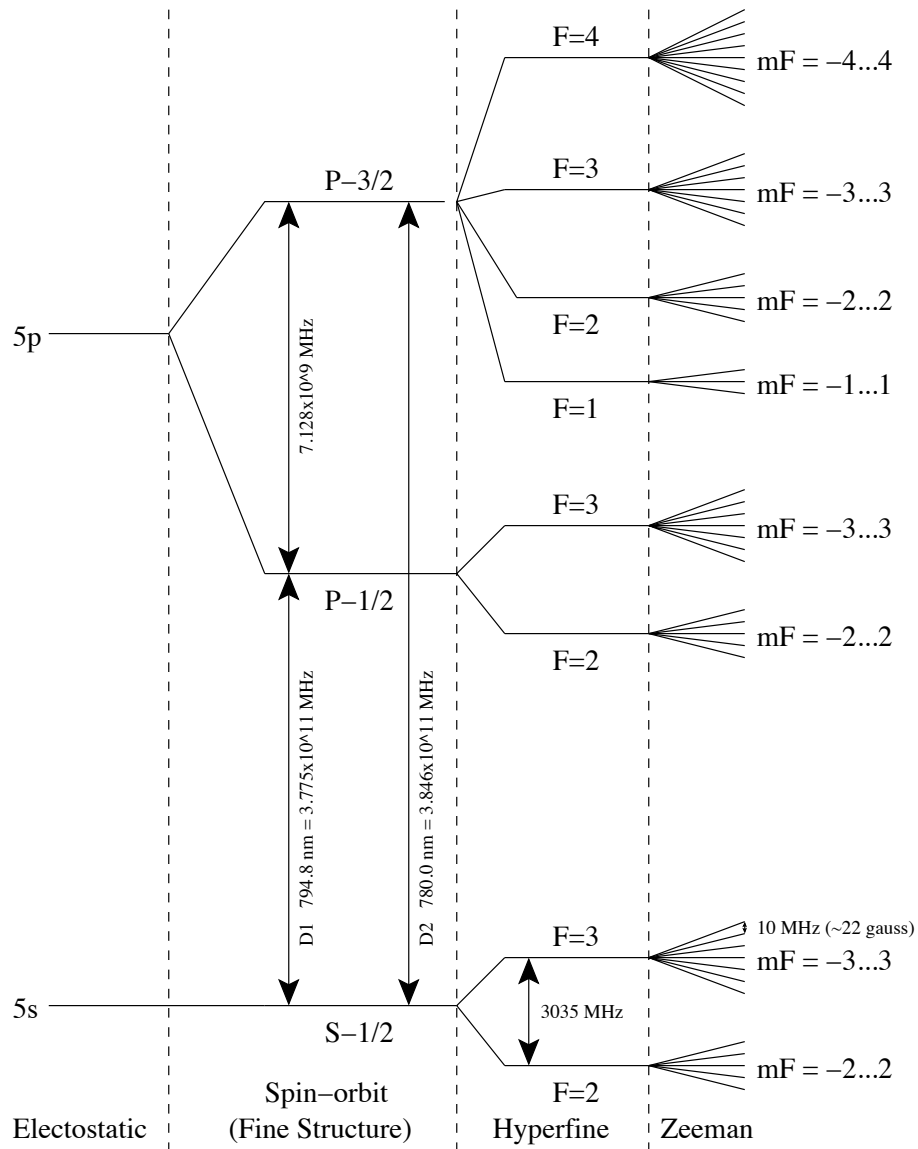


Figure 1.1: Qualitative Energy Level Diagram for Rubidium-85 ($I = 5/2$) in a Weak Field

$$|F, m_F\rangle = \sum_{m_J=-\frac{1}{2}}^{+\frac{1}{2}} |m_F - m_J, m_J\rangle \langle m_F - m_J, m_J | F, m_F\rangle \quad (1.230)$$

$$b_1^\pm(m_F) = \left\langle m_F - \frac{1}{2}, +\frac{1}{2} | I \pm \frac{1}{2}, m_F \right\rangle \quad (1.231)$$

$$b_2^\pm(m_F) = \left\langle m_F + \frac{1}{2}, -\frac{1}{2} | I \pm \frac{1}{2}, m_F \right\rangle \quad (1.232)$$

$$\left| I \pm \frac{1}{2}, m_F \right\rangle = b_1^\pm \left| m_F - \frac{1}{2}, +\frac{1}{2} \right\rangle + b_2^\pm \left| m_F + \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (1.233)$$

The values for $a_{1,2}^\pm$ come from the diagonalization of eqn. (1.203) where λ_\pm are the eigenvalues given by eqn. (1.205), α and β are defined by eqns. (1.201) and (1.202), and $b_{1,2}^\pm$ are from eqns. (C.9) and (C.10):

$$a_1^\pm = \frac{2\beta x}{\sqrt{(1 + 2\alpha x \mp \lambda)^2 + 4\beta^2 x^2}} \quad (1.234)$$

$$a_2^\pm = \frac{1 + 2\alpha x \mp \lambda}{\sqrt{(1 + 2\alpha x \mp \lambda)^2 + 4\beta^2 x^2}} \quad (1.235)$$

$$a_1^\pm = \pm a_2^\mp \quad (1.236)$$

$$b_1^\pm = \pm \sqrt{\frac{I \pm m_F + \frac{1}{2}}{[I]}} \quad (1.237)$$

$$b_2^\pm = + \sqrt{\frac{I \mp m_F + \frac{1}{2}}{[I]}} \quad (1.238)$$

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

$$a_1 \equiv a_1^+ = a_2^- \quad (1.239)$$

$$a_2 \equiv a_2^+ = -a_1^- \quad (1.240)$$

$$b_1 \equiv b_1^+ = b_2^- \quad (1.241)$$

$$b_2 \equiv b_2^+ = -b_1^- \quad (1.242)$$

$$\left| I \pm \frac{1}{2}, m_F \right\rangle = b_1 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm b_2 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \quad (1.243)$$

$$|m_F^\pm\rangle = a_1 \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 \left| I \mp \frac{1}{2}, m_F \right\rangle \quad (1.244)$$

Eqn. (1.244) represents the decomposition of the eigenstates $\{|m_F^\pm\rangle\}$ in the zero field hyperfine coupled basis $\{|F, m_F\rangle\}$, whereas eqn. (1.243) represents the decomposition in the zero field uncoupled IJ basis $\{|m_I, m_J\rangle\}$:

$$\begin{aligned} |m_F^\pm\rangle &= a_1 \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 \left| I \mp \frac{1}{2}, m_F \right\rangle \\ &= a_1 \left(b_1 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm b_2 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right) \\ &\quad \pm a_2 \left(b_1 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \mp b_2 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \right) \\ &= (a_1 b_1 - a_2 b_2) \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm (a_1 b_2 + a_2 b_1) \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \end{aligned} \quad (1.245)$$

Isotope	$F = I - \frac{1}{2}$	transition	$F = I + \frac{1}{2}$	transition	m_F
^{39}K			2	+2 \leftrightarrow +1	+2
	1	+1 \leftrightarrow 0	2	+1 \leftrightarrow 0	+1
	1	0 \leftrightarrow -1	2	0 \leftrightarrow -1	0
			2	-1 \leftrightarrow -2	-1
^{85}Rb			3	+3 \leftrightarrow +2	+3
	2	+2 \leftrightarrow +1	3	+2 \leftrightarrow +1	+2
	2	+1 \leftrightarrow 0	3	+1 \leftrightarrow 0	+1
	2	0 \leftrightarrow -1	3	0 \leftrightarrow -1	0
	2	-1 \leftrightarrow -2	3	-1 \leftrightarrow -2	-1
			3	-2 \leftrightarrow -3	-2

Table 1.2: Transitions are labeled by the higher m_F state.

1.3.5 Transition Frequencies: EPR Spectrum

Introduction

EPR stands for *Electron Paramagnetic Resonance*. At low field, it refers to the transitions between adjacent states within a particular manifold. Transitions between $m_F \leftrightarrow m_F - 1$ will be labeled by the higher state m_F . For example, refer to table (1.2) for the applicable transitions within the ground state for potassium-39 and rubidium-85. Recall that:

$$g_S = -2 [1 + \mathcal{O}(10^{-3})] \quad (1.246)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{B}{h \nu_{hfs}} \quad (1.247)$$

The frequency corresponding to these transitions within the $F = I \pm \frac{1}{2}$ manifold are:

$$\nu_+ = -\frac{g_I \mu_N B}{h} + \frac{\nu_{hfs}}{2} \left(\sqrt{1 + \frac{4m_F}{[I]} x + x^2} - \sqrt{1 + \frac{4(m_F - 1)}{[I]} x + x^2} \right) \quad (1.248)$$

$$-\nu_- = -\frac{g_I \mu_N B}{h} - \frac{\nu_{hfs}}{2} \left(\sqrt{1 + \frac{4m_F}{[I]} x + x^2} - \sqrt{1 + \frac{4(m_F - 1)}{[I]} x + x^2} \right) \quad (1.249)$$

$$\nu_- = +\frac{g_I \mu_N B}{h} + \frac{\nu_{hfs}}{2} \left(\sqrt{1 + \frac{4m_F}{[I]} x + x^2} - \sqrt{1 + \frac{4(m_F - 1)}{[I]} x + x^2} \right) \quad (1.250)$$

$$\nu_{\pm} = \mp \frac{g_I \mu_N B}{h} + \frac{\nu_{hfs}}{2} \left(\sqrt{1 + \frac{4m_F}{[I]} x + x^2} - \sqrt{1 + \frac{4(m_F - 1)}{[I]} x + x^2} \right) \quad (1.251)$$

where the overall sign was chosen to give a positive frequency for ν_{\pm} .

End Transition Frequencies

Transitions involving the edge states are called “end” transitions. The frequencies for these transitions can be written in a simpler form by taking advantage of this formula:

$$m_F = \pm \left(I + \frac{1}{2} \right) \rightarrow 4m_F = \pm 2[I] \rightarrow \sqrt{1 + \frac{4m_F}{[I]} x + x^2} = 1 \pm x \quad (1.252)$$

The frequency of the $m_F = I + 1/2 \leftrightarrow I - 1/2$ end transition is:

$$\nu_{+I+1/2} = -\frac{g_I \mu_N B}{h} + \frac{\nu_{hfs}}{2} \left(1 + x - \sqrt{1 + \frac{4(I - 1/2)}{[I]} x + x^2} \right) \quad (1.253)$$

while the frequency of the $m_F = -(I + 1/2) + 1 \leftrightarrow -(I + 1/2)$ end transition is:

$$\nu_{-I-1/2} = -\frac{g_I \mu_N B}{h} + \frac{\nu_{hfs}}{2} \left(\sqrt{1 - \frac{4(I-1/2)}{[I]} x + x^2} - 1 + x \right) \quad (1.254)$$

We can collapse both of equations into one equation to give:

$$\nu_{\pm} = \frac{\nu_{hfs}}{2} \left[x \left(\frac{1 + \frac{g_I \mu_N}{g_S \mu_B}}{1 - \frac{g_I \mu_N}{g_S \mu_B}} \right) \pm 1 \mp \sqrt{1 \pm 2 \left(\frac{2I-1}{2I+1} \right) x + x^2} \right] \quad (1.255)$$

where the \pm now refers to edge state $m_F = \pm (I + \frac{1}{2})$ involved in the end transition.

End Transition Frequency Inversion Formula

Because the equation for the frequency of an end transition involves only one square root term, the equation can be inverted to give the field as a function of frequency. Expressing eqn. (1.255) in terms of x and isolating the square root term:

$$\nu_{\pm} = \frac{\nu_{hfs}}{2} \left[x \underbrace{\left(\frac{1 + \frac{g_I \mu_N}{g_S \mu_B}}{1 - \frac{g_I \mu_N}{g_S \mu_B}} \right)}_a \pm 1 \mp \sqrt{1 \pm 2 \underbrace{\left(\frac{2I-1}{2I+1} \right)}_b x + x^2} \right] \quad (1.256)$$

$$\nu = \frac{\nu_{hfs}}{2} (ax + s - s\sqrt{1 + 2sbx + x^2}) \quad (1.257)$$

$$s = \pm 1 \rightarrow s^2 = 1 \quad (1.258)$$

$$n = 2 \frac{\nu}{\nu_{hfs}} = ax + s - s\sqrt{1 + 2sbx + x^2} \quad (1.259)$$

$$n - ax - s = -s\sqrt{1 + 2sbx + x^2} \quad (1.260)$$

Now both sides of the equation can be squared, leaving an equation that is second order in x :

$$(n - ax - s)^2 = \left(-s\sqrt{1 + 2sbx + x^2} \right)^2 \quad (1.261)$$

$$n^2 + a^2 x^2 + 1 - 2nax - 2sn + 2sax = 1 + 2sbx + x^2 \quad (1.262)$$

$$0 = 2sbx + x^2 - n^2 - a^2 x^2 + 2nax + 2sn - 2sax \quad (1.263)$$

$$0 = (1 - a^2) x^2 + 2(sb - sa + na) x + 2sn - n^2 \quad (1.264)$$

$$0 = (1 - a^2) x^2 - 2s(a - b - san) x + sn(2 - sn) \quad (1.265)$$

This is solved by using the quadratic formula from section 5.5 of *Numerical Recipes* [8]:

$$\mathcal{A}x^2 + \mathcal{B}x + \mathcal{C} = 0 \quad (1.266)$$

$$q \equiv -\frac{1}{2} \left[\mathcal{B} + \text{sgn}(\mathcal{B}) \sqrt{\mathcal{B}^2 - 4\mathcal{A}\mathcal{C}} \right] \quad (1.267)$$

$$x_1 = \frac{q}{\mathcal{A}} \quad \& \quad x_2 = \frac{\mathcal{C}}{q} \quad (1.268)$$

In principle, the "traditional" quadratic formula is formally equivalent to the solutions (1.268). However, in practice, solutions to the quadratic formula are typically computed on devices that are susceptible to round off errors caused the subtraction of two very nearly identical numbers. The solutions of the form given above are robust against round off errors.

Only one of the two solutions is correct. Since the B field defined the axis of quantization used to derive the Breit-Rabi equation, it is positive by definition. Therefore the correct solution is the one for which

Isotope	I	upper F	End Transition	g_I	ν_{hfs} MHz
${}^6\text{Li}$	1	3/2	$s3/2 \leftrightarrow s1/2$	+0.822 056	228.205 26
${}^7\text{Li}$	3/2	2	$s2 \leftrightarrow s1$	+2.170 960	803.504 09
${}^{23}\text{Na}$	3/2	2	$s2 \leftrightarrow s1$	+1.478 347	1 771.626 13
${}^{39}\text{K}$	3/2	2	$s2 \leftrightarrow s1$	+0.260 973	461.719 72
${}^{40}\text{K}$	4	9/2	$s9/2 \leftrightarrow s7/2$	-0.324 5	-1 142.92
${}^{41}\text{K}$	3/2	2	$s2 \leftrightarrow s1$	+0.143 247	254.013 87
${}^{85}\text{Rb}$	5/2	3	$s3 \leftrightarrow s2$	+0.541 208	3 035.732 00
${}^{87}\text{Rb}$	3/2	2	$s2 \leftrightarrow s1$	+1.834 133	6 834.682 60
${}^{133}\text{Cs}$	7/2	4	$s4 \leftrightarrow s3$	+0.736 857	9 192.631 77

Table 1.3: Upper Manifold End Transitions for which Equation (1.273) is valid with $s = \pm$

$B > 0$. Since $\mu_B \gg \mu_N$, the sign of x is given by the sign of $-g_S B$. Since $g_S \approx -2$, x and B have the same sign. The sign of x_1 is given by the sign of $-\mathcal{B}/\mathcal{A}$ while the sign of x_2 is given by the sign of $-\mathcal{C}/\mathcal{B}$.

The value of the parameter a is 1 with a small correction of order 10^{-3} whose sign depends on g_I . Consequently, \mathcal{A} is nearly 0 and the sign of \mathcal{A} is equal to the sign of g_I . The value of the parameter b is always less than 1. If $2I \ll 10^3$, then $b < a$. If we also stipulate that $0 < \nu < \nu_{hfs}/2$, then $n < 1$. All this put together insures $(a - b - san) > 0$ which implies \mathcal{B} has the same sign as $-s$. Finally, the sign of \mathcal{C} is s because $(2 - sn) > 0$. Therefore, under these conditions, the sign of x_1 is s/g_I , whereas the sign of x_2 is positive. Since the correct solution must be positive regardless of s , it is $x_2 = \mathcal{C}/q$.

The discriminant $\mathcal{B}^2 - 4\mathcal{A}\mathcal{C}$ is given by:

$$[-2s(a - b - san)]^2 - 4[1 - a^2][sn(2 - sn)] = 4[b^2 + a^2 - 2ab + 2absn - 2sn + n^2] \quad (1.269)$$

$$= 4[(a - b)^2 - 2sn(1 - ab - sn/2)] \quad (1.270)$$

Plugging this into q , canceling factors of 2 inside q , and canceling a factor of s in \mathcal{C} & q gives:

$$x = (g_I\mu_N - g_S\mu_B) \frac{B}{h\nu_{hfs}} = \frac{C}{q} = \frac{n(2 - sn)}{a(1 - sn) - b + \sqrt{(a - b)^2 - 2sn(1 - ab - sn/2)}} \quad (1.271)$$

where $s = \pm 1$ and as a reminder:

$$n = 2\nu/\nu_{hfs} \quad a = \frac{1 + \frac{g_I\mu_N}{g_S\mu_B}}{1 - \frac{g_I\mu_N}{g_S\mu_B}} \quad b = \frac{2I - 1}{2I + 1} = \frac{[I] - 2}{[I]} \quad (1.272)$$

Multiplying the top and bottom by $[I]$, writing a as $1 - \epsilon$, and solving for B gives:

$$B = \left(\frac{[I]h\nu}{g_I\mu_N} \right) \frac{\epsilon(1 - f)}{1 - [I] \left\{ f(1 - \epsilon) + \frac{\epsilon}{2} \right\} + \sqrt{(1 - [I]\frac{\epsilon}{2})^2 - 2f[I] \left(1 - \epsilon + [I]\frac{(\epsilon - f)}{2} \right)}} \quad (1.273)$$

where $s = \pm 1$ is the sign of the edge state involved in the transition and:

$$[I] = 2I + 1 \quad f = s\nu/\nu_{hfs} \quad \epsilon = 1 - a = \frac{2g_I\mu_N}{g_I\mu_N - g_S\mu_B} = g_I \frac{\mu_N}{\mu_B} \left[\frac{-2}{g_S} \right] \left(1 - \frac{g_I\mu_N}{g_S\mu_B} \right)^{-1} \quad (1.274)$$

Twin Transition Frequency Difference

The upper manifold has two more $\Delta m_F = \pm 1$ transitions than the lower manifold. These extra transitions are the end transitions. All other upper manifold transitions have a “twin” transition in the lower manifold. The twins transitions sit side by side on the same row in table (1.2). The difference in frequencies between twin transitions depends only on the magnitude of the field:

$$\Delta\nu_{\text{twin}} = \nu_{\text{lower}} - \nu_{\text{upper}} = +2g_I \frac{\mu_N}{h} B \quad (1.275)$$

Note that for any pair of twin transitions, the lower manifold transition has the larger frequency. For example, the twin frequency differences for ^{39}K and ^{85}Rb at 10 gauss are:

$$^{39}\text{K} : \nu(F=1, m_F = \pm 1 \leftrightarrow 0) - \nu(F=2, m_F = \pm 1 \leftrightarrow 0) = 3.98 \text{ kHz} \quad (1.276)$$

$$^{85}\text{Rb} : \nu(F=2, m_F = \pm 2 \leftrightarrow \pm 1 \leftrightarrow 0) - \nu(F=3, m_F = \pm 2 \leftrightarrow \pm 1 \leftrightarrow 0) = 8.25 \text{ kHz} \quad (1.277)$$

Low Field Frequency Expansion

To expand the frequency at low field up to sixth order in x :

$$\begin{aligned} \nu_{\pm} &= \frac{\nu_{\text{hfs}}}{2} \Delta \mp \frac{g_I \mu_N B}{h} \\ \Delta &= \sqrt{1 + 2ax + x^2} - \sqrt{1 + 2a'x + x^2} \\ &= (a - a')x + \left(-\frac{a^2 - a'^2}{2}\right)x^2 \\ &\quad + \left(-\frac{a - a'}{2} + \frac{a^3 - a'^3}{2}\right)x^3 \\ &\quad + \left(3\frac{a^2 - a'^2}{4} - 5\frac{a^4 - a'^4}{8}\right)x^4 \\ &\quad + \left(3\frac{a - a'}{8} - 5\frac{a^3 - a'^3}{4} + 7\frac{a^5 - a'^5}{8}\right)x^5 \\ &\quad + \left(-15\frac{a^2 - a'^2}{16} + 35\frac{a^4 - a'^4}{16} - 21\frac{a^6 - a'^6}{16}\right)x^6 \end{aligned} \quad (1.278)$$

The difference in each term is with $b = [I]$:

$$a^n - a'^n = \left(\frac{2m_F}{[I]}\right)^n - \left(\frac{2(m_F - 1)}{[I]}\right)^n = \left[\frac{2}{b}\right]^n [m_F^n - (m_F - 1)^n] \quad (1.279)$$

Factoring out b^n from each term:

$$\begin{aligned} \frac{\Delta}{2} &= \frac{x}{b} + [1 - 2m_F] \frac{x^2}{b^2} + 2 \left[1 - 3m_F + 3m_F^2 - \frac{b^2}{4}\right] \frac{x^3}{b^3} \\ &\quad + \left[5(1 - 4m_F + 6m_F^2 - 4m_F^3) - \frac{3b^2}{2}(1 - 2m_F)\right] \frac{x^4}{b^4} \\ &\quad + \left[14(1 - 5m_F + 10m_F^2 - 10m_F^3 + 5m_F^4) - 5b^2(1 - 3m_F + 3m_F^2) + \frac{3b^4}{8}\right] \frac{x^5}{b^5} \\ &\quad + \left[42(1 - 6m_F + 15m_F^2 - 20m_F^3 + 15m_F^4 - 6m_F^5)\right] \frac{x^6}{b^6} \\ &\quad + \left[-\frac{35b^2}{2}(1 - 4m_F + 6m_F^2 - 4m_F^3) + \frac{15b^4}{8}(1 - 2m_F)\right] \frac{x^6}{b^6} \end{aligned} \quad (1.280)$$

Putting this altogether gives (to sixth order in x), the frequency of transition for the $F = I \pm 1/2$ manifold at a given (low) field B :

$$\frac{\nu_{\pm}}{\nu_{hfs}} = \sum_{n=1}^6 c_n \frac{x^n}{[I]^n} \quad (1.281)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{B}{h \nu_{hfs}} \quad (1.282)$$

$$[I] = 2I + 1 \quad (1.283)$$

$$c_1 = \frac{1 \pm \frac{g_I \mu_N}{g_S \mu_B} ([I] \mp 1)}{1 - \frac{g_I \mu_N}{g_S \mu_B}} = 1 \mp \mathcal{O}(10^{-3}) \quad (1.284)$$

$$c_2 = 1 - 2m_F \quad (1.285)$$

$$c_3 = 2 \left(1 - 3m_F + 3m_F^2 - \frac{[I]^2}{4} \right) \quad (1.286)$$

$$c_4 = 5(1 - 4m_F + 6m_F^2 - 4m_F^3) - \frac{3[I]^2}{2}(1 - 2m_F) \quad (1.287)$$

$$c_5 = 14(1 - 5m_F + 10m_F^2 - 10m_F^3 + 5m_F^4) - 5[I]^2(1 - 3m_F + 3m_F^2) + \frac{3[I]^4}{8} \quad (1.288)$$

$$c_6 = 42(1 - 6m_F + 15m_F^2 - 20m_F^3 + 15m_F^4 - 6m_F^5) - \frac{35[I]^2}{2}(1 - 4m_F + 6m_F^2 - 4m_F^3) + \frac{15[I]^4}{8}(1 - 2m_F) \quad (1.289)$$

where \pm refers to the manifold.

Low Field Frequency Inversion Formula

If we drop all terms higher than second order, then we can get an inversion formula for equation (1.281) for *any* transition at low field. Thus applying the quadratic formula (1.268) and noting that $\mu_N/\mu_B \ll 1 \rightarrow c_1 \approx 1$ and $g_S \approx -2$, we get the field corresponding to a particular transition frequency at low fields:

$$B \approx \left(\frac{h\nu}{\mu_B} \right) \frac{[I]}{1 + \sqrt{1 + 4(1 - 2m_F)\nu/\nu_{hfs}}} \quad (1.290)$$

Table (1.4) illustrates how accurate this approximate equation is. For ^{85}Rb , its better than 0.25% up to $\nu = 16$ MHz. For ^{39}K , its better than 0.50% up to $\nu = 10$ MHz.

Low Field Adjacent Transition Frequency Difference

At low fields to lowest order, the frequency difference between two adjacent transitions depends on B^2 :

$$\left| \frac{\nu(m_F + 1 \leftrightarrow m_F) - \nu(m_F \leftrightarrow m_F - 1)}{\nu_{hfs}} \right| = 2 \frac{x^2}{[I]^2} = 2 \left[(g_I \mu_N - g_S \mu_B) \frac{B}{[I] h \nu_{hfs}} \right]^2 \quad (1.291)$$

At $B = 10$ G, $\Delta\nu = 14.4$ kHz for ^{85}Rb and $\Delta\nu = 212$ kHz for ^{39}K .

Low Field Frequency Derivative with respect to Field

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

$$\frac{d\nu}{dB} = \mp \frac{g_I \mu_N}{h} + \frac{(g_I \mu_N - g_S \mu_B)}{2h[I]} \left(\frac{2m_F + [I]x}{\sqrt{1 + \frac{4m_F}{[I]}x + x^2}} - \frac{2m_F - 2 + [I]x}{\sqrt{1 + \frac{4(m_F-1)}{[I]}x + x^2}} \right) \quad (1.292)$$

^{39}K		$\nu = 10 \text{ MHz}$			$\nu = 25 \text{ MHz}$		
F	m_F	B (full)	B (1.290)	% diff.	B (full)	B (1.290)	% diff.
2	-1	13.422	13.465	+0.32	30.923	31.276	+1.14
1	0	14.011	13.993	-0.13	34.514	33.974	-1.56
2	0	14.018	13.993	-0.18	34.532	33.974	-1.62
1	+1	14.633	14.613	-0.13	38.564	37.901	-1.72
2	+1	14.642	14.613	-0.19	38.590	37.901	-1.79
2	+2	15.292	15.363	+0.46	43.095	44.883	+4.15

^{85}Rb		$\nu = 6.5 \text{ MHz}$			$\nu = 16 \text{ MHz}$		
F	m_F	B (full)	B (1.290)	% diff.	B (full)	B (1.290)	% diff.
3	-2	13.779	13.786	+0.05	33.403	33.436	+0.10
2	-1	13.814	13.844	+0.22	33.700	33.769	+0.21
3	-1	13.838	13.844	+0.04	33.758	33.769	+0.03
2	0	13.873	13.903	+0.21	34.057	34.116	+0.17
3	0	13.898	13.903	+0.04	34.116	34.116	-0.00
2	+1	13.933	13.962	+0.21	34.417	34.478	+0.18
3	+1	13.957	13.962	+0.03	34.479	34.478	-0.00
2	+2	13.992	14.023	+0.22	34.781	34.855	+0.21
3	+2	14.017	14.023	+0.04	34.845	34.855	+0.03
3	+3	14.078	14.085	+0.05	35.215	35.250	+0.10

Table 1.4: Comparison of calculation of B given ν . All the fields are in gauss. The “full” calculation is solving Eqn. (blah) numerically. The approximate calculation is Eqn. (1.290). Comparisons are made at $B \approx 15 \text{ G}$ & 35 G . For ^{39}K this corresponds to $\nu = 10 \text{ MHz}$ & 25 MHz . For ^{85}Rb this corresponds to $\nu = 6.5 \text{ MHz}$ & 16 MHz .

The derivative can be “expanded” in x at low field by taking the derivative of equation (1.281) term by term. To fifth order in field, the derivative of the frequency with respect to the field is:

$$\frac{d\nu_{\pm}}{dB} = \frac{(g_I\mu_N - g_S\mu_B)}{h[I]} \sum_{n=0}^5 b_n \frac{x^n}{[I]^n} \quad (1.293)$$

$$x = (g_I\mu_N - g_S\mu_B) \frac{B}{h\nu_{hfs}} \quad (1.294)$$

$$[I] = 2I + 1 \quad (1.295)$$

$$b_0 = \frac{1 \pm \frac{g_I\mu_N}{g_S\mu_B} ([I] \mp 1)}{1 - \frac{g_I\mu_N}{g_S\mu_B}} = 1 \mp \mathcal{O}(10^{-3}) \quad (1.296)$$

$$b_1 = 2(1 - 2m_F) \quad (1.297)$$

$$b_2 = 6 \left(1 - 3m_F + 3m_F^2 - \frac{[I]^2}{4} \right) \quad (1.298)$$

$$b_3 = 20(1 - 4m_F + 6m_F^2 - 4m_F^3) - 6[I]^2(1 - 2m_F) \quad (1.299)$$

$$b_4 = 70(1 - 5m_F + 10m_F^2 - 10m_F^3 + 5m_F^4) - 25[I]^2(1 - 3m_F + 3m_F^2) + \frac{15[I]^4}{8} \quad (1.300)$$

$$b_5 = 252(1 - 6m_F + 15m_F^2 - 20m_F^3 + 15m_F^4 - 6m_F^5) - 105[I]^2(1 - 4m_F + 6m_F^2 - 4m_F^3) + \frac{45[I]^4}{4}(1 - 2m_F) \quad (1.301)$$

These coefficients have simple forms for the end transitions. Plugging in $m_F = I + 1/2$ for $I + 1/2 \leftrightarrow I - 1/2$ and $m_F = -I + 1/2$ for $-I + 1/2 \leftrightarrow -I - 1/2$, the coefficients for the expansion of the derivative of the EPR frequency are:

$$b_0 = \frac{1 + \frac{g_I\mu_N}{g_S\mu_B}(2I)}{1 - \frac{g_I\mu_N}{g_S\mu_B}} = 1 - \mathcal{O}(10^{-3}) \quad (1.302)$$

$$b_1 = \mp 4I \quad (1.303)$$

$$b_2 = 6I(2I - 1) \quad (1.304)$$

$$b_3 = \mp 8I(4I^2 - 6I + 1) \quad (1.305)$$

$$b_4 = 10I(2I - 1)(4I^2 - 10I + 1) \quad (1.306)$$

$$b_5 = \mp 12I(16I^4 - 80I^3 + 80I^2 - 20I + 1) \quad (1.307)$$

where \pm refers to the edge state $m_F = \pm(I + \frac{1}{2})$ involved in the transition.

Chapter 2

The Structure of Polarized Light

2.1 Representing Electromagnetic Plane Waves

2.1.1 Real Representation

The electric and magnetic field components of an electromagnetic plane wave traveling in the z -direction with arbitrary polarization in a uniform and isotropic medium can be written as:

$$\vec{E}(\vec{r}, t) = E_x(z, t)\hat{x} + E_y(z, t)\hat{y} = E_{0x}\hat{x}\cos(kz - \omega t) + E_{0y}\hat{y}\cos(kz - \omega t + \phi) \quad (2.1)$$

$$\vec{B}(\vec{r}, t) = \sqrt{\mu\epsilon} [\hat{z} \times \vec{E}(\vec{r}, t)] = \mu\vec{H}(\vec{r}, t) \quad (2.2)$$

$$= \sqrt{\mu\epsilon} [E_{0x}\hat{y}\cos(kz - \omega t) - E_{0y}\hat{x}\cos(kz - \omega t + \phi)] \quad (2.3)$$

In SI, the energy flux (energy per unit time per unit area or instantaneous power density) associated with the EM wave is given by the Poynting vector:

$$\vec{S}(\vec{r}, t) = \vec{E}(\vec{r}, t) \times \vec{H}(\vec{r}, t) = \frac{1}{\mu} \vec{E}(\vec{r}, t) \times \vec{B}(\vec{r}, t) = \sqrt{\frac{\epsilon}{\mu}} \vec{E}(\vec{r}, t) \times [\hat{z} \times \vec{E}(\vec{r}, t)] \quad (2.4)$$

$$= \sqrt{\frac{\epsilon}{\mu}} \left(\hat{z} [\vec{E}(\vec{r}, t) \cdot \vec{E}(\vec{r}, t)] - \vec{E}(\vec{r}, t) [\hat{z} \cdot \vec{E}(\vec{r}, t)] \right) \quad (2.5)$$

$$= \hat{z} \sqrt{\frac{\epsilon}{\mu}} [\vec{E}(\vec{r}, t) \cdot \vec{E}(\vec{r}, t)] \quad (2.6)$$

$$= \hat{z} \sqrt{\frac{\epsilon}{\mu}} E_{0x}^2 \left[\cos^2(kz) \cos^2(\omega t) + \sin^2(kz) \sin^2(\omega t) + \frac{1}{2} \sin(2kz) \sin(2\omega t) \right] \\ + \hat{z} \sqrt{\frac{\epsilon}{\mu}} E_{0y}^2 \left[\cos^2(kz + \phi) \cos^2(\omega t) + \sin^2(kz + \phi) \sin^2(\omega t) + \frac{1}{2} \sin(2kz + 2\phi) \sin(2\omega t) \right] \quad (2.7)$$

We'll define the intensity as the magnitude of the time averaged energy flux (or time averaged power density):

$$I \equiv \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} \hat{z} \cdot \vec{S}(\vec{r}, t) dt \quad (2.8)$$

$$\frac{1}{2} = \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} \cos^2(\omega t) dt = \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} \sin^2(\omega t) dt \quad (2.9)$$

$$I = \sqrt{\frac{\epsilon}{\mu}} \left(\frac{E_{0x}^2}{2} [\cos^2(kz) + \sin^2(kz)] + \frac{E_{0y}^2}{2} [\cos^2(kz + \phi) + \sin^2(kz + \phi)] \right) \quad (2.10)$$

$$= \frac{1}{2} \sqrt{\frac{\epsilon}{\mu}} [E_{0x}^2 + E_{0y}^2] = \sqrt{\frac{\epsilon}{\mu}} \left\langle |\vec{E}|^2 \right\rangle_{\text{time}} \quad (2.11)$$

where the time averaged magnitude of the electric field vector is given as:

$$\sqrt{\langle |\vec{E}|^2 \rangle_{\text{time}}} = \sqrt{\frac{E_{0x}^2 + E_{0y}^2}{2}} \quad (2.12)$$

2.1.2 Complex Representation: The Jones Calculus

We will use the Jones calculus [9, 10, 11] 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 a monochromatic electromagnetic plane wave with propagation vector $\vec{k} = k\hat{z}$ at time t is:

$$\vec{E}(z, t) = E_x(z, t)\hat{x} + E_y(z, t)\hat{y} = |E\rangle e^{ikz - i\omega t} \quad (2.13)$$

$$E_x(z, t) = E_{0x} \exp(ikz - i\omega t + i\alpha_x) \quad (2.14)$$

$$E_y(z, t) = E_{0y} \exp(ikz - i\omega t + i\alpha_y) \quad (2.15)$$

$$|E\rangle \equiv \begin{bmatrix} E_{0x} e^{i\alpha_x} \\ E_{0y} e^{i\alpha_y} \end{bmatrix} \quad (2.16)$$

where the relative phase shift is $\alpha = \alpha_x - \alpha_y$. Note that it is assumed that the real part of \vec{E} is taken when the physical field is needed. At a fixed point in space and over one period ($= \frac{2\pi}{\omega}$) in time, \vec{E} sweeps out an ellipse in the xy -plane given by (Born, Max and Emil Wolf. Principles of Optics, 7th (Expanded) Edition. Cambridge: Cambridge University Press, 1999. page 26, equation 15):

$$\left(\frac{E_x}{E_{0x}}\right)^2 + \left(\frac{E_y}{E_{0y}}\right)^2 - 2\left(\frac{E_x}{E_{0x}}\right)\left(\frac{E_y}{E_{0y}}\right)\cos(\alpha) = \sin^2(\alpha) \quad (2.17)$$

In this representation, computing the modulus square of the electric field vector gives:

$$\vec{E}^* \cdot \vec{E} = \langle E|E\rangle = E_{0x}^2 + E_{0y}^2 \quad (2.18)$$

The time averaged modulus squared of electric field vector is therefore:

$$|\vec{E}|_{\text{time}}^2 \equiv \frac{\vec{E}^* \cdot \vec{E}}{2} = \frac{E_{0x}^2 + E_{0y}^2}{2} \quad (2.19)$$

and finally the intensity is:

$$I = \sqrt{\frac{\epsilon}{\mu}} \langle \vec{E}^* \cdot \vec{E} \rangle_{\text{time}} = \sqrt{\frac{\epsilon}{\mu}} \frac{\langle E|E\rangle}{2} = \frac{\langle B|B\rangle}{2\mu\sqrt{\epsilon\mu}} \quad (2.20)$$

2.2 Linear Polarization

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

$$\alpha = \pm n\pi \quad (2.21)$$

or in other words the two components are in phase. Eqn. (2.17) becomes degenerate,

$$\left(\frac{E_x}{E_{0x}}\right)^2 + \left(\frac{E_y}{E_{0y}}\right)^2 \mp 2\left(\frac{E_x}{E_{0x}}\right)\left(\frac{E_y}{E_{0y}}\right) = 0 \quad (2.22)$$

with solutions

$$\frac{E_y}{E_{0y}} = \mp \frac{E_x}{E_{0x}} \quad (2.23)$$

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

$$|\mathcal{P}\rangle = |x\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (2.24)$$

Vertical linearly polarized light is denoted by

$$|\mathcal{S}\rangle = |y\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (2.25)$$

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

$$|\theta\rangle = \begin{bmatrix} \cos(\theta) \\ \sin(\theta) \end{bmatrix} \quad (2.26)$$

2.3 Circular Polarization

When the relative phase shift is a quarter wave,

$$\alpha = \pm(2n + 1)\frac{\pi}{2} \quad (2.27)$$

and the magnitudes of the two components are identical,

$$E_{0x} = E_{0y} \quad (2.28)$$

then eqn. (2.17) reduces to an equation for a circle:

$$E_x^2 + E_y^2 = 1 \quad (2.29)$$

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,

$$|\mathcal{R}\rangle = |+\rangle = \frac{\sqrt{2}}{2} \begin{bmatrix} 1 \\ +i \end{bmatrix} \quad (2.30)$$

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

$$|\mathcal{L}\rangle = |-\rangle = \frac{\sqrt{2}}{2} \begin{bmatrix} 1 \\ -i \end{bmatrix} \quad (2.31)$$

is anti-parallel. 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 xy -plane at a fixed point in space. In the standard optics convention, for right circularly polarized light, \vec{E} rotates counterclockwise in the xy -plane at a fixed moment in time as you move forward in the direction of propagation. See fig. (2.1). Unless otherwise noted, *the helicity convention* will be used. See page 400 of *Waves* [12] for further discussion regarding handedness convention.

2.4 Stokes Parameters

Since the polarization vector of light has two components with complex coefficients, four real numbers are required to describe it completely. These real numbers are called Stokes parameters. Unfortunately many different conventions exist in the literature. For our purposes, the most useful convention in the circular polarization basis for arbitrarily polarized light is:

$$|E\rangle = E_0 e^{i\phi_p} \left[\sqrt{\frac{1+P}{2}} e^{-i\theta} |\mathcal{R}\rangle + \sqrt{\frac{1-P}{2}} e^{+i\theta} |\mathcal{L}\rangle \right] \quad (2.32)$$

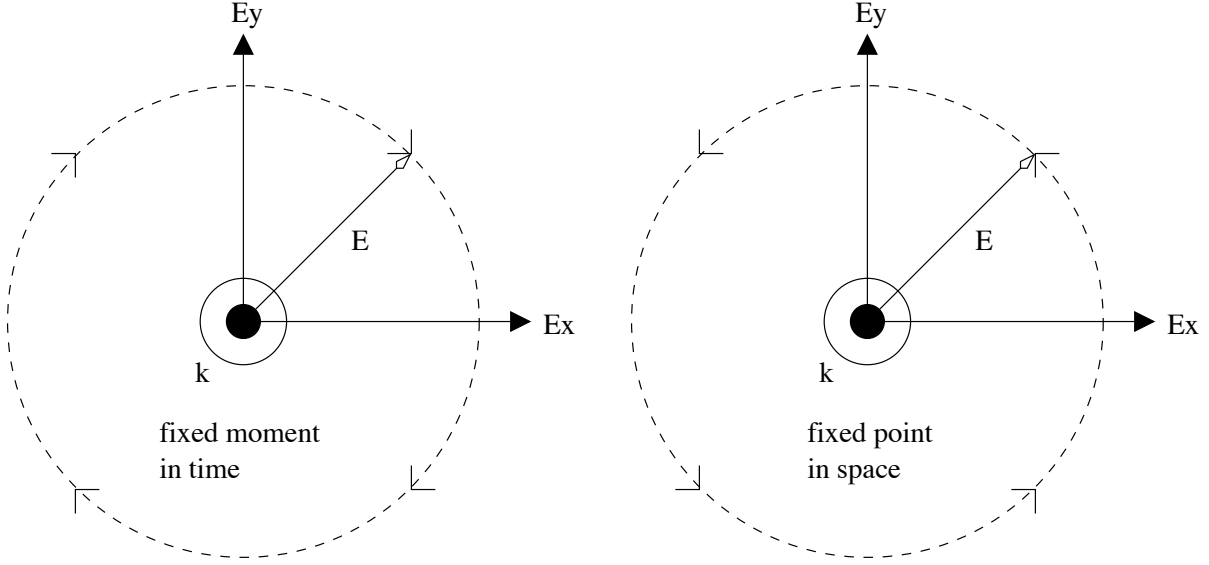


Figure 2.1: Right (helicity) circularly polarized light. Left: fixed time, forward in space. Right: fixed space, forward in time.

where ϕ_p is just an overall phase factor that rarely contains any useful information about the light. Equivalently in the linear polarization basis, it is written as:

$$|E\rangle = E_0 e^{i\phi_p} \left[\left(\sqrt{1-P} \frac{e^{+i\theta}}{2} + \sqrt{1+P} \frac{e^{-i\theta}}{2} \right) |\mathcal{P}\rangle + \left(\sqrt{1-P} \frac{e^{+i\theta}}{2i} - \sqrt{1+P} \frac{e^{-i\theta}}{2i} \right) |\mathcal{S}\rangle \right] \quad (2.33)$$

The magnitude of \vec{E} is:

$$\sqrt{\langle E|E\rangle} = \sqrt{\langle E_{\mathcal{R}}|E_{\mathcal{R}}\rangle + \langle E_{\mathcal{L}}|E_{\mathcal{L}}\rangle} = \sqrt{\left(\frac{1+P}{2}\right) E_0^2 + \left(\frac{1-P}{2}\right) E_0^2} = E_0 \quad (2.34)$$

The degree of circular polarization of the light is:

$$\frac{\langle E_{\mathcal{R}}|E_{\mathcal{R}}\rangle - \langle E_{\mathcal{L}}|E_{\mathcal{L}}\rangle}{\langle E|E\rangle} = \frac{\left(\frac{1+P}{2}\right) E_0^2 - \left(\frac{1-P}{2}\right) E_0^2}{E_0^2} = P \quad (2.35)$$

where $P = +(-)1$ for pure right (left) circular polarization and $P = 0$ for pure linear polarization. In the linear basis for pure linear polarization:

$$|E\rangle = E_0 e^{i\phi_p} \left[\left(\frac{e^{+i\theta}}{2} + \frac{e^{-i\theta}}{2} \right) |\mathcal{P}\rangle + \left(\frac{e^{+i\theta}}{2i} - \frac{e^{-i\theta}}{2i} \right) |\mathcal{S}\rangle \right] = E_0 e^{i\phi_p} [\cos(\theta) |\mathcal{P}\rangle + \sin(\theta) |\mathcal{S}\rangle] \quad (2.36)$$

where θ is the angle of the linear polarization vector with respect to the $|\mathcal{P}\rangle$ -axis. In general for elliptically polarized light, θ is the angle that the major axis of the polarization ellipse makes with the $|\mathcal{P}\rangle$ -axis.

2.5 Mirrors

Mirrors are produced by applying one or more layers of a thin film coating onto a substrate. The index of refraction and thickness of the thin film is chosen to maximize reflection. The reflectivity of the mirror and the phase shift induced in the light depends on the polarization of the light and its angle of incidence. The mirrors we commonly use (Newport Corporation, 1791 Deere Ave, Irvine, CA 92606, 1-800-222-6440) have a minimum reflectivity of 99% for \mathcal{P} polarized light and 98% for \mathcal{S} polarized light in the 700–950 nm

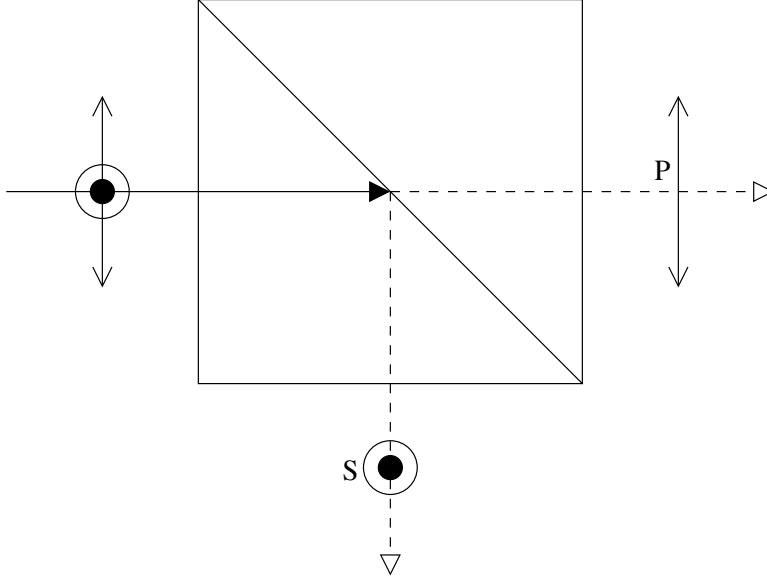


Figure 2.2: Top view of BSPC

range for angles from 0–45 degrees (broadband dielectric coating BD.2). Specifically, at 45 degrees and at a wavelength of around 800 nm, the reflectivities for \mathcal{P} & \mathcal{S} polarized light are 99.5% and 99.9%. Since the reflectivity is defined as the ratio of output to input intensities, the reflection coefficient is the square root of the reflectivity:

$$r_P = \sqrt{R_P} \approx 0.9975 \quad (2.37)$$

$$r_S = \sqrt{R_S} \approx 0.9995 \quad (2.38)$$

If the light is circularly polarized or a mix of \mathcal{S} and \mathcal{P} linear polarizations, then it is necessary to include a small relative phase shift factor, δ_m . Unfortunately, this value is not given in the optics catalogs and must be obtained empirically if needed. A simplified form for the mirror matrix is then:

$$\hat{M} = \begin{bmatrix} r_P & 0 \\ 0 & r_S e^{i\delta_m} \end{bmatrix} \quad (2.39)$$

A fully general mirror matrix would be, in principle, complex and may even contain small non-zero off diagonal elements.

2.6 Beam Splitting Polarizing Cubes

2.6.1 Matrix Representation

An ideal beam splitting polarizing cube (BSPC) simply splits an incoming beam into its two linearly polarized components. Once separated, the two beam paths are orthogonal, see fig. (2.2). The transmitted beam is selected by

$$\hat{C}_t = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \quad (2.40)$$

and the reflected beam is selected by

$$\hat{C}_r = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \quad (2.41)$$

For the ideal case, the transmitted and reflected beams are pure \mathcal{P} & \mathcal{S} linear polarizations respectively. In practice the splitting and polarizing are imperfect. According to RMI (Dr. Zhiming Lu, zlu@rmico.com,

Rocky Mountain Instruments, 106 Laser Drive, Lafayette, CO, 80026, 303-664-5000), our 2" BSPC has an extinction ratio for the transmitted beam of $\geq 1000 : 1$ whereas for the reflected beam it is $\leq 20 : 1$. The transmittance is about $\geq 95\%$, whereas the reflectance is about $\geq 99.9\%$. Therefore a more realistic form of \hat{C} can be written. For example, for the transmitted beam:

$$\hat{C}_t = \begin{bmatrix} t_1 & 0 \\ 0 & t_2 \end{bmatrix} \quad (2.42)$$

$$T_t = \frac{I_{\text{transmitted}}}{I_{\text{input}\mathcal{P}}} = t_1^2 + t_2^2 \quad (2.43)$$

$$e_t = \frac{I_{\text{transmitted}\mathcal{P}}}{I_{\text{transmitted}\mathcal{S}}} = \frac{t_1^2}{t_2^2} \quad (2.44)$$

where t is the transmittance and e_t is the extinction ratio for the transmitted beam. Solving for t_1 & t_2 in terms of t & e_t and doing the same for the reflected beam, the more general cube matrices become:

$$\hat{C}_t = \begin{bmatrix} \sqrt{\frac{T_t}{1+e_t}} & 0 \\ 0 & \sqrt{\frac{T_t}{1+e_t}} \end{bmatrix} \quad (2.45)$$

$$\hat{C}_r = \begin{bmatrix} \sqrt{\frac{T_r}{1+e_r}} & 0 \\ 0 & \sqrt{\frac{T_r}{1+e_r^{-1}}} \end{bmatrix} \quad (2.46)$$

Given the specifications for our cube, the matrices are:

$$\hat{C}_t \approx \begin{bmatrix} 0.974 & 0 \\ 0 & 0.031 \end{bmatrix} \quad (2.47)$$

$$\hat{C}_r \approx \begin{bmatrix} 0.213 & 0 \\ 0 & 0.951 \end{bmatrix} \quad (2.48)$$

The fully general cube matrices could be, in principle, complex and have non-zero off diagonal elements.

2.6.2 Measuring the degree of circular polarization

One can measure the degree of circular polarization of a beam of light by using a rotatable beam splitting polarizing cube. Note that an input light polarization angle of θ with respect to the cube axis is equivalent to having the cube axis be $-\theta$ from the light polarization \mathcal{P} axis. Therefore varying θ is equivalent to rotating the cube. If the incident light is normal to the cube, then the intensity of the light transmitted through the cube is given by:

$$\begin{aligned} I_t &= \left| \hat{C}_t |E\rangle \right|^2 = t_1^2 \langle E_{\mathcal{P}} | E_{\mathcal{P}} \rangle + t_2^2 \langle E_{\mathcal{S}} | E_{\mathcal{S}} \rangle \\ &= \frac{E_0^2 T_t e_t}{1+e_t} \left(\frac{1-P+1+P+2\sqrt{1-P^2} \cos(2\theta)}{4} \right) + \frac{E_0^2 T_t}{1+e_t} \left(\frac{1-P+1+P-2\sqrt{1-P^2} \cos(2\theta)}{4} \right) \\ &= \frac{E_0^2 T_t}{2} \left[1 + \left(\frac{e_t-1}{e_t+1} \right) \sqrt{1-P^2} \cos(2\theta) \right] \end{aligned} \quad (2.49)$$

The maximum and minimum transmitted intensities are:

$$I_{\text{max}} = \frac{E_0^2 T_t}{2} \left[1 + \left(\frac{e_t-1}{e_t+1} \right) \sqrt{1-P^2} \right] \quad (2.50)$$

$$I_{\text{min}} = \frac{E_0^2 T_t}{2} \left[1 - \left(\frac{e_t-1}{e_t+1} \right) \sqrt{1-P^2} \right] \quad (2.51)$$

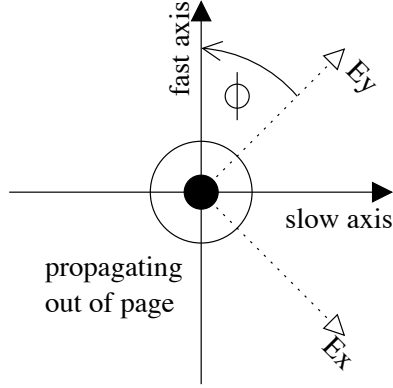


Figure 2.3: Coordinate System of a Waveplate #check#time or space convention fast axis?

Defining the cube efficiency f_c and forming the cube asymmetry A_c yields a polarization “Pythagorean” expression:

$$f_c \equiv \frac{e_t - 1}{e_t + 1} \quad (2.52)$$

$$A_c \equiv \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} = f_c \sqrt{1 - P^2} \quad (2.53)$$

$$1 = P^2 + \left(\frac{A_c}{f_c}\right)^2 \quad (2.54)$$

where P is the degree of circular polarization.

2.7 Waveplates

2.7.1 Matrix Representation

A waveplate is an optical element that has different indices of refraction along two orthogonal axes, see fig. (2.3). This results in a net phase shift between the linear 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,

$$\hat{R}(\phi) = \begin{bmatrix} \cos(\phi) & \sin(\phi) \\ -\sin(\phi) & \cos(\phi) \end{bmatrix} \quad (2.55)$$

followed by a relative phase retardation of β radians,

$$\hat{W}(\beta) = \begin{bmatrix} \exp\left(+i\frac{\beta}{2}\right) & 0 \\ 0 & \exp\left(-i\frac{\beta}{2}\right) \end{bmatrix} \quad (2.56)$$

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

$$\hat{W}(\phi, \beta) = \hat{R}(-\phi)\hat{W}(\beta)\hat{R}(\phi) \quad (2.57)$$

$$= \exp\left(-i\frac{\beta}{2}\right) \begin{bmatrix} 1 + 2i \exp\left(i\frac{\beta}{2}\right) \sin\left(\frac{\beta}{2}\right) \cos^2(\phi) & i \exp\left(i\frac{\beta}{2}\right) \sin\left(\frac{\beta}{2}\right) \sin(2\phi) \\ i \exp\left(i\frac{\beta}{2}\right) \sin\left(\frac{\beta}{2}\right) \sin(2\phi) & 1 + 2i \exp\left(i\frac{\beta}{2}\right) \sin\left(\frac{\beta}{2}\right) \sin^2(\phi) \end{bmatrix} \quad (2.58)$$

Note that for one complete wave, $\beta = 2\pi$. Typically the fast axis is taken to be vertical.

2.7.2 Half Waveplate

A half-waveplate has a retardance $\beta = \frac{2\pi}{2} = \pi$. When it is orientated at an angle of ϕ from a set of reference axes, the waveplate matrix becomes:

$$\hat{W}_{\frac{1}{2}}(\phi) = i \begin{bmatrix} \cos(2\phi) & \sin(2\phi) \\ \sin(2\phi) & -\cos(2\phi) \end{bmatrix} \quad (2.59)$$

This operation implies that each linear polarization component of some arbitrarily polarized light is rotated by twice the angle between the linear polarization axis and the waveplate fast axis. If the the linear polarization is either \mathcal{S} or \mathcal{P} , then a half-waveplate at an angle ϕ with respect to the polarization axis rotates the linear polarization by an angle of 2ϕ . A half-waveplate at $\pm 45^\circ$ simplify flips $\mathcal{P} \leftrightarrow \mathcal{S}$. For pure circularly polarized light, a half-waveplate orientated at *any* angle simply flips $\mathcal{L} \leftrightarrow \mathcal{R}$.

2.7.3 Quarter Waveplate

For a quarter-waveplate with retardance $\beta = \frac{2\pi}{4} = \frac{\pi}{2}$, orientated at an angle of 45° , the matrix becomes:

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right) = \frac{\sqrt{2}}{2} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \quad (2.60)$$

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

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right)|\mathcal{P}\rangle = |\mathcal{R}\rangle \quad (2.61)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right)|\mathcal{R}\rangle = i|\mathcal{S}\rangle \quad (2.62)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right)|\mathcal{S}\rangle = i|\mathcal{L}\rangle \quad (2.63)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right)|\mathcal{L}\rangle = |\mathcal{P}\rangle \quad (2.64)$$

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. Note that in the RHS of the two middle equations, there is an overall phase factor (i) which for our purposes is unimportant.

2.7.4 Photoelastic Modulator

A photoelastic modulator is a variable retardance waveplate. The retardance can be fixed at a constant value or (more importantly) modulated at a frequency $\nu_{\text{mod}} (= \Omega_{\text{mod}}/2\pi)$:

$$\beta(t) = \beta_0 \sin(\Omega_{\text{mod}}t + \phi_{\text{mod}}) \quad (2.65)$$

The PEM that we have (Hinds Instruments, 3175 NW Alcock, Hillsboro, OR 97124, 503-690-2000) oscillates at 50 kHz. The ability to modulate the phase retardance and therefore modulate the polarization of the incident light makes a PEM (in conjunction with a lock-in amplifier) useful as a high precision polarimeter. Note the following useful relationships from p. 361 of *Abramowitz & Stegun* [13]:

$$\begin{aligned} \sin(\beta_0 \sin(\Omega_{\text{mod}}t)) &= 2 \sum_{n=0}^{\infty} J_{2n+1}(\beta_0) \sin((2n+1)\Omega_{\text{mod}}t) \\ &= 2J_1(\beta_0) \sin(\Omega_{\text{mod}}t) + \dots \end{aligned} \quad (2.66)$$

$$\begin{aligned} \sin(\beta_0 \cos(\Omega_{\text{mod}}t)) &= 2 \sum_{n=0}^{\infty} (-)^n J_{2n+1}(\beta_0) \cos((2n+1)\Omega_{\text{mod}}t) \\ &= 2J_1(\beta_0) \cos(\Omega_{\text{mod}}t) - \dots \end{aligned} \quad (2.67)$$

$$\begin{aligned}
\cos(\beta_0 \sin(\Omega_{\text{mod}} t)) &= J_0(\beta_0) + 2 \sum_{n=1}^{\infty} J_{2n}(\beta_0) \cos(2n\Omega_{\text{mod}} t) \\
&= J_0(\beta_0) + 2J_2(\beta_0) \cos(2\Omega_{\text{mod}} t) + \dots
\end{aligned} \tag{2.68}$$

$$\begin{aligned}
\cos(\beta_0 \cos(\Omega_{\text{mod}} t)) &= J_0(\beta_0) + 2 \sum_{n=1}^{\infty} (-)^n J_{2n}(\beta_0) \cos(2n\Omega_{\text{mod}} t) \\
&= J_0(\beta_0) - 2J_2(\beta_0) \cos(2\Omega_{\text{mod}} t) + \dots
\end{aligned} \tag{2.69}$$

Chapter 3

The Effect on Alkali Atoms Due to Semiclassical Interactions With Polarized Light

3.1 Density Matrix

3.1.1 Definition & Basic Properties

To discuss the change in the relative populations of different states due to transitions, it is useful to first introduce the density matrix [14]. The density matrix is often used to represent a large ensemble of systems in a statistical mixture of pure quantum states, for example, a vapor of polarized alkali atoms. To be explicit, given a statistical probability p_k of being in the pure quantum state $|\psi_k\rangle$, the density matrix is defined as

$$\rho \equiv \sum_k p_k |\Psi_k\rangle \langle \Psi_k| \quad (3.1)$$

where $|\Psi_k\rangle$ is, in general, a superposition of eigenstates:

$$|\Psi_k\rangle = \sum_n c_{kn}(t) |n\rangle \quad \& \quad \langle \Psi_k| = \sum_m c_{km}^*(t) \langle m| \quad (3.2)$$

The complex coefficients $c_{kn}(t)$ contain all of the time dependence. For notational convenience we'll drop the (t) and expanding the density matrix in this eigenbasis gives

$$\rho = \sum_{k,m,n} p_k c_{km}^* c_{kn} |n\rangle \langle m| \quad (3.3)$$

where the matrix elements are

$$\rho_{ba} = \langle b | \rho | a \rangle = \sum_{k,m,n} p_k c_{km}^* c_{kn} \langle b | n \rangle \langle m | a \rangle = \sum_k p_k c_{ka}^* c_{kb} \quad (3.4)$$

The diagonal elements ($b = a$) have a simple and straightforward physical interpretation: they are the combined statistical and quantum mechanical probabilities of being in the eigenstate $|a\rangle$. We've assumed that everything has been normalized properly:

$$\sum_n c_{kn}^* c_{kn} = \sum_n |c_{kn}|^2 = 1 \quad \& \quad \sum_k p_k = 1 \quad (3.5)$$

Off-diagonal elements ($b \neq a$) are called coherences and are complex conjugates of each other

$$\rho_{ba} = \rho_{ab}^* \quad \rightarrow \quad \rho = \rho^\dagger \quad (3.6)$$

which implies that the density matrix is Hermitian, by construction.

3.1.2 Time Evolution: Liouville Equation

The time evolution of the density matrix is easily derived by first differentiating with respect to time t

$$\frac{d\rho}{dt} = \dot{\rho} = \sum_k p_k \left(\frac{\partial |\Psi_k\rangle}{\partial t} \langle \Psi_k| + |\Psi_k\rangle \frac{\partial \langle \Psi_k|}{\partial t} \right) \quad (3.7)$$

and then applying Schrodinger equation

$$\frac{\partial |\Psi_k\rangle}{\partial t} = -\frac{i}{\hbar} \mathcal{H} |\Psi_k\rangle \quad \& \quad \frac{\partial \langle \Psi_k|}{\partial t} = +\frac{i}{\hbar} \langle \Psi_k| \mathcal{H} \quad (3.8)$$

where \mathcal{H} is the full Hamiltonian of the system. The end result is known as the Liouville equation:

$$\dot{\rho} = -\frac{i}{\hbar} (\mathcal{H}\rho - \rho\mathcal{H}) = -\frac{i}{\hbar} [\mathcal{H}, \rho] \quad (3.9)$$

We'll write \mathcal{H} as the sum of the free Hamiltonian \mathcal{H}_0 and the interaction term \mathcal{W} :

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{W} \quad \& \quad \mathcal{H}_0 |n\rangle = \hbar\omega_n |n\rangle \quad (3.10)$$

where the energy associated with the eigenstate n in the free Hamiltonian is $\hbar\omega_n$. Expanding ρ in the eigenbasis of \mathcal{H}_0 and collecting terms gives:

$$\dot{\rho} = -\frac{i}{\hbar} \sum_{k,n,m} p_k c_{km}^* c_{kn} \{ (\hbar\omega_{nm} + \mathcal{W}) |n\rangle \langle m| - |n\rangle \langle m| \mathcal{W} \} \quad (3.11)$$

where we've set $\omega_{nm} = \omega_n - \omega_m$. Placing this result inside $\langle b | \dots | a \rangle$ gives the projection:

$$\dot{\rho}_{ba} = -\frac{i}{\hbar} \sum_{k,n,m} p_k c_{km}^* c_{kn} \{ (\hbar\omega_{nm} \langle b | n \rangle + \langle b | \mathcal{W} | n \rangle) \langle m | a \rangle - \langle b | n \rangle \langle m | \mathcal{W} | n \rangle \} \quad (3.12)$$

Reducing the sums over n and m by noting $\langle j | k \rangle = \delta_{jk}$ gives a set of coupled differential equations:

$$\dot{\rho}_{ba} = -i\omega_{ba}\rho_{ba} - \frac{i}{\hbar} \sum_n (\rho_{na} \langle b | \mathcal{W} | n \rangle - \rho_{bn} \langle n | \mathcal{W} | a \rangle) \quad (3.13)$$

where we've relabeled the dummy variable of the last term $m \rightarrow n$. When there is no interaction ($\mathcal{W} = 0$), the equations become uncoupled:

$$\dot{\rho}_{ba} = -i\omega_{ba}\rho_{ba} \quad (3.14)$$

and are easily solved:

$$\rho_{ba}(t) = \rho_{ba}(0) \exp(-i\omega_{ba}t) \quad \text{for coherences } (b \neq a) \quad (3.15)$$

$$\rho_{aa}(t) = \rho_a(t) = \rho_a(0) = \text{constant} \quad \text{for populations } (b = a) \quad (3.16)$$

3.1.3 Expectation Values: Trace

The expectation value of some operator \mathcal{U} for a state $|\Psi_k\rangle$ is given by $\langle \mathcal{U} \rangle_k = \langle \Psi_k | \mathcal{U} | \Psi_k \rangle$. For a system in a statistical mixture of pure quantum states, we have to average $\langle \mathcal{U} \rangle_k$ over all k :

$$\langle \mathcal{U} \rangle = \sum_k p_k \langle \mathcal{U} \rangle_k = \sum_k p_k \langle \Psi_k | \mathcal{U} | \Psi_k \rangle = \sum_{k,n,m} p_k c_{km}^* c_{kn} \langle m | \mathcal{U} | n \rangle = \sum_{n,m} \langle n | \rho | m \rangle \langle m | \mathcal{U} | n \rangle \quad (3.17)$$

We can write this sum in a more illuminating way by inserting three copies of the complete projection operator $1 = \sum_a |a\rangle \langle a|$:

$$\sum_{n,m} \langle n | \rho | m \rangle \langle m | \mathcal{U} | n \rangle = \sum_{n,m} \langle n | \left(\sum_a |a\rangle \langle a| \right) \rho \left(\sum_b |b\rangle \langle b| \right) |m\rangle \langle m | \mathcal{U} \left(\sum_\ell |\ell\rangle \langle \ell| \right) |n\rangle \quad (3.18)$$

When we group the sums appropriately, we find:

$$\sum_n \langle n | \left(\sum_{a,b} |a\rangle \langle a| \rho |b\rangle \langle b| \right) \left(\sum_{m,\ell} |m\rangle \langle m| \mathcal{U} |\ell\rangle \langle \ell| \right) |n\rangle = \sum_n \langle n | \rho \mathcal{U} |n\rangle \quad (3.19)$$

The action defined by $\sum_n \langle n | (\dots) |n\rangle$ is simply the sum of the diagonal elements of the enclosed matrix, in other words: the trace $\text{Tr}(\dots)$. To summarize, in the density matrix formulation, the expectation value of some operator \mathcal{U} is given by the trace of the product $\rho \mathcal{U}$:

$$\langle \mathcal{U} \rangle = \text{Tr}(\mathcal{U} \rho) = \text{Tr}(\rho \mathcal{U}) = \sum_{n,m} \langle n | \rho |m\rangle \langle m | \mathcal{U} |n\rangle \quad (3.20)$$

3.2 General Electromagnetic Dipole Interaction

3.2.1 General Form

Dipole Moment Operator

The interaction of light with an alkali atom can be written semiclassically as:

$$\mathcal{W} = -\vec{m} \cdot \Re \vec{F}(\vec{r}, t) \quad (3.21)$$

where \vec{F} is the field component of the incident light *in the complex representation* and \vec{m} is a dipole moment operator of the form:

$$\vec{m} = \sum_q m_0 \mathcal{U}_q \hat{\varepsilon}_q^* \quad (3.22)$$

where m_0 is magnitude of the moment and $\{\hat{\varepsilon}_q^*\}$ are unit basis vectors. The operator associated with the dipole moment, \mathcal{U}_q , connects the eigenstate m with the eigenstate $m + q$:

$$\mathcal{U}_q = \sum_{m,n} \delta_{m+q,n} |n\rangle \langle n| \mathcal{U}_q |m\rangle \langle m| = \sum_m |m+q\rangle \langle m+q| \mathcal{U}_q |m\rangle \langle m| \quad (3.23)$$

Electromagnetic Field

A subtle point to note is that the interaction depends only on *the real part of the field*. To be explicit, the real part of the field in the complex representation is:

$$\Re \vec{F}(\vec{r}, t) = \Re \vec{F}_0 \exp(i\vec{k} \cdot \vec{r} - \omega t) = F_0 \left[\hat{F}_0 \exp(i\vec{k} \cdot \vec{r} - i\omega t) + \hat{F}_0^* \exp(-i\vec{k} \cdot \vec{r} + i\omega t) \right] \quad (3.24)$$

where F_0 is the real magnitude of the field, \hat{F}_0 is the complex unit polarization vector, \vec{k} is the wave vector of the light, \vec{r} is its direction of propagation, and ω is the angular frequency.

Dipole Approximation

We'll make the dipole approximation by noting:

$$|\vec{k} \cdot \vec{r}| = kr = \frac{2\pi r}{\lambda} \approx \frac{2\pi 5a_0}{\lambda} \approx \frac{2\pi 5(0.053 \text{ nm})}{780 \text{ nm}} \approx 0.002 \ll 1 \quad (3.25)$$

where a_0 is the Bohr radius ($5a_0$ is the characteristic scale of an K or Rb atom) and λ is the wavelength of the light. Shorter wavelengths correspond to the transitions with the larger energy differences. The transitions with the largest energy differences that we'll be discussing are the *D1* and *D2* transitions of alkali atoms. For K and Rb, this is around 780 nm, therefore, the dipole approximation is a very good one under our conditions. Physically, this means that the amplitude of the electromagnetic wave hitting the atom does

not vary much in amplitude over the size scale of the atom. As a consequence, we'll drop the $\vec{k} \cdot \vec{r}$ term and write the interaction as:

$$\mathcal{W} = -m_0 F_0 \sum_q \mathcal{U}_q \left[\hat{\varepsilon}_q^* \cdot \hat{F}_0 \exp(-i\omega t) + \hat{\varepsilon}_q \cdot \hat{F}_0^* \exp(+i\omega t) \right] = -\hbar\Omega \sum_{q,s} \{ u_q^s \exp(+is\omega t) \mathcal{U}_q \} \quad (3.26)$$

where $s = \pm 1$ and we've made the following substitutions:

$$\hbar\Omega = m_0 F_0 \quad u_q^- = \hat{\varepsilon}_q^* \cdot \hat{F}_0 \quad u_q^+ = \hat{\varepsilon}_q \cdot \hat{F}_0^* \quad (3.27)$$

Since \mathcal{W} is Hermitian, $(\mathcal{U}_q)^\dagger = \mathcal{U}_{-q}$ and consequently $(u_q^s)^* = u_{-q}^{-s}$.

3.2.2 Coherences

Plugging the general dipole interaction, Eqn. (3.26), into the Liouville equation, Eqn. (3.13), gives:

$$\dot{\rho}_{ba} = -i\omega_{ba}\rho_{ba} + i\Omega \sum_{q,s,n,m} u_q^s \exp(+is\omega t) \{ \dots \} \quad (3.28)$$

$$\dots = \rho_{na} \langle b | m+q \rangle \langle m+q | \mathcal{U}_q | m \rangle \langle m | n \rangle - \rho_{bn} \langle n | m+q \rangle \langle m+q | \mathcal{U}_q | m \rangle \langle m | a \rangle$$

Reducing the sum over n and m gives:

$$\dot{\rho}_{ba} = -i\omega_{ba}\rho_{ba} + i\Omega \sum_{q,s} u_q^s \exp(+is\omega t) \{ \rho_{b-q,a} \langle b | \mathcal{U}_q | b-q \rangle - \rho_{b,a+q} \langle a+q | \mathcal{U}_q | a \rangle \} \quad (3.29)$$

For the $q = b - a$ term in the sum, the matrix elements of ρ in that term are populations. For the remaining terms in the sum, $q \neq b - a$ and the matrix elements of ρ in those terms are coherences. As we'll see shortly, this is a vital difference, so we'll explicitly separate the $q = b - a$ term from the sum:

$$\dot{\rho}_{ba} = -i\omega_{ba}\rho_{ba} + i\Omega \sum_s \exp(+is\omega t) \left(U_{\text{pop}}^{s,q=b-a} + \sum_q U_{\text{coh}}^{s,q \neq b-a} \right) \quad (3.30)$$

$$U_{\text{pop}}^{s,q=b-a} = u_{b-a}^s (\rho_a - \rho_b) \langle b | \mathcal{U}_{b-a} | a \rangle \quad (3.31)$$

$$U_{\text{coh}}^{s,q \neq b-a} = u_q^s \{ \rho_{b-q,a} \langle b | \mathcal{U}_q | b-q \rangle - \rho_{b,a+q} \langle a+q | \mathcal{U}_q | a \rangle \} \quad (3.32)$$

Relaxation

Up to now, we've only considered transitions due to our interaction term \mathcal{W} . In reality, there are other processes that cause transitions that drive the system toward thermodynamic equilibrium. We'll account for these "relaxation" processes by adding a relaxation term "by-hand:"

$$\dot{\rho}_{ba} = -i\omega_{ba}\rho_{ba} - \gamma_{ba}\rho_{ba} + i\Omega \sum_s \exp(+is\omega t) \left(U_{\text{pop}}^{s,q=b-a} + \sum_q U_{\text{coh}}^{s,q \neq b-a} \right) \quad (3.33)$$

where γ_{ba} is the relaxation rate and, by construction, $\gamma_{ba} = \gamma_{ab}$.

Solving this set of differential equations would be much easier if they weren't coupled (contained different coherences). To a very good approximation, we can decouple these equations by making the following arguments. First, we'll make an educated guess for the form of the coherences $\rho_{ba}(t)$. When there is no interaction, the entire time dependence of the coherences is given by $\exp(-i\omega_{ba}t)$. Since we're now driving the system with a frequency of ω , it is not unreasonable to think that the time dependence of the coherences is now $\exp(\mp i\omega t)$, where the negative (positive) sign is chosen when ω_{ba} is positive (negative). Plugging in $C_{ba}(t) \exp(\mp i\omega t)$ for the coherences $b \neq a$ on both sides of the equation give:

$$\begin{aligned} (\mp i\omega C_{ba} + \dot{C}_{ba}) \exp(\mp i\omega t) &= -i(\omega_{ba} - i\gamma_{ba}) C_{ba} \exp(\mp i\omega t) \\ &+ i\Omega \sum_s \exp(+is\omega t) \left(U_{\text{pop}}^{s,q=b-a} + \exp(\mp i\omega t) \sum_q \bar{U}_{\text{coh}}^{s,q \neq b-a} \right) \end{aligned} \quad (3.34)$$

where the terms in the sum over q proportional to coherences is given by:

$$\bar{U}_{\text{coh}}^{s,q \neq b-a} = u_q^s \{C_{b-q,a} \langle b | \mathcal{U}_q | b-q \rangle - C_{b,a+q} \langle a+q | \mathcal{U}_q | a \rangle\} \quad (3.35)$$

Multiplying both sides by $\exp(\pm i\omega t)$, dividing by i , and moving a few things around gives:

$$-i\dot{C}_{ba} = (\pm\omega - \omega_{ba} + i\gamma_{ba})C_{ba} + \Omega \sum_s \exp(+i(s \pm 1)\omega t) \left(U_{\text{pop}}^{s,q=b-a} + \exp(\mp i\omega t) \sum_q \bar{U}_{\text{coh}}^{s,q \neq b-a} \right) \quad (3.36)$$

Rotating Wave Approximation

We're now in a position to take the second step, which is called the rotating wave approximation [15]: we simply drop any of the remaining oscillatory terms, namely ones with a factor of $\exp(\pm ni\omega t)$ with $n \neq 0$:

$$-i\dot{C}_{ba} = (\pm\omega - \omega_{ba} + i\gamma_{ba})C_{ba} + \Omega U_{\text{pop}}^{s=\mp, q=b-a} \quad (3.37)$$

This is a completely uncoupled set of equations! The only term left that could possibly have any time dependence is C_{ba} . The last step in solving these equations is to choose C_{ba} to be a constant:

$$-i\dot{C}_{ba} = 0 = (\pm\omega - \omega_{ba} + i\gamma_{ba})C_{ba} + \Omega U_{\text{pop}}^{s=\mp, q=b-a} \quad (3.38)$$

$$= (\pm\omega - \omega_{ba} + i\gamma_{ba})C_{ba} + \Omega u_{b-a}^{\mp} (\rho_a - \rho_b) \langle b | \mathcal{U}_{b-a} | a \rangle \quad (3.39)$$

This is just an algebraic equation which is solved very simply by:

$$C_{ba} = \frac{u_{b-a}^{\mp} \Omega (\rho_b - \rho_a) \langle b | \mathcal{U}_{b-a} | a \rangle}{\pm\omega - \omega_{ba} + i\gamma_{ba}} \quad (3.40)$$

which immediately gives:

$$\rho_{ba} = \frac{u_{b-a}^{\mp} \Omega (\rho_b - \rho_a) \langle b | \mathcal{U}_{b-a} | a \rangle}{\pm\omega - \omega_{ba} + i\gamma_{ba}} \exp(\mp i\omega t) \quad (3.41)$$

3.2.3 Changes in Population

Since we have a solution for the coherences ($b \neq a$), we now consider the coupled differential equations for the populations ($b = a$):

$$\dot{\rho}_a = -i\omega_{aa}\rho_a + i\Omega \sum_s \exp(+is\omega t) \left(U_{\text{pop}}^{s,q=a-a} + \sum_q U_{\text{coh}}^{s,q \neq a-a} \right) \quad (3.42)$$

$$U_{\text{pop}}^{s,q=a-a} = u_{a-a}^s (\rho_a - \rho_a) \langle a | \mathcal{U}_{a-a} | a \rangle = 0 \quad (3.43)$$

$$U_{\text{coh}}^{s,q \neq a-a} = u_q^s \{ \rho_{a-q,a} \langle a | \mathcal{U}_q | a-q \rangle - \rho_{a,a+q} \langle a+q | \mathcal{U}_q | a \rangle \} \quad (3.44)$$

Up to now, we've been a little sloppy with the notation $q = b - a$, etc. What we have meant is that the operator associated with q is the "difference" between eigenstates b and a . In practice, q , b , and a can be made into numbers if b and a happen to be observables and not just labels for the eigenstates. This can be done if we label eigenstates as J, m where J & m represent eigenvalues associated with that eigenstate. Before going on, we should rewrite the coherences in this new notation:

$$\rho_{K_{a+q}J_a} = \frac{u_q^{\mp} \Omega (\rho_{K_{a+q}} - \rho_{J_a}) \langle K, a+q | \mathcal{U}_q | J, a \rangle}{\pm\omega - \omega_{K_{a+q}J_a} + i\gamma_{K_{a+q}J_a}} \exp(\mp i\omega t) \quad (3.45)$$

where we've made the substitution $b = a + q$. The complex conjugate of this coherence is:

$$\rho_{K_{a+q}J_a}^* = \rho_{J_a K_{a+q}} = \frac{(u_q^{\mp})^* \Omega (\rho_{K_{a+q}} - \rho_{J_a}) \langle J, a | \mathcal{U}_{-q} | K, a+q \rangle}{\pm\omega - \omega_{K_{a+q}J_a} - i\gamma_{J_a K_{a+q}}} \exp(\pm i\omega t) \quad (3.46)$$

Dropping terms that contain $\omega_{aa} = 0$ & $(\rho_a - \rho_a)$, the differential equations for the populations is rewritten as:

$$\dot{\rho}_{Ja} = i\Omega \sum_{K,s,q} u_q^s \exp(+is\omega t) \{ \rho_{Ka-q,Ja} \langle J, a | \mathcal{U}_q | K, a - q \rangle - \rho_{Ja, Ka+q} \langle K, a + q | \mathcal{U}_q | J, a \rangle \} \quad (3.47)$$

These equations are coupled only to coherences, which we already have expressions for. Before plugging in the coherences, we'll derive an alternate form of the first sum by reversing the sum by $s, q \rightarrow -s, -q$ using the Hermiticity of \mathcal{W} & ρ in the form of $u_{-q}^{-s} = (u_q^s)^*$, $\rho_{Ka+q,Ja} = \rho_{Ja, Ka+q}^*$, & $\mathcal{U}_{-q} = \mathcal{U}_q^\dagger$:

$$\begin{aligned} \sum_{s,q} u_q^s \exp(+is\omega t) \rho_{Ka-q,Ja} \langle J, a | \mathcal{U}_q | K, a - q \rangle &= \sum_{s,q} u_{-q}^{-s} \exp(-is\omega t) \rho_{Ka+q,Ja} \langle J, a | \mathcal{U}_{-q} | K, a + q \rangle \\ &= \sum_{s,q} [u_q^s \exp(+is\omega t) \rho_{Ja, Ka+q} \langle K, a + q | \mathcal{U}_q | J, a \rangle]^* \end{aligned} \quad (3.48)$$

This shows that the first sum is just the complex conjugate of the second sum. Using the identity $z^* - z = -2i\Im\{z\}$, we can now write $\dot{\rho}_{Ja}$ as just the imaginary part of the second sum:

$$\dot{\rho}_{Ja} = 2\Omega \sum_{K,s,q} \Im \{ u_q^s \exp(+is\omega t) \rho_{Ja, Ka+q} \langle K, a + q | \mathcal{U}_q | J, a \rangle \} \quad (3.49)$$

Plugging in the form of the coherence $\rho_{Ja, Ka+q} = \rho_{Ka+q,Ja}^*$, gives:

$$\dot{\rho}_{Ja} = 2\Omega^2 \sum_{K,s,q} \Im \left\{ u_q^s (u_q^\mp)^* \exp(+i(s \pm 1)\omega t) \frac{(\rho_{Ka+q} - \rho_{Ja}) \langle K, a + q | \mathcal{U}_q | J, a \rangle^*}{\pm\omega - \omega_{Ka+qJa} - i\gamma_{Ka+qJa}} \langle K, a + q | \mathcal{U}_q | J, a \rangle \right\} \quad (3.50)$$

Applying the rotating wave approximation once again, namely keeping only the $s = \mp 1$ terms, gives:

$$\dot{\rho}_{Ja} = 2\Omega^2 \sum_{K,q} |u_q^\mp|^2 (\rho_{Ka+q} - \rho_{Ja}) |\langle K, a + q | \mathcal{U}_q | J, a \rangle|^2 \Im \left\{ (\pm\omega - \omega_{Ka+qJa} - i\gamma_{Ka+qJa})^{-1} \right\} \quad (3.51)$$

After collecting all common factors, we find that the denominator is the only complex quantity. We can find the imaginary part of it by multiplying the top & bottom by the complex conjugate of the bottom. This finally gives:

$$\dot{\rho}_{Ja} = 2\Omega^2 \sum_{K,q} \frac{\gamma_{Ka+qJa} (\rho_{Ka+q} - \rho_{Ja}) |u_q^\mp|^2 |\langle K, a + q | \mathcal{U}_q | J, a \rangle|^2}{(\pm\omega - \omega_{Ka+qJa})^2 + \gamma_{Ka+qJa}^2} \quad (3.52)$$

3.2.4 Expectation Value of the Dipole Moment Operator

It is often useful to calculate the expectation value of the very operators causing the transitions. For the case of a general harmonic interaction, this means calculating the expectation value of \mathcal{U}_q :

$$\langle \mathcal{U}_q \rangle = \sum_{K,n,J,m} \langle K, n | \rho | J, m \rangle \langle J, m | \mathcal{U}_q | K, n \rangle = \sum_{K,n,J} \langle K, n | \rho | J, n + q \rangle \langle J, n + q | \mathcal{U}_q | K, n \rangle \quad (3.53)$$

There are two different cases which result in either a sum over populations or a sum over coherences. For the case ($K = J$ & $q = 0$), we get a sum over populations:

$$\langle \mathcal{U}_0 \rangle = \sum_{n,J} \rho_{Jn} \langle J, n | \mathcal{U}_0 | J, n \rangle \quad (3.54)$$

For all cases other than ($K = J$ & $q = 0$), we get a sum over coherences due to $\sum_q \mathcal{U}_q$, which we've already calculated, and plugging them in gives:

$$\langle \mathcal{U}_q \rangle = \sum_{K,n,J} \left\{ \frac{\Omega (\rho_{Jn+q} - \rho_{Kn}) (u_q^\mp)^* |\langle J, n + q | \mathcal{U}_q | K, n \rangle|^2}{\pm\omega - \omega_{Jn+qKn} - i\gamma_{Jn+qKn}} \times \exp(\pm i\omega t) \right\} \quad (3.55)$$

3.2.5 Electric Dipole Interaction for the $2S+1L_J$ Orbital States

The interaction between the atom and the electric field component of the light is:

$$\mathcal{W} = -\vec{d} \cdot \Re \vec{E}(\vec{r}, t) \quad (3.56)$$

The electric dipole operator \vec{d} is given by the sum $\sum_k q_k \vec{r}_k$, where q_k & \vec{r}_k are the charge & relative position of the k -th particle in the atom. If we take the nucleus to be infinitely heavy and measure the position of the electrons relative to it, then the dipole operator is reduced to the sum over all electrons. Since we're only going to be considering transitions of the single valence electron of an alkali atom, the sum further reduces to a single term which results in $\vec{d} = -e\vec{r}$. The position vector of the valence electron, \vec{r} , can be expanded in the irreducible spherical vector basis $\sum_{q=-1}^{+1} r_q \hat{\varepsilon}_q^*$. We can now identify the parameters from the general dipole interaction, Eqn. (3.26), as:

$$\mathcal{U}_q = r_q \quad \hbar\Omega = -eE_0 \quad u_q^- = \hat{\varepsilon}_q^* \cdot \hat{E}_0 \quad u_q^+ = \hat{\varepsilon}_q^* \cdot \hat{E}_0^* \quad (3.57)$$

The relevant atomic states are the $S_{1/2}$ ground state and the mixed $P_{1/2}$ & $P_{3/2}$ excited states, see Sec. (1.2.4). Therefore the electric dipole transition matrix elements are $\langle P_{\pm}, m+q | r_q | S, m \rangle$ and their complex conjugates for all m & q .

3.2.6 Magnetic Dipole Interaction for the $|F, m\rangle$ Hyperfine States

The interaction between the atom and the magnetic field component of the light is:

$$\mathcal{W} = -\vec{\mu} \cdot \Re \vec{B}(\vec{r}, t) \quad (3.58)$$

In this case, the light is in the form of radio-frequency (RF) waves. The magnetic moment operator is the sum of nuclear magnetic moment $\vec{\mu}_I$ and the total electronic magnetic moment $\vec{\mu}_J$. Since $|\vec{\mu}_I| \ll |\vec{\mu}_J|$, we'll ignore the coupling to the nuclear spin. In the $S_{1/2}$ ground state of an alkali atom, $J = S = 1/2 (L = 0)$ and therefore the magnetic moment can be written in terms of the spin-1/2 angular momentum operators:

$$\vec{\mu} = g_S \mu_B \vec{S} = -g_S \mu_B (S_x \hat{x} + S_y \hat{y} + S_z \hat{z}) = g_S \mu_B (S_+ \hat{\varepsilon}_+^* + S_- \hat{\varepsilon}_-^* + S_z \hat{\varepsilon}_0^*) \quad (3.59)$$

where $S_{\pm} = S_x \pm iS_y$ and the unit vectors $\hat{\varepsilon}_q$ are *not* the same unit vectors used for the electric dipole operator from the previous section:

$$\hat{\varepsilon}_{\pm}^* = \frac{\hat{x} \mp i\hat{y}}{2} \quad \hat{\varepsilon}_0 = \hat{z} \quad (3.60)$$

We can now identify the parameters from the general dipole interaction, Eqn. (3.26), as:

$$\mathcal{U}_q = S_q \quad \hbar\Omega = g_S \mu_B B_{\text{rf}} \quad u_q^- = \hat{\varepsilon}_q^* \cdot \hat{B}_{\text{rf}} \quad u_q^+ = \hat{\varepsilon}_q^* \cdot \hat{B}_{\text{rf}}^* \quad (3.61)$$

The relevant atomic states are the mixed hyperfine states in the $F = I \pm 1/2$ manifolds, see Sec. (1.3.4). We will only consider RF frequencies small enough to induce transitions *within* a manifold and *not between* manifolds. Therefore the magnetic dipole transition matrix elements are $\langle F, m+q | S_q | F, m \rangle$ and their complex conjugates for all m & q .

3.3 Electric Dipole Matrix Elements: Oscillator Strength

3.3.1 Wigner-Eckart Theorem

The probability that an electric dipole transition occurs from an initial state a to a final state b is proportional to the modulus squared matrix element of the component of the dipole operator that is parallel to the polarization vector of the light:

$$\left| \langle b | \vec{\varepsilon} \cdot \vec{d} | a \rangle \right|^2 = \left| \langle b | \vec{\varepsilon} \cdot (-e\hat{r}) | a \rangle \right|^2 = e^2 \left| \langle b | \vec{\varepsilon} \cdot \hat{r} | a \rangle \right|^2 \quad (3.62)$$

When the dipole operator, or analogously the radius vector operator, is written as a tensor of rank one (see appendix B), the matrix element can be evaluated using the Wigner-Eckart theorem. The theorem was originally derived from group theory considerations and factorizes the matrix element of a tensor operator T_q^k between states labeled with quantum numbers n_i, n_f and angular momentum (J_i, m_i) and (J_f, m_f) into two parts:

$$\langle J_f, m_f | \hat{T}_q^k | J_i, m_i \rangle = \text{CG} \left(\vec{J}_i + \vec{k} = \vec{J}_f ; m_i, q, m_f \right) \times \text{R.M.E.} (n_f, J_f; n_i, J_i) \quad (3.63)$$

The first part is simply a Clebsch-Gordon coefficient for the addition of angular momenta such that $\vec{J}_i + \vec{k} = \vec{J}_f$ with m_i, m_f, q . The second part, called the reduced matrix element, is a term *with the essential property that it is independent of m_i, q, m_f* . The exact form of the reduced matrix element is somewhat arbitrary so long as it is independent of m_i, q, m_f and behaves mathematically appropriately. By this, we mean that the matrix element is a complex number or equivalently the modulus square matrix element is non-negative. One form of the reduced matrix element that is often *chosen* in textbooks (for example equation XIII.125 of *Messiah* [16]) is:

$$\text{R.M.E.} = \frac{1}{\sqrt{[J_f]}} \times \langle n_f, J_f \| T^k \| n_i, J_i \rangle \quad (3.64)$$

For the present discussion, we will drop the n_i and n_f labels because the D1 and D2 transitions of alkali metals occur within the same n . To insure positive definiteness of the modulus square matrix element, we'll explicitly give ourselves flexibility with the phase:

$$\text{R.M.E.} = \frac{(\pm)_{fi}}{\sqrt{[J_f]}} \times i \times \langle J_f \| T^k \| J_i \rangle \quad (3.65)$$

The phase ambiguity of the reduced matrix element is related to the choice made in defining the phase convention of the Clebsch-Gordon coefficients. Using the notation of *Messiah*, the Wigner-Eckart Theorem [17, 18] can be expressed as:

$$\langle J_f, m_f | \hat{T}_q^k | J_i, m_i \rangle = i \frac{(\pm)_{fi}}{\sqrt{[J_f]}} \langle (J_i, k) m_i, q | J_f, m_f \rangle \langle J_f \| T^k \| J_i \rangle \quad (3.66)$$

3.3.2 Phase Convention and Positive Definiteness

Care must be taken in *choosing* the phase convention when evaluating these matrix elements using the Wigner-Eckart theorem. Let's consider the modulus square matrix element of a component q of the radius vector operator \vec{r} in the spherical tensor basis ($k = 1$):

$$|\langle J_f, m_f | r_q | J_i, m_i \rangle|^2 = \langle J_f, m_f | r_q | J_i, m_i \rangle^* \langle J_f, m_f | r_q | J_i, m_i \rangle \quad (3.67)$$

$$= \langle J_i, m_i | r_q^* | J_f, m_f \rangle \langle J_f, m_f | r_q | J_i, m_i \rangle \quad (3.68)$$

$$= (-1)^q \langle J_i, m_i | r_{-q} | J_f, m_f \rangle \langle J_f, m_f | r_q | J_i, m_i \rangle \quad (3.69)$$

Before expanding these matrix elements using the WET, we'll introduce the Wigner $3j$ symbol [18] which is related to the Clebsch-Gordon coefficients by:

$$\begin{pmatrix} J_i & k & J_f \\ m_i & q & -m_f \end{pmatrix} = \frac{(-1)^{J_i - k + m_f}}{\sqrt{[J_f]}} \langle (J_i, k) m_i, q | J_f, m_f \rangle \delta_{m_i + q = m_f} \quad (3.70)$$

where the Kronecker Delta insures that angular momentum is conserved ($m_i + q = m_f$). Their utility lies in the fact that they make the symmetry properties of Clebsch-Gordon coefficients more apparent under the cyclic permutation of all three columns, the interchange of two columns, and the replacement of the second row with its negative:

$$\begin{pmatrix} J_i & k & J_f \\ m_i & q & -m_f \end{pmatrix} = \begin{pmatrix} J_f & J_i & k \\ -m_f & m_i & q \end{pmatrix} = \begin{pmatrix} k & J_f & J_i \\ q & -m_f & m_i \end{pmatrix} \quad (3.71)$$

$$= (-1)^{J_i + k + J_f} \begin{pmatrix} k & J_i & J_f \\ q & m_i & -m_f \end{pmatrix} \quad (3.72)$$

$$= (-1)^{J_i + k + J_f} \begin{pmatrix} J_i & k & J_f \\ -m_i & -q & m_f \end{pmatrix} \quad (3.73)$$

Expanding the modulus squared matrix element using Wigner $3j$ symbol, enforcing $m_f = m_i + q$, and moving things around:

$$|\langle r_q \rangle|^2 = (-1)^q \langle J_i, m_i | r_{-q} | J_f, m_i + q \rangle \langle J_f, m_i + q | r_q | J_i, m_i \rangle \quad (3.74)$$

$$\begin{aligned} &= (-1)^q i(\pm)_{if} (-1)^{J_f - 1 + m_i} \begin{pmatrix} J_f & 1 & J_i \\ m_i + q & -q & -m_i \end{pmatrix} \langle J_i \| r \| J_f \rangle \\ &\quad \times (i)(\pm)_{fi} (-1)^{J_i - 1 + m_i + q} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} \langle J_f \| r \| J_i \rangle \end{aligned} \quad (3.75)$$

$$= (\pm)_{fi} (\pm)_{if} (-1)^{J_f + J_i + 2m_i + 1} \begin{pmatrix} J_f & 1 & J_i \\ m_i + q & -q & -m_i \end{pmatrix} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} |\langle J_f \| r \| J_i \rangle|^2 \quad (3.76)$$

$$= (\pm)_{fi} (\pm)_{if} (-1)^{2J_f + 2J_i + 2m_i + 2} \begin{pmatrix} J_i & 1 & J_f \\ -m_i & -q & m_i + q \end{pmatrix} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} |\langle J_f \| r \| J_i \rangle|^2 \quad (3.77)$$

$$= (\pm)_{fi} (\pm)_{if} (-1)^{3J_f + 3J_i + 2m_i + 1} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} |\langle J_f \| r \| J_i \rangle|^2 \quad (3.78)$$

$$= (\pm)_{fi} (\pm)_{if} (-1)^{3J_f + 3J_i + 2m_i + 1} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix}^2 |\langle J_f \| r \| J_i \rangle|^2 \quad (3.79)$$

The last two terms are positive. For the left hand side of the equation to be positive (as it should be), the following must be true for D1 transitions ($J_i, |m_i|, J_f = \frac{1}{2}$):

$$+1 = [(\pm)_{fi} (\pm)_{if}]_{\frac{1}{2}} (-1)^{\frac{3}{2} + \frac{3}{2} \pm 1 + 1} \quad (3.80)$$

$$= [(\pm)_{fi} (\pm)_{if}]_{\frac{1}{2}} (-1)^{4 \pm 1} \quad (3.81)$$

$$= -[(\pm)_{fi} (\pm)_{if}]_{\frac{1}{2}} \quad (3.82)$$

$$s_1 = [(\pm)_{fi}]_{\frac{1}{2}} = -[(\pm)_{if}]_{\frac{1}{2}} \quad (3.83)$$

For D2 transitions, the corresponding relations are ($J_i, |m_i| = \frac{1}{2}; J_f = \frac{3}{2}$):

$$+1 = [(\pm)_{fi} (\pm)_{if}]_{\frac{3}{2}} (-1)^{\frac{9}{2} + \frac{3}{2} \pm 1 + 1} \quad (3.84)$$

$$= [(\pm)_{fi} (\pm)_{if}]_{\frac{3}{2}} (-1)^{7 \pm 1} \quad (3.85)$$

$$= [(\pm)_{fi} (\pm)_{if}]_{\frac{3}{2}} \quad (3.86)$$

$$s_2 = [(\pm)_{fi}]_{\frac{3}{2}} = [(\pm)_{if}]_{\frac{3}{2}} \quad (3.87)$$

In both cases, we have hidden the sign in an s factor. The positive definiteness of the modulus square matrix element defines for the phase convention of the reduced matrix element. For a D1 transition, the reduced matrix elements for a matrix element and its complex conjugate must have opposite signs. However, the reduced matrix elements for a D2 matrix element and its complex conjugate must have the same sign.

3.3.3 Connecting the Radial Integral to Physical Observables

The double barred term $\langle b \| T^k \| a \rangle$ of the reduced matrix element (also sometimes called the reduced matrix element itself) is a radial integral. In practice, rather than being calculated from first principles, the value of the radial integral for the radius vector between atomic states is inferred from measurements of the natural atomic lifetimes. The spontaneous decays of the $P_{\frac{1}{2}}$ and $P_{\frac{3}{2}}$ excited states for neutral alkali atoms are dominated by the D1 and D2 transitions. Therefore the lifetime τ of these states are nearly equal to the inverse of the spontaneous decay probability rate (as known as the Einstein A coefficient), see equation 4.23

of *Corney* [19]:

$$\tau_b^{-1} = A_b = \frac{e^2 \omega_{ab}^3}{3\pi \epsilon_0 \hbar c^3} \frac{\sum_{m_b}}{[J_b]} \sum_{m_a} \left| \langle J_a, m_a | \hat{r} | J_b, m_b \rangle \right|^2 \quad (3.88)$$

$$= \frac{4\alpha \omega_{ab}^3}{3c^2} \underbrace{\frac{\sum_{m_b}}{[J_b]}}_{\text{mean}} \underbrace{\sum_{m_a}}_{\text{sum}} \left| \langle J_a, m_a | \hat{r} | J_b, m_b \rangle \right|^2 \quad (3.89)$$

where A_b is averaged over all the initial (upper m_b) states and summed over all the final (lower m_a) states. Typical lifetimes for alkali metals are tens of nanoseconds, see table blah. Another form of the averaged, summed modulus square matrix element is the oscillator strength. In the classical picture, an atom is modeled as a collection of many damped oscillators with frequencies that correspond to all possible atomic transitions. An atom in a state a can make transitions to other states through a subset of oscillators that connect that state with all other states. The fraction of oscillators that connect state a to another state b is called the oscillator strength. For absorption (emission), the oscillator strength is chosen to be positive (negative) by convention. Just as for the probability rate, the modulus square matrix element is averaged over initial (lower m_a) states and summed over final (upper m_b) states. For transitions from initial state a to final state b , where the sign is chosen based on the physical process under consideration, the oscillator strength is:

$$f_{a \rightarrow b} = \pm \frac{2m\omega_{ab}}{3\hbar} \frac{\sum_{m_a}}{2J_a + 1} \sum_{m_b} \left| \langle J_a, m_b | \hat{r} | J_a, m_b \rangle \right|^2 \quad (3.90)$$

By convention, we will always refer to the absorption oscillator strength unless otherwise noted. In addition, since we will always be discussing transitions from the $S_{\frac{1}{2}}$ ground states to one of either the $P_{\frac{1}{2}}$ or $P_{\frac{3}{2}}$ excited states, the oscillator strength will simply be labeled by the J of the final excited state.

Both the oscillator strength and the spontaneous decay rate involve sums over the initial and final m states. This sum, which depends only on J_a , J_b , and the reduced matrix element, is called the line strength (first introduced on page 98 of *Condon & Shortley* [20]) and for transitions between the lower state a and the higher state b , it is given by:

$$S_{ab} = S_{ba} = \sum_{m_a} \sum_{m_b} \left| \langle J_a, m_a | e \hat{r} | J_b, m_b \rangle \right|^2 \quad (3.91)$$

$$= \sum_{m_a} \sum_{m_b} \left| \langle J_b, m_b | e \hat{r} | J_a, m_a \rangle \right|^2 \quad (3.92)$$

$$= \frac{3\hbar e^2}{2m\omega_{ab}} \cdot [J_a] f_b \quad (3.93)$$

$$= \frac{3c^2 [J_b] e^2}{4\alpha \omega_{ab}^3} \cdot \frac{1}{\tau_b} \quad (3.94)$$

$$= \frac{3\pi \epsilon_0 \hbar c^3 [J_b]}{\omega_{ab}^3} \cdot A_b \quad (3.95)$$

Note that the line strength is explicitly defined as a positive quantity. This insures that the absorption oscillator strength f_b , spontaneous lifetime τ_b , and the spontaneous probability rate are all positive. Evaluating the line strength using WET:

$$S_{ab} = \sum_{m_a} \sum_{m_b} \left| \langle J_b, m_b | e \hat{r} | J_a, m_a \rangle \right|^2 \quad (3.96)$$

$$= \sum_{m_a} \sum_{m_b} \left| \langle J_b, m_b | e \sum_q (-1)^q \hat{r}_q \hat{\epsilon}_{-q} | J_a, m_a \rangle \right|^2 \quad (3.97)$$

$$= \sum_{m_a} \sum_{m_b} \langle J_a, m_a | e \sum_{q'} (-1)^{q'} \hat{r}_{q'} \hat{\epsilon}_{-q'} | J_b, m_b \rangle \cdot \langle J_b, m_b | e \sum_q (-1)^q \hat{r}_q \hat{\epsilon}_{-q} | J_a, m_a \rangle \quad (3.98)$$

$$= \sum_{m_a} \sum_{m_b} \sum_q (-1)^q \langle J_a, m_a | e^{\hat{r}_{-q}} | J_b, m_b \rangle \langle J_b, m_b | e^{\hat{r}_q} | J_a, m_a \rangle \quad (3.99)$$

$$= \pm s_{a,b}^2 i^2 \sum_{m_a, m_b, q} (-1)^q \frac{\langle (J_b, 1) m_b, -q | J_a, m_a \rangle}{\sqrt{[J_a]}} \langle J_a || e^{\hat{r}} || J_b \rangle \frac{\langle (J_a, 1) m_a, q | J_b, m_b \rangle}{\sqrt{[J_b]}} \langle J_b || e^{\hat{r}} || J_a \rangle \quad (3.100)$$

$$= |\langle J_b || e^{\hat{r}} || J_a \rangle|^2 \cdot \varsigma_b \quad (3.101)$$

$$\varsigma_b = \mp \sum_{m_a, q} \frac{(-1)^q}{\sqrt{[J_a][J_b]}} \langle (J_b, 1) m_a + q, -q | J_a, m_a \rangle \langle (J_a, 1) m_a, q | J_b, m_a + q \rangle \quad (3.102)$$

where the lower (upper) sign is taken for D1 (D2) transitions to insure positive definiteness. Again since we will always be discussing transitions from the $S_{\frac{1}{2}}$ ground states to one of either the $P_{\frac{1}{2}}$ or $P_{\frac{3}{2}}$ excited states, the Clebsch-Gordon sum ς will simply be labeled by the J of the final excited state. This gives us the following equivalent relationships between the modulus squared reduced matrix element (which is difficult to calculate accurately from theory) with physical observables (which we determine empirically) for transitions from the lower level a to the higher level b :

$$|\langle J_b || r || J_a \rangle|^2 = \frac{S_{ab}}{\varsigma_{ab} e^2} \quad (3.103)$$

$$= \frac{3\hbar}{2m\omega_{ab}} \cdot \frac{[J_a] f_b}{\varsigma_b} \quad (3.104)$$

$$= \frac{3c^2}{4\alpha\omega_{ab}^3} \cdot \frac{[J_b]}{\varsigma_b \tau_b} \quad (3.105)$$

$$= \frac{3\pi\epsilon_0 \hbar c^3}{e^2 \omega_{ab}^3} \cdot \frac{[J_b] A_b}{\varsigma_b} \quad (3.106)$$

3.3.4 Evaluation of the Clebsch-Gordon Coefficients and Sums

The general forms of the D1 matrix elements are:

$$\left\langle P_{\frac{1}{2}}, q \pm \frac{1}{2} \left| r_q \right| S_{\frac{1}{2}}, \pm \frac{1}{2} \right\rangle = \left\langle \left(\frac{1}{2}, 1 \right) \pm \frac{1}{2}, q \left| \frac{1}{2}, q \pm \frac{1}{2} \right. \right\rangle \left(i \frac{s_1}{\sqrt{2}} \right) \langle P_{\frac{1}{2}} || r || S_{\frac{1}{2}} \rangle \quad (3.107)$$

$$= -i \frac{s_1}{\sqrt{2}} \left\langle \left(1, \frac{1}{2} \right) q, \pm \frac{1}{2} \left| \frac{1}{2}, q \pm \frac{1}{2} \right. \right\rangle \langle P_{\frac{1}{2}} || r || S_{\frac{1}{2}} \rangle \quad (3.108)$$

$$= \pm i s_1 \sqrt{\frac{1 \mp q}{6}} \langle P_{\frac{1}{2}} || r || S_{\frac{1}{2}} \rangle \quad (3.109)$$

$$\left\langle S_{\frac{1}{2}}, q \pm \frac{1}{2} \left| r_q \right| P_{\frac{1}{2}}, \pm \frac{1}{2} \right\rangle = \left\langle \left(\frac{1}{2}, 1 \right) \pm \frac{1}{2}, q \left| \frac{1}{2}, q \pm \frac{1}{2} \right. \right\rangle \left(-i \frac{s_1}{\sqrt{2}} \right) \langle S_{\frac{1}{2}} || r || P_{\frac{1}{2}} \rangle \quad (3.110)$$

$$= i \frac{s_1}{\sqrt{2}} \left\langle \left(1, \frac{1}{2} \right) q, \pm \frac{1}{2} \left| \frac{1}{2}, q \pm \frac{1}{2} \right. \right\rangle \langle S_{\frac{1}{2}} || r || P_{\frac{1}{2}} \rangle \quad (3.111)$$

$$= \mp i s_1 \sqrt{\frac{1 \mp q}{6}} \langle S_{\frac{1}{2}} || r || P_{\frac{1}{2}} \rangle \quad (3.112)$$

$$(3.113)$$

The general forms of the D2 matrix elements are:

$$\left\langle P_{\frac{3}{2}}, q \pm \frac{1}{2} \left| r_q \right| S_{\frac{1}{2}}, \pm \frac{1}{2} \right\rangle = \left\langle \left(\frac{1}{2}, 1 \right) \pm \frac{1}{2}, q \left| \frac{3}{2}, q \pm \frac{1}{2} \right. \right\rangle \left(i \frac{s_2}{2} \right) \langle P_{\frac{3}{2}} || r || S_{\frac{1}{2}} \rangle \quad (3.114)$$

$$= i \frac{s_2}{2} \left\langle \left(1, \frac{1}{2} \right) q, \pm \frac{1}{2} \left| \frac{3}{2}, q \pm \frac{1}{2} \right. \right\rangle \langle P_{\frac{3}{2}} || r || S_{\frac{1}{2}} \rangle \quad (3.115)$$

$$= i s_2 \sqrt{\frac{2 \pm q}{12}} \langle P_{\frac{3}{2}} || r || S_{\frac{1}{2}} \rangle \quad (3.116)$$

$$\langle S_{\frac{1}{2}}, m \pm 1 | r_{\pm} | P_{\frac{3}{2}}, m \rangle = \left\langle \left(\frac{3}{2}, 1 \right) m, \pm 1 \middle| \frac{1}{2}, m \pm 1 \right\rangle \left(i \frac{s_2}{\sqrt{2}} \right) \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (3.117)$$

$$= i s_2 \sqrt{\frac{(\frac{1}{2} \mp m)(\frac{3}{2} \mp m)}{24}} \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (3.118)$$

$$\langle S_{\frac{1}{2}}, \pm \frac{1}{2} | r_0 | P_{\frac{3}{2}}, \pm \frac{1}{2} \rangle = \left\langle \left(\frac{3}{2}, 1 \right) \pm \frac{1}{2}, 0 \middle| \frac{1}{2}, \pm \frac{1}{2} \right\rangle \left(i \frac{s_2}{\sqrt{2}} \right) \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (3.119)$$

$$= -i s_2 \sqrt{\frac{1}{6}} \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (3.120)$$

The D1 matrix elements are:

$$\langle S_{\frac{1}{2}}, +\frac{1}{2} | r_+ | P_{\frac{1}{2}}, -\frac{1}{2} \rangle = \langle P_{\frac{1}{2}}, -\frac{1}{2} | r_- | S_{\frac{1}{2}}, +\frac{1}{2} \rangle = +i s_1 \sqrt{\frac{1}{3}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.121)$$

$$-\langle S_{\frac{1}{2}}, +\frac{1}{2} | r_0 | P_{\frac{1}{2}}, +\frac{1}{2} \rangle = \langle P_{\frac{1}{2}}, +\frac{1}{2} | r_0 | S_{\frac{1}{2}}, +\frac{1}{2} \rangle = +i s_1 \sqrt{\frac{1}{6}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.122)$$

$$-\langle S_{\frac{1}{2}}, -\frac{1}{2} | r_0 | P_{\frac{1}{2}}, -\frac{1}{2} \rangle = \langle P_{\frac{1}{2}}, -\frac{1}{2} | r_0 | S_{\frac{1}{2}}, -\frac{1}{2} \rangle = -i s_1 \sqrt{\frac{1}{6}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.123)$$

$$\langle S_{\frac{1}{2}}, -\frac{1}{2} | r_- | P_{\frac{1}{2}}, +\frac{1}{2} \rangle = \langle P_{\frac{1}{2}}, +\frac{1}{2} | r_+ | S_{\frac{1}{2}}, -\frac{1}{2} \rangle = -i s_1 \sqrt{\frac{1}{3}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.124)$$

$$\langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle = \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.125)$$

The D2 matrix elements are:

$$\langle S_{\frac{1}{2}}, +\frac{1}{2} | r_+ | P_{\frac{3}{2}}, -\frac{1}{2} \rangle = \langle P_{\frac{3}{2}}, -\frac{1}{2} | r_- | S_{\frac{1}{2}}, +\frac{1}{2} \rangle = +i s_2 \sqrt{\frac{1}{12}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.126)$$

$$\langle S_{\frac{1}{2}}, -\frac{1}{2} | r_+ | P_{\frac{3}{2}}, -\frac{3}{2} \rangle = \langle P_{\frac{3}{2}}, -\frac{3}{2} | r_- | S_{\frac{1}{2}}, -\frac{1}{2} \rangle = +i s_2 \frac{1}{2} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.127)$$

$$-\langle S_{\frac{1}{2}}, +\frac{1}{2} | r_0 | P_{\frac{3}{2}}, +\frac{1}{2} \rangle = \langle P_{\frac{3}{2}}, +\frac{1}{2} | r_0 | S_{\frac{1}{2}}, +\frac{1}{2} \rangle = +i s_2 \sqrt{\frac{1}{6}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.128)$$

$$-\langle S_{\frac{1}{2}}, -\frac{1}{2} | r_0 | P_{\frac{3}{2}}, -\frac{1}{2} \rangle = \langle P_{\frac{3}{2}}, -\frac{1}{2} | r_0 | S_{\frac{1}{2}}, -\frac{1}{2} \rangle = +i s_2 \sqrt{\frac{1}{6}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.129)$$

$$\langle S_{\frac{1}{2}}, -\frac{1}{2} | r_- | P_{\frac{3}{2}}, +\frac{1}{2} \rangle = \langle P_{\frac{3}{2}}, +\frac{1}{2} | r_+ | S_{\frac{1}{2}}, -\frac{1}{2} \rangle = +i s_2 \sqrt{\frac{1}{12}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.130)$$

$$\langle S_{\frac{1}{2}}, +\frac{1}{2} | r_- | P_{\frac{3}{2}}, +\frac{3}{2} \rangle = \langle P_{\frac{3}{2}}, +\frac{3}{2} | r_+ | S_{\frac{1}{2}}, +\frac{1}{2} \rangle = +i s_2 \frac{1}{2} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.131)$$

$$\langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle = \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.132)$$

Note that the radial integral is real. Putting these results together allows us to evaluate the Clebsch-Gordon sums:

$$\varsigma_{\frac{1}{2}} = s_1^2 \left[-\frac{i}{\sqrt{3}} \frac{i}{\sqrt{3}} + \frac{-i}{\sqrt{6}} \frac{i}{\sqrt{6}} + \frac{i}{\sqrt{6}} \frac{-i}{\sqrt{6}} - \frac{-i}{\sqrt{3}} \frac{-i}{\sqrt{3}} \right] = +1 \quad (3.133)$$

$$\varsigma_{\frac{3}{2}} = s_2^2 \left[-\frac{i}{\sqrt{12}} \frac{i}{\sqrt{12}} - \frac{i}{2} \frac{i}{2} + \frac{-i}{\sqrt{6}} \frac{i}{\sqrt{6}} + \frac{-i}{\sqrt{6}} \frac{i}{\sqrt{6}} - \frac{i}{\sqrt{12}} \frac{i}{\sqrt{12}} - \frac{i}{2} \frac{i}{2} \right] = +1 \quad (3.134)$$

Therefore the radial integrals for the D1 and D2 transitions are:

$$|\langle P_J \| r \| S_{\frac{1}{2}} \rangle|^2 = \frac{3\hbar}{m\omega_J} f_J \quad (3.135)$$

3.3.5 The Radial Integral in the coupled LS basis

In the uncoupled basis, there is only one radial integral between the S and P states. First we must fix the phase convention of the uncoupled matrix elements:

$$|\langle r_q \rangle|^2 = (-1)^q \left\langle \pm \frac{1}{2} \left| \right|_S \langle 0 |_L r_{-q} | q \rangle_L \left| \pm \frac{1}{2} \right\rangle_S \left\langle \pm \frac{1}{2} \left| \right|_S \langle q |_L r_q | 0 \rangle_L \left| \pm \frac{1}{2} \right\rangle_S \right. \quad (3.136)$$

$$= (-1)^q \langle 0 |_L r_{-q} | q \rangle_L \langle q |_L r_q | 0 \rangle_L \quad (3.137)$$

$$= (\pm)_{PS} (\pm)_{SP} (-1)^{3+1} \begin{pmatrix} 0 & 1 & 1 \\ 0 & q & -q \end{pmatrix}^2 |\langle P \| r \| S \rangle|^2 \quad (3.138)$$

$$+1 = (\pm)_{PS} (\pm)_{SP} (-1)^4 \quad (3.139)$$

$$= (\pm)_{PS} (\pm)_{SP} \quad (3.140)$$

$$s = (\pm)_{PS} = (\pm)_{SP} \quad (3.141)$$

When the radial integral is evaluated in the coupled LS basis J , there is radial integral for each J . The relationship between the radial integrals evaluated in the two different basis sets can be shown by an expansion in the uncoupled basis and by application of the WET:

$$\left\langle P_{\frac{3}{2}}, +\frac{3}{2} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \langle +1 |_L \left\langle +\frac{1}{2} \left| \right|_S r_+ | 0 \rangle_L \left| +\frac{1}{2} \right\rangle_S \right. \quad (3.142)$$

$$= \langle +1 | r_+ | 0 \rangle_L \left\langle +\frac{1}{2} \left| \right| +\frac{1}{2} \right\rangle_S \quad (3.143)$$

$$= \langle (0, 1) 0, +1 | 1, +1 \rangle \left(\frac{is}{\sqrt{3}} \right) \langle P \| r \| S \rangle \quad (3.144)$$

$$= \frac{is}{\sqrt{3}} \langle P \| r \| S \rangle \quad (3.145)$$

$$= +is_2 \frac{1}{2} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.146)$$

$$\left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = \left(\sqrt{\frac{2}{3}} \langle +1 |_L \left\langle -\frac{1}{2} \left| \right|_S - \sqrt{\frac{1}{3}} \langle 0 |_L \left\langle +\frac{1}{2} \left| \right|_S r_+ | 0 \rangle_L \left| -\frac{1}{2} \right\rangle_S \right. \right. \quad (3.147)$$

$$= \sqrt{\frac{2}{3}} \langle +1 | r_+ | 0 \rangle_L \left\langle -\frac{1}{2} \left| \right| -\frac{1}{2} \right\rangle_S - \sqrt{\frac{1}{3}} \langle 0 | r_+ | 0 \rangle_L \left\langle +\frac{1}{2} \left| \right| -\frac{1}{2} \right\rangle_S \quad (3.148)$$

$$= \sqrt{\frac{2}{3}} \langle +1 | r_+ | 0 \rangle_L \quad (3.149)$$

$$= \sqrt{\frac{2}{3}} \langle (0, 1) 0, +1 | 1, +1 \rangle \left(\frac{is}{\sqrt{3}} \right) \langle P \| r \| S \rangle \quad (3.150)$$

$$= \frac{is\sqrt{2}}{3} \langle P \| r \| S \rangle \quad (3.151)$$

$$= -is_1 \sqrt{\frac{1}{3}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (3.152)$$

We can do the same calculation for the complex conjugates of the same matrix elements:

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_- \right| P_{\frac{3}{2}}, +\frac{3}{2} \right\rangle = \langle 0 |_L \left\langle +\frac{1}{2} \left| \right|_S r_- | +1 \rangle_L \left| +\frac{1}{2} \right\rangle_S \right. \quad (3.153)$$

$$= \frac{is}{\sqrt{3}} \langle S \| r \| P \rangle \quad (3.154)$$

$$= +is_2 \frac{1}{2} \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (3.155)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \langle 0 |_L \left\langle -\frac{1}{2} \left| \right|_S r_- \left(\sqrt{\frac{2}{3}} | +1 \rangle_L \left| -\frac{1}{2} \right\rangle_S - \sqrt{\frac{1}{3}} | 0 \rangle_L \left| +\frac{1}{2} \right\rangle_S \right) \right. \quad (3.156)$$

$$= \frac{is\sqrt{2}}{3} \langle S \| r \| P \rangle \quad (3.157)$$

$$= -is_1 \sqrt{\frac{1}{3}} \langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle \quad (3.158)$$

Note that the reduced matrix element in the uncoupled LS basis does not have any sign ambiguity due to positive definiteness, because for the transitions under consideration, the Clebsch-Gordon coefficient is always $+1$. Note also that the radial integral in the uncoupled basis is real. Since the radial integral is independent of m_L and m_J , we only had to evaluate one matrix element for each J . Summarizing these results:

$$s_2 \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle = +s \frac{2}{\sqrt{3}} \langle P \| r \| S \rangle \quad (3.159)$$

$$s_2 \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle = +s \frac{2}{\sqrt{3}} \langle S \| r \| P \rangle \quad (3.160)$$

$$s_1 \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle = -s \sqrt{\frac{2}{3}} \langle P \| r \| S \rangle \quad (3.161)$$

$$s_1 \langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle = -s \sqrt{\frac{2}{3}} \langle S \| r \| P \rangle \quad (3.162)$$

where $s_1^2 = s_2^2 = s^2 = +1$. This implies the following relationships between the quantities relating to D1 and D2 transitions:

$$s_1 s_2 = -1 \quad (3.163)$$

$$\frac{\langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle}{\langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle} = -\sqrt{2} \frac{s_1}{s_2} = +\sqrt{2} \quad (3.164)$$

$$\langle P_J \| r \| S_{\frac{1}{2}} \rangle = \langle S_{\frac{1}{2}} \| r \| P_J \rangle = +\sqrt{\frac{3\hbar}{m\omega_J}} f_J \quad (3.165)$$

$$\frac{S_{\frac{3}{2}}}{S_{\frac{1}{2}}} = 2 \quad (3.166)$$

$$\frac{f_{\frac{3}{2}}}{f_{\frac{1}{2}}} = 2 \left(\frac{\omega_{\frac{3}{2}}}{\omega_{\frac{1}{2}}} \right) \quad (3.167)$$

$$\frac{\tau_{\frac{3}{2}}}{\tau_{\frac{1}{2}}} = \left(\frac{\omega_{\frac{1}{2}}}{\omega_{\frac{3}{2}}} \right)^3 \quad (3.168)$$

$$\frac{A_{\frac{3}{2}}}{A_{\frac{1}{2}}} = \left(\frac{\omega_{\frac{3}{2}}}{\omega_{\frac{1}{2}}} \right)^3 \quad (3.169)$$

3.3.6 Explicit Forms of the Matrix Elements

First we'll calculate the modulus square matrix elements neglecting fine structure mixing. This is easily done given the following matrix elements in terms of the oscillator strength. The D1 matrix elements are:

$$\left\langle S_{\frac{1}{2}, +\frac{1}{2}} \left| r_+ \right| P_{\frac{1}{2}, -\frac{1}{2}} \right\rangle = \left\langle P_{\frac{1}{2}, -\frac{1}{2}} \left| r_- \right| S_{\frac{1}{2}, +\frac{1}{2}} \right\rangle = +is_1 \sqrt{\frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}}} \quad (3.170)$$

$$-\left\langle S_{\frac{1}{2}, +\frac{1}{2}} \left| r_0 \right| P_{\frac{1}{2}, +\frac{1}{2}} \right\rangle = \left\langle P_{\frac{1}{2}, +\frac{1}{2}} \left| r_0 \right| S_{\frac{1}{2}, +\frac{1}{2}} \right\rangle = +is_1 \sqrt{\frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}}} \quad (3.171)$$

$$-\left\langle S_{\frac{1}{2}, -\frac{1}{2}} \left| r_0 \right| P_{\frac{1}{2}, -\frac{1}{2}} \right\rangle = \left\langle P_{\frac{1}{2}, -\frac{1}{2}} \left| r_0 \right| S_{\frac{1}{2}, -\frac{1}{2}} \right\rangle = -is_1 \sqrt{\frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}}} \quad (3.172)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = -is_1 \sqrt{\frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}}} \quad (3.173)$$

The D2 matrix elements are:

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}}} \quad (3.174)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_+ \right| P_{\frac{3}{2}}, -\frac{3}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{3}{2} \left| r_- \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}}} \quad (3.175)$$

$$-\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_0 \right| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}}} \quad (3.176)$$

$$-\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_0 \right| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}}} \quad (3.177)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}}} \quad (3.178)$$

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_- \right| P_{\frac{3}{2}}, +\frac{3}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{3}{2} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}}} \quad (3.179)$$

The modulus squared matrix elements for transitions involving the absorption of photon with helicity +1 are calculated below:

$$\left| \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}} \quad (3.180)$$

$$\left| \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (3.181)$$

$$\left| \left\langle P_{\frac{3}{2}}, +\frac{3}{2} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (3.182)$$

The modulus squared matrix elements for transitions involving the absorption of photon with helicity 0 are calculated below:

$$\left| \left\langle P_{\frac{1}{2}}, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}} \quad (3.183)$$

$$\left| \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}} \quad (3.184)$$

$$\left| \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}} \quad (3.185)$$

$$\left| \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}} \quad (3.186)$$

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

$$\left| \left\langle P_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}} \quad (3.187)$$

$$\left| \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (3.188)$$

$$\left| \left\langle P_{\frac{3}{2}}, -\frac{3}{2} \left| r_- \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (3.189)$$

Because some of the excited eigenstates are mixed, now we'll evaluate the modulus squared matrix element in a general form.

$$|\langle r_q \rangle|^2 = \left| \left(c_1^* \langle P_{\frac{3}{2}}, m+q \mid + c_2^* \langle P_{\frac{1}{2}}, m+q \mid \right) r_q \mid S_{\frac{1}{2}}, m \rangle \right|^2 \quad (3.190)$$

$$= \left| c_1^* \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle + c_2^* \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \right|^2 \quad (3.191)$$

$$\begin{aligned} &= |c_1|^2 \left| \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \right|^2 + |c_2|^2 \left| \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \right|^2 \\ &\quad + c_1^* \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \cdot c_2 \langle S_{\frac{1}{2}}, m \mid r_q^* \mid P_{\frac{1}{2}}, m+q \rangle \\ &\quad + c_1 \langle S_{\frac{1}{2}}, m \mid r_q^* \mid P_{\frac{3}{2}}, m+q \rangle \cdot c_2^* \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \end{aligned} \quad (3.192)$$

The c_1 and c_2 are the fine mixing coefficients which are real:

$$\begin{aligned} |\langle r_q \rangle|^2 &= c_1^2 \left| \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \right|^2 + c_2^2 \left| \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \right|^2 \\ &\quad + (-1)^q c_1 c_2 \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \langle S_{\frac{1}{2}}, m \mid r_{-q} \mid P_{\frac{1}{2}}, m+q \rangle \\ &\quad + (-1)^q c_1 c_2 \langle S_{\frac{1}{2}}, m \mid r_{-q} \mid P_{\frac{3}{2}}, m+q \rangle \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \end{aligned} \quad (3.193)$$

Noting the following relationship:

$$\langle P_J, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle = (-1)(-1)^q \langle S_{\frac{1}{2}}, m \mid r_{-q} \mid P_J, m+q \rangle \quad (3.194)$$

the cross terms can be written:

$$\begin{aligned} \text{cross terms} &= (-1)^q c_1 c_2 \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \langle S_{\frac{1}{2}}, m \mid r_{-q} \mid P_{\frac{1}{2}}, m+q \rangle \\ &\quad + (-1)^q c_1 c_2 \langle S_{\frac{1}{2}}, m \mid r_{-q} \mid P_{\frac{3}{2}}, m+q \rangle \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \end{aligned} \quad (3.195)$$

$$\begin{aligned} &= (-1)^q c_1 c_2 \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle (-1)(-1)^q \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \\ &\quad + (-1)^q c_1 c_2 (-1)(-1)^q \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \end{aligned} \quad (3.196)$$

$$= (-1)^{1+q+q} 2c_1 c_2 \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \quad (3.197)$$

$$= -2c_1 c_2 \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \quad (3.198)$$

Therefore the general form of the modulus square matrix element accounting for fine structure mixing is:

$$\begin{aligned} |\langle r_q \rangle|^2 &= c_1^2 \left| \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \right|^2 + c_2^2 \left| \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \right|^2 \\ &\quad - 2c_1 c_2 \langle P_{\frac{3}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \langle P_{\frac{1}{2}}, m+q \mid r_q \mid S_{\frac{1}{2}}, m \rangle \end{aligned} \quad (3.199)$$

For the following, we've used equations (1.89) and (3.167). For the transitions involving light with -1 helicity:

$$\left| \left\langle P_+, -\frac{3}{2} \mid r_- \mid S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (3.200)$$

$$\left| \left\langle P_-, -\frac{1}{2} \mid r_- \mid S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}} \right) \left[1 + a_1 a_2^+ \sqrt{2} - \frac{(a_2^+)^2}{2} \right] \quad (3.201)$$

$$\left| \left\langle P_+, -\frac{1}{2} \mid r_- \mid S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \right) \left[1 - a_1 a_2^+ 2\sqrt{2} + (a_2^+)^2 \right] \quad (3.202)$$

For the transitions involving light with 0 helicity:

$$\left| \left\langle P_-, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \quad (3.203)$$

$$\left| \left\langle P_+, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \quad (3.204)$$

$$\left| \left\langle P_-, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}} \right) \left[1 + a_1 a_2^+ 2\sqrt{2} + (a_2^+)^2 \right] \quad (3.205)$$

$$\left| \left\langle P_+, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}} \right) \left[1 - a_1 a_2^+ \sqrt{2} - \frac{(a_2^+)^2}{2} \right] \quad (3.206)$$

For the transitions involving light with +1 helicity:

$$\left| \left\langle P_-, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \quad (3.207)$$

$$\left| \left\langle P_+, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \quad (3.208)$$

$$\left| \left\langle P_+, +\frac{3}{2} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (3.209)$$

3.4 Magnetic Dipole Matrix Elements

The main field B defines the z -axis. In order to probe $\Delta m_F \pm 1$ transitions, a small set of coils creates an RF field in a direction *transverse* to the main B -field. In our lab, the RF field produced at the center of our cell by a 1.3 cm radius, 20 turn coil with a resistance of 3.9 Ω & an inductance of 0.5 μH driven at 16 VPP at a frequency of about 7 MHz is on order of hundreds of microgauss to a few milligauss. Therefore, we can treat the RF field \vec{B}_{rf} as a time dependent perturbation to our original Hamiltonian:

$$\mathcal{H}_{EPR} = \mathcal{H} + \mathcal{W} \quad (3.210)$$

$$\mathcal{W} = -\vec{\mu}_I \cdot \vec{B}_{rf} - \vec{\mu}_J \cdot \vec{B}_{rf} \quad (3.211)$$

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:

$$W_{fi} = \frac{\hbar}{2} \langle m_F - 1 | \omega_I \hat{I}_- + \omega_J \hat{J}_- | m_F \rangle \quad (3.212)$$

$$= \frac{\hbar}{2} \langle m_F - 1 | \omega_I \hat{F}_- + (\omega_J - \omega_I) \hat{J}_- | m_F \rangle \quad (3.213)$$

$$= \frac{\hbar}{2} \langle f | \omega_I \hat{F}_- + (\omega_J - \omega_I) \hat{J}_- | i \rangle \quad (3.214)$$

$$\omega_I = -\frac{g_I \mu_N B_{RF}}{\hbar} \quad (3.215)$$

$$\omega_J = -\frac{g_S \mu_B B_{RF}}{\hbar} \quad (3.216)$$

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

$$\langle \hat{F}_- \rangle = \langle m_F^\pm - 1 | \hat{F}_- | m_F^\pm \rangle \quad (3.217)$$

$$\begin{aligned}
&= \left[a_1(m_F - 1) \left\langle I \pm \frac{1}{2}, m_F - 1 \right| \pm a_2(m_F - 1) \left\langle I \mp \frac{1}{2}, m_F - 1 \right| \right] \\
&\quad \hat{F}_- \left[a_1(m_F) \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2(m_F) \left| I \mp \frac{1}{2}, m_F \right\rangle \right] \tag{3.218}
\end{aligned}$$

$$\begin{aligned}
&= \left[a_1(m_F - 1) \left\langle I \pm \frac{1}{2}, m_F - 1 \right| \pm a_2(m_F - 1) \left\langle I \mp \frac{1}{2}, m_F - 1 \right| \right] \\
&\quad \left[f_{\pm} a_1(m_F) \left| I \pm \frac{1}{2}, m_F - 1 \right\rangle \pm f_{\mp} a_2(m_F) \left| I \mp \frac{1}{2}, m_F - 1 \right\rangle \right] \tag{3.219}
\end{aligned}$$

$$= f_{\pm} a_1(m_F) a_1(m_F - 1) + f_{\mp} a_2(m_F) a_2(m_F - 1) \tag{3.220}$$

$$= f_{\pm} a_1 f a_{1i} + f_{\mp} a_2 f a_{2i} \tag{3.221}$$

$$f_{\pm} = \sqrt{\left(I + \frac{1}{2}\right) \left(I + \frac{1}{2} \pm 1\right) - m_F(m_F - 1)} \tag{3.222}$$

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

$$\begin{aligned}
\langle \hat{J}_- \rangle^{\pm} &= \langle m_F^{\pm} - 1 | \hat{J}_- | m_F^{\pm} \rangle \tag{3.223} \\
&= (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - 1 \mp \frac{1}{2}, \pm \frac{1}{2} \right| \pm (a_{1f} b_{2f} + a_{2f} b_{1f}) \\
&\quad \times \left\langle m_F - 1 \pm \frac{1}{2}, \mp \frac{1}{2} \right| \hat{J}_- \left[(a_{1i} b_{1i} - a_{2i} b_{2i}) \right. \\
&\quad \left. \times \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm (a_{1i} b_{2i} + a_{2i} b_{1i}) \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right] \tag{3.224}
\end{aligned}$$

$$\begin{aligned}
\langle \hat{J}_- \rangle^{+} &= (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - \frac{3}{2}, +\frac{1}{2} \right| + (a_{1f} b_{2f} + a_{2f} b_{1f}) \\
&\quad \times \left\langle m_F - \frac{1}{2}, -\frac{1}{2} \right| \left[\sqrt{\frac{1}{2} \frac{3}{2} + \frac{1}{2} \frac{1}{2}} \left[(a_{1i} b_{1i} - a_{2i} b_{2i}) \left| m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \right. \right. \tag{3.225}
\end{aligned}$$

$$= [a_{1f} b_{2f} + a_{2f} b_{1f}] \times [a_{1i} b_{1i} - a_{2i} b_{2i}] \tag{3.226}$$

$$\begin{aligned}
\langle \hat{J}_- \rangle^{-} &= (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - \frac{1}{2}, -\frac{1}{2} \right| - (a_{1f} b_{2f} + a_{2f} b_{1f}) \\
&\quad \times \left\langle m_F - \frac{3}{2}, +\frac{1}{2} \right| \left[\sqrt{\frac{1}{2} \frac{3}{2} + \frac{1}{2} \frac{1}{2}} \left[- (a_{1i} b_{2i} + a_{2i} b_{1i}) \left| m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \right. \right. \tag{3.227}
\end{aligned}$$

$$= [a_{2f} b_{2f} - a_{1f} b_{1f}] \times [a_{1i} b_{2i} + a_{2i} b_{1i}] \tag{3.228}$$

Note the following relations:

$$b_{2f} b_{1i} = \frac{\sqrt{\left(I + \frac{1}{2}\right) \left(I + \frac{3}{2}\right) - m_F(m_F - 1)}}{2I + 1} = \frac{f_+}{2I + 1} \tag{3.229}$$

$$b_{1f} b_{2i} = \frac{\sqrt{\left(I + \frac{1}{2}\right) \left(I - \frac{1}{2}\right) - m_F(m_F - 1)}}{2I + 1} = \frac{f_-}{2I + 1} \tag{3.230}$$

$$b_{1f} b_{1i} = \frac{\sqrt{\left(I + \frac{1}{2}\right) \left(I - \frac{1}{2}\right) + m_F(m_F - 1) + 2m_F \left(I + \frac{1}{2}\right)}}{2I + 1} = \frac{g_-}{2I + 1} \tag{3.231}$$

$$b_{2f} b_{2i} = \frac{\sqrt{\left(I + \frac{1}{2}\right) \left(I + \frac{3}{2}\right) + m_F(m_F - 1) - 2m_F \left(I + \frac{1}{2}\right)}}{2I + 1} = \frac{g_+}{2I + 1} \tag{3.232}$$

$$g_{\pm} = \sqrt{\left(I + \frac{1}{2}\right) \left(I + \frac{1}{2} \pm 1\right) + m_F(m_F - 1) \mp 2m_F \left(I + \frac{1}{2}\right)} \tag{3.233}$$

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

$$\langle \hat{J}_- \rangle^+ = [a_{1f}b_{2f} + a_{2f}b_{1f}] \times [a_{1i}b_{1i} - a_{2i}b_{2i}] \quad (3.234)$$

$$= a_{1f}a_{1i} \frac{f_+}{2I+1} + a_{2f}a_{1i} \frac{g_-}{2I+1} - a_{1f}a_{2i} \frac{g_+}{2I+1} - a_{2f}a_{2i} \frac{f_-}{2I+1} \quad (3.235)$$

$$\langle \hat{J}_- \rangle^- = [a_{2f}b_{2f} - a_{1f}b_{1f}] \times [a_{1i}b_{2i} + a_{2i}b_{1i}] \quad (3.236)$$

$$= a_{2f}a_{1i} \frac{g_+}{2I+1} - a_{1f}a_{1i} \frac{f_-}{2I+1} + a_{2f}a_{2i} \frac{f_+}{2I+1} - a_{1f}a_{2i} \frac{g_-}{2I+1} \quad (3.237)$$

$$\langle \hat{J}_- \rangle^\pm = \pm a_{1f}a_{1i} \frac{f_\pm}{2I+1} + a_{2f}a_{1i} \frac{g_\mp}{2I+1} - a_{1f}a_{2i} \frac{g_\pm}{2I+1} \mp a_{2f}a_{2i} \frac{f_\mp}{2I+1} \quad (3.238)$$

Putting this altogether,

$$\begin{aligned} W_{fi} &= \frac{\hbar}{2} \omega_I (f_\pm a_{1f} a_{1i} + f_\mp a_{2f} a_{2i}) + \frac{\hbar}{2} (\omega_J - \omega_I) \\ &\times \left(\pm a_{1f} a_{1i} \frac{f_\pm}{2I+1} + a_{2f} a_{1i} \frac{g_\mp}{2I+1} - a_{1f} a_{2i} \frac{g_\pm}{2I+1} \mp a_{2f} a_{2i} \frac{f_\mp}{2I+1} \right) \end{aligned} \quad (3.239)$$

$$\begin{aligned} &= \frac{\hbar}{2} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I+1} \right) f_\pm a_{1f} a_{1i} + \frac{\hbar}{2} \left(\frac{2I\omega_I + (1 \pm 1)\omega_I \mp \omega_J}{2I+1} \right) \\ &\times f_\mp a_{2f} a_{2i} + \frac{\hbar}{2} \left(\frac{\omega_J - \omega_I}{2I+1} \right) (g_\mp a_{2f} a_{1i} - g_\pm a_{1f} a_{2i}) \end{aligned} \quad (3.240)$$

Using the small field approximations from before:

$$a_1 = 1 - \frac{\beta^2}{2} x^2 \quad (3.241)$$

$$a_2 = -\beta x + 2\alpha\beta x^2 \quad (3.242)$$

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

$$\begin{aligned} |W_{fi}|^2 &\simeq \frac{\hbar^2}{4} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I+1} \right)^2 f_\pm^2 - \frac{\hbar^2}{4} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I+1} \right) \\ &\times \left(\frac{\omega_J - \omega_I}{2I+1} \right) f_\pm (g_\mp \beta_f - g_\pm \beta_i) x + \mathcal{O}(x^2) \end{aligned} \quad (3.243)$$

3.5 Population Differences

3.5.1 Two State Systems: Polarization

Polarization

For a system with only two states, for example the two Zeeman levels $m_J = \pm 1$ of the $S_{1/2}$ ground state, we can label the populations as ρ_\pm . Their sum and difference are given by:

$$\rho_+ + \rho_- = \text{Tr}(\rho) = 1 \quad \rho_+ - \rho_- = P \quad (3.244)$$

where P is called the polarization. Using these two equations, it is straightforward to find the populations of the two states:

$$\rho_\pm = \frac{1 \pm P}{2} \quad (3.245)$$

The polarization P and the expectation value of S_z are related by:

$$\langle S_z \rangle = \text{Tr}(\rho S_z) = \text{Tr} \left\{ \begin{bmatrix} \rho_+ & 0 \\ 0 & \rho_- \end{bmatrix} \begin{bmatrix} +\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} \right\} = \text{Tr} \left\{ \begin{bmatrix} +\frac{\rho_+}{2} & 0 \\ 0 & -\frac{\rho_-}{2} \end{bmatrix} \right\} = \frac{\rho_+ - \rho_-}{2} = \frac{P}{2} \quad (3.246)$$

Thermal Equilibrium

At thermal equilibrium, for a canonical ensemble (fixed number of particles in equilibrium with a heat reservoir at a common temperature T), the population of each state is given by:

$$\rho_n = \frac{\exp\left(-\frac{E_n}{kT}\right)}{Z} \quad Z = \sum_n \exp\left(-\frac{E_n}{kT}\right) \quad (3.247)$$

where Z is the partition function. Specifying to our two level case, the energies for $S_{1/2}$ states are:

$$E_{\pm} = E\left(\left|S_{\frac{1}{2}}, \pm\frac{1}{2}\right\rangle\right) = E_0^S \pm \left[\frac{g_S}{-2}\right] \mu_B B \quad (3.248)$$

This gives for the relative population of each state at thermodynamic equilibrium:

$$Z = \exp\left(-\frac{E_+}{kT}\right) + \exp\left(-\frac{E_-}{kT}\right) \quad (3.249)$$

$$= \exp\left(-\frac{E_0^S + \left[\frac{g_S}{-2}\right] \mu_B B}{kT}\right) + \exp\left(-\frac{E_0^S - \left[\frac{g_S}{-2}\right] \mu_B B}{kT}\right) \quad (3.250)$$

$$= \exp\left(-\frac{E_0^S}{kT}\right) \left[\exp\left(-\left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right) + \exp\left(+\left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right) \right] \quad (3.251)$$

$$\rho_{\pm} = \frac{\exp\left(-\frac{E_0^S}{kT}\right) \exp\left(\mp \left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right)}{\exp\left(-\frac{E_0^S}{kT}\right) \left[\exp\left(+\left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right) + \exp\left(-\left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right) \right]} \quad (3.252)$$

$$= \frac{\exp\left(\mp \left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right)}{\exp\left(+\left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right) + \exp\left(-\left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right)} \quad (3.253)$$

$$= \frac{\exp(m_J \beta)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \quad (3.254)$$

We have introduced the β parameter which we'll call the "spin temperature," even though it is a unitless quantity, is inversely proportional to temperature at thermal equilibrium, and is, in this case, negative. It's usefulness far outweighs those peccadilloes and will be more apparent when we discuss the role of nuclear spin in spin-exchange collisions in section (3.5.2). For the $S_{\frac{1}{2}}$ ground states at thermal equilibrium, the spin temperature is:

$$\beta = \frac{g_S \mu_B B}{kT} = \left[\frac{g_S}{-2}\right] \left(\frac{-2\mu_B B}{kT}\right) \quad (3.255)$$

We can express the polarization as a function of the spin temperature:

$$P = \frac{\exp\left(+\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} - \frac{\exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \quad (3.256)$$

$$= \frac{\exp\left(+\frac{\beta}{2}\right) - \exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \quad (3.257)$$

$$P = \tanh\left(\frac{\beta}{2}\right) \quad (3.258)$$

We'll see later on that this result is true regardless of the mechanism that producing the polarization. Inverting to get the spin temperature as a function of polarization:

$$P = \frac{\exp\left(+\frac{\beta}{2}\right) - \exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} = \frac{x - \frac{1}{x}}{x + \frac{1}{x}} = \frac{x^2 - 1}{x^2 + 1} \quad (3.259)$$

$$Px^2 + P = x^2 - 1 \quad (3.260)$$

$$(P-1)x^2 = -P-1 \quad (3.261)$$

$$x^2 = \left[\exp\left(+\frac{\beta}{2}\right) \right]^2 = \frac{1+P}{1-P} \quad (3.262)$$

$$\beta = \log\left(\frac{1+P}{1-P}\right) \quad (3.263)$$

3.5.2 Multiple State Systems: Spin Temperature

It has been shown [21] that under the optical pumping, spin exchange, high pressure conditions that exist within a cell, the populations are given by:

$$\rho_{m_F} = \frac{e^{\beta m_F}}{Z_F} = \frac{e^{\beta m_J}}{Z_J} \frac{e^{\beta m_I}}{Z_I} \quad (3.264)$$

where $m_F = m_J + m_I$ and the partition function, in general, is given by [22]:

$$Z_J = \sum_{m=-J}^{+J} e^{\beta m} = \frac{\sinh(\beta[J]/2)}{\sinh(\beta/2)} = \frac{(1+P)^{[J]} - (1-P)^{[J]}}{2P(1-P^2)^J} \quad (3.265)$$

where P is the polarization and $[J] = 2J + 1$.

The motivation of using β , spin temperature, is best described by the original 1959 reference by Anderson, Pipkin, & Baird [23]:

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

$$\rho = \frac{\exp[-(I_{1z} + S_{1z})\beta] \exp[-(I_{2z} + S_{2z})\beta]}{\text{Tr}\{\exp[-(I_{1z} + S_{1z})\beta] \exp[-(I_{2z} + S_{2z})\beta]\}},$$

where β is such that the total z component of the angular momentum of the system is given by $\text{Tr}[(I_{1s} + S_{1z} + I_{2z} + S_{2z})\rho]$. 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.

To calculate the population difference between states m and $m-1$, we first must calculate the population of states with m . In our case, $J = S = 1/2$ & $[J] = 2$, and consequently $Z_{1/2}$ is

$$Z_{1/2} = \frac{(1+P)^2 - (1-P)^2}{2P\sqrt{1-P^2}} = \frac{2}{\sqrt{(1-P)(1+P)}} = \frac{2}{1+P} \sqrt{\frac{1+P}{1-P}} = \frac{2\exp(\beta/2)}{1+P} \quad (3.266)$$

Plugging this in for the population of the m state gives [24]:

$$\rho_m = \frac{\exp(\beta m)}{Z_I Z_S} = \frac{\exp(\beta(m-1/2))}{Z_I} \frac{1+P}{2} = Q_{I\bar{m}} \frac{1+P}{2} \quad Q_{I\bar{m}} = \frac{\exp(\beta\bar{m})}{Z_I} \quad (3.267)$$

where P is the polarization, I is the nuclear spin, and $\bar{m} = (m + m - 1)/2 = m - 1/2$ is the mean m of the transition. For the adjacent state $m - 1$, the population is:

$$\rho_{m-1} = \frac{\exp(\beta(m - 1 - 1/2))}{Z_I} \frac{1 + P}{2} = Q_{I\bar{m}} \frac{1 + P}{2} \exp(-\beta) = Q_{I\bar{m}} \frac{1 + P}{2} \left(\frac{1 - P}{1 + P} \right) = Q_{I\bar{m}} \frac{1 - P}{2} \quad (3.268)$$

Putting this altogether gives the population difference between the states m and $m - 1$ as:

$$\rho_m - \rho_{m-1} = Q_{I\bar{m}} \left(\frac{1 + P}{2} - \frac{1 - P}{2} \right) = Q_{I\bar{m}} P \quad (3.269)$$

Chapter 4

The Effect on Polarized Light Due to Spin-Polarized Alkali Atoms

4.1 General Formula for Atomic Polarizability

As we've seen before, we can write the electric field component of an electromagnetic wave in the complex representation as:

$$\vec{E} = E_0 \hat{E}_0 \exp(i\vec{k} \cdot \vec{r} - i\omega t) \quad (4.1)$$

The speed of wave is given the ratio $\omega/|\vec{k}|$. The effect of a uniform, isotropic, and linear medium on a beam of light is given by the (possibly complex) index of refraction of the medium, n :

$$|\vec{k}| = \frac{\omega}{c} n = \frac{2\pi n}{\lambda_{\text{vac}}} \quad (4.2)$$

where \vec{k} is the wave vector of the light and λ_{vac} is the wavelength of the light in vacuum. However, in general, different components of the light polarization vector have different values of \vec{k} depending on the symmetry properties of an anisotropic medium. The symmetry of a vapor of alkali metal in a magnetic field is described by the spherical vector basis; therefore there are in general three different wave vectors of the light in an alkali vapor:

$$|\vec{k}_q| = \frac{\omega}{c} n_q \quad (4.3)$$

where $q = 0, \pm 1$ labels the components relative to the atomic coordinate system. If \vec{k} is imaginary, then its useful to split it into its real and imaginary parts:

$$\vec{E} = E_0 \hat{E}_0 \exp(-\Im\{\vec{k} \cdot \vec{r}\}) \exp(i\Re\{\vec{k} \cdot \vec{r}\} - i\omega t) \quad (4.4)$$

The real part of the index of refraction yields the dispersion relation which affects the phase of the wave. A difference in the real part for $q = \pm 1$ gives rise to circular birefringence; whereas, a difference in the real part between the $q = 0$ and $q = \pm$ gives rise to linear birefringence. The imaginary part of the index of refraction yields the attenuation constant which affects the amplitude of the wave. A difference in the imaginary part for $q = \pm 1$ gives rise to circular dichroism; whereas, a difference in the imaginary part between $q = 0$ and $q = \pm 1$ gives rise to linear dichroism. The details of the atomic system, beyond its symmetry, are hidden in the index of refraction:

$$n_q = \sqrt{\frac{\epsilon_q \mu_q}{\epsilon_0 \mu_0}} \quad (4.5)$$

where ϵ_q & μ_q are the dielectric constant & permeability of the medium and ϵ_0 & μ_0 are the dielectric constant & permeability of free space.

Applying Maxwell's equations, *in the complex representation*:

$$\vec{D} = \vec{\epsilon} \vec{E} = \epsilon_0 \vec{E} + \vec{P} = \epsilon_0 \vec{E} + [\mathcal{A}] \langle \vec{d} \rangle \quad (4.6)$$

where \vec{P} is the electric polarization of the medium and $[\mathcal{A}]$ is the atomic number density of the medium. The dipole moment, \vec{d} , is evaluated as the expectation value of the quantum mechanical dipole operator averaged over every atom or molecule in the medium. The expectation value for the electric dipole operator is given by:

$$\Re \langle \vec{d} \rangle = -e \langle \vec{r} \rangle = -e \sum_q \langle r_q \rangle \varepsilon_q^* \quad (4.7)$$

Plugging in the result from Eqn. (3.55), where $\mathcal{U}_q = r_q$:

$$\Re \langle \vec{d} \rangle = -e \sum_{K,n,J,q} \left\{ \frac{\Omega (\rho_{Jn+q} - \rho_{Kn}) (u_q^\mp)^* |\langle J, n+q | r_q | K, n \rangle|^2}{\pm\omega - \omega_{Jn+qKn} - i\gamma_{Jn+qKn}} \times \exp(\pm i\omega t) \right\} \varepsilon_q^* \quad (4.8)$$

Using Eqn. (3.57) to identify the rest of the parameters:

$$\Re \langle \vec{d} \rangle = \frac{e^2}{\hbar} \sum_{K,n,J,q} \hat{\varepsilon}_q^* \left\{ \frac{(\rho_{Jn+q} - \rho_{Kn}) |\langle J, n+q | r_q | K, n \rangle|^2}{\pm\omega - \omega_{Jn+qKn} - i\gamma_{Jn+qKn}} \right\} \varepsilon_q \cdot E_0 \hat{E}_0^\pm \exp(\pm i\omega t) = \frac{e^2}{\hbar} (\Sigma_1 + \Sigma_2) \quad (4.9)$$

where $(u_q^\mp)^* = \hat{\varepsilon}_q \hat{E}_0^\pm$ and $\hat{E}_0 = \hat{E}_0^-$ & $\hat{E}_0^* = \hat{E}_0^+$. When $|K, n\rangle$ are the $|S, \pm 1/2\rangle$ ground states, then the sum becomes:

$$\Sigma_1 = \sum_{n,s,q} \hat{\varepsilon}_q^* \left\{ \frac{(\rho_{Psn+q} - \rho_{Sn}) |\langle P_s, n+q | r_q | S, n \rangle|^2}{+\omega - \omega_{Psn+qSn} + i\gamma_{Psn+qSn}} \right\} \varepsilon_q \cdot E_0 \hat{E}_0^* \exp(+i\omega t) \quad (4.10)$$

where $s = \pm$ labels the mixed fine structure state. When $|J, n+q\rangle$ are the $|S, \pm 1/2\rangle$ ground states, then the sum becomes:

$$\Sigma_2 = \sum_{s,n,q} \hat{\varepsilon}_q^* \left\{ \frac{(\rho_{Sn+q} - \rho_{Psn}) |\langle S, n+q | r_q | P_s, n \rangle|^2}{-\omega - \omega_{Sn+qPsn} - i\gamma_{Sn+qPsn}} \right\} \varepsilon_q \cdot E_0 \hat{E}_0 \exp(-i\omega t) \quad (4.11)$$

Reversing the sum, relabeling the sum variables, and multiplying the top & bottom by -1 , the sum becomes:

$$\Sigma_2 = \sum_{s,n,q} \hat{\varepsilon}_q^* \left\{ \frac{(\rho_{Psn+q} - \rho_{Sn}) |\langle P_s, n+q | r_q | S, n \rangle|^2}{+\omega - \omega_{Psn+qSn} + i\gamma_{Psn+qSn}} \right\} \varepsilon_q \cdot E_0 \hat{E}_0 \exp(-i\omega t) \quad (4.12)$$

Finally, putting the two sums together again, we get:

$$\Re \langle \vec{d} \rangle = \frac{e^2}{\hbar} \sum_{s,n,q} \hat{\varepsilon}_q^* \left\{ \frac{(\rho_{Sn} - \rho_{Psn+q}) |\langle P_s, n+q | r_q | S, n \rangle|^2}{\omega_{Psn+qSn} - \omega - i\gamma_{Psn+qSn}} \right\} \varepsilon_q \cdot \left[E_0 \hat{E}_0 \exp(-i\omega t) + \left(E_0 \hat{E}_0 \exp(-i\omega t) \right)^* \right] \quad (4.13)$$

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

$$\Re \vec{d} = \vec{\alpha} \cdot \Re \vec{E} = \sum_q \hat{\varepsilon}_q^* \alpha_q \hat{\varepsilon}_q \left[\frac{\vec{E} + C.C.}{2} \right] \quad (4.14)$$

which immediately yields the components of the atomic polarizability tensor:

$$\alpha_q = \frac{e^2}{\hbar} \sum_{s,n} \left\{ \frac{(\rho_{Sn} - \rho_{Psn+q}) |\langle P_s, n+q | r_q | S, n \rangle|^2}{\omega_{Psn+qSn} - \omega - i\gamma_{Psn+qSn}} \right\} \quad (4.15)$$

4.2 Explicit Calculation of Atomic Polarizability

4.2.1 Description of Terms

To calculate the polarizability, we need to use many of the results from the previous sections:

1. the populations of the states, Sec. (3.5.1)
2. the transition matrix elements, Sec. (3.3)
3. the frequencies of the transitions, Sec. (1.2.5)

Putting these together, we see that every term in the sum looks like this:

$$\left(\frac{e^2}{\hbar}\right) \frac{\overbrace{\left[\frac{(\Delta\rho)}{m\omega_n} \left(\frac{T\hbar f_n}{m\omega_n} \right) (1 + c_1 a_1 a_2 + c_2 a_2^2) \right]}^{\text{matrix element squared}}}{\omega_n - \delta_2 - \omega - i\gamma_n} = (4\pi\epsilon_0 r_e c^2) \left(\frac{(\Delta\rho) T f_n}{\omega_n} \right) \underbrace{\left(\frac{1 + c_1 a_1 a_2 + c_2 a_2^2}{\omega_n - \delta_2 - \omega - i\gamma_n} \right)}_{\text{field dependent}} \quad (4.16)$$

where ϵ_0 is the electric permittivity of free space, r_e is the classical electron radius, c is the speed of light in a vacuum, e is the elementary charge, \hbar is Planck's constant divided by 2π , $(\Delta\rho)$ is the difference in population between the ground & excited states, $T = \{1/4, 1/2, 3/4, 1\}$, $c_1 = \pm\{2, 2\sqrt{2}\}$, & $c_2 = \{-1/2, +1\}$ are numerical constants that depends on the specific transition, f_n is the oscillator strength for the Dn transition, m is the mass of the electron, ω_n is the zero-field transition frequency for the Dn transition, δ_2 is the frequency shift due to the magnetic field & depends on the specific transition, ω is the incident light frequency, γ is the full width half maximum for the Dn transition, and a_1 & a_2 are the fine structure mixing coefficients and depend on the specific transition. When we say "specific" transition, we mean that it depends on the specific m_J s involved; on the other hand, when we say "Dn" transition, it only depends on the L_J s involved, where $n = 1$ or 2 . The last term is magnetic field dependent.

We'll specify the populations of the $|S, \pm\rangle$, $|P_-, \pm\rangle$, & $|P_+, (\pm 1/2, \pm 3/2)\rangle$ states. Under our spin-exchange optical pumping conditions inside the cells, the optical pumping rate is 1 MHz or less and the non-radiative quenching rate due to N_2 molecules is 1 GHz. This limits the populations of the $|P_{\pm}, (\pm 1/2, \pm 3/2)\rangle$ excited states to $\approx 1/1000$. We can safely treat this as zero and set $\rho_{P_{sn+q}} = 0$. Therefore, we only need to calculate the population of the $|S, \pm\rangle$ ground states. These are given by the electron spin polarization P as:

$$\rho_{S,\pm} = \frac{1 \pm P}{2} \quad (4.17)$$

Note that we can write everything in terms of the D1 oscillator strength f_1 by using:

$$f_n/\omega_n = n f_1/\omega_1 \quad C^{-1} = 4\pi\epsilon_0 r_e c^2 f_1/\omega_1 \quad (4.18)$$

4.2.2 Expansion to Second Order in Magnetic Field

Before we can expand the last term to second order in field, we'll first need to specify the field dependence of each parameter. For convenience, the field will be represented by the fine structure scaling parameter y . We are considering the fine structure mixing for the P states, so $L = 1$ and taking $g_S = -2$ gives $y = \mu_B B / (\hbar\omega_{so})$, where the fine structure splitting is given by $A_{so}[L]/2 = \hbar\omega_{so}$. The field dependence of the fine structure mixing coefficients a_1 & a_2 and frequency shift δ_2 to second order in y (field) is:

$$a_1 = 1 - \beta_0 y^2 \quad (4.19)$$

$$a_2 = -\beta_1 y + \beta_2 y^2 \quad (4.20)$$

$$\delta_2 = \omega_{so}(a y + b y^2) \quad (4.21)$$

where $\beta_0 = 1/9$, $\beta_1 = \sqrt{2}/3$, $\beta_2 = \pm\sqrt{2}/9$, $a = \pm\{1/3, 2/3, 1, 4/3, 5/3\}$, and $b = \pm 2/9$ depending on the transition involved. First we'll multiply the top and bottom by the complex conjugate of the bottom:

$$G = G(y) = \frac{1 + c_1 a_1 a_2 + c_2 a_2^2}{\omega_n - \delta_2 - \omega - i\gamma_n} = \left(\frac{1 + c_1 a_1 a_2 + c_2 a_2^2}{\omega_n - \delta_2 - \omega - i\gamma_n} \right) \left(\frac{\omega_n - \delta_2 - \omega + i\gamma_n}{\omega_n - \delta_2 - \omega + i\gamma_n} \right) \quad (4.22)$$

which allows us to write G as a sum of its real and imaginary parts:

$$G = \frac{(1 + c_1 a_1 a_2 + c_2 a_2^2) (\omega_n - \omega - \delta_2 + i\gamma_n)}{(\omega_n - \omega - \delta_2)^2 + \gamma_n^2} = \frac{(1 + c_1 a_1 a_2 + c_2 a_2^2) (-\Delta_n - \delta_2 + i\gamma_n)}{(-\Delta_n - \delta_2)^2 + \gamma_n^2} \quad (4.23)$$

where $\Delta_n = \omega - \omega_n$ is the detuning. We now need to remove the field dependence from the bottom. To separate the bottom into a sum of field dependent and independent terms, we expand the square:

$$(-\Delta_n - \delta_2)^2 + \gamma_n^2 = \Delta_n^2 + 2\Delta_n\delta_2 + \delta_2^2 + \gamma_n^2 = D_n^2 + \delta_1 \quad (4.24)$$

where $D_n^2 = \Delta_n^2 + \gamma_n^2$ and $\delta_1 = 2\Delta_n\delta_2 + \delta_2^2$. Expanding the bottom to second order in y :

$$\frac{1}{D_n^2 + \delta_1} = D_n^{-2} \left(1 + \frac{\delta_1}{D_n^2}\right)^{-1} = D_n^{-2} \left(1 - \frac{\delta_1}{D_n^2} + \frac{\delta_1^2}{D_n^4}\right) \quad (4.25)$$

where $D_n^2 = \Delta_n^2 + \gamma_n^2$ is the field independent denominator of G . Altogether, this gives:

$$G = \frac{(1 + c_1 a_1 a_2 + c_2 a_2^2)(-\Delta_n - \delta_2 + i\gamma_n)}{(-\Delta_n - \delta_2)^2 + \gamma_n^2} = D_n^{-2} (-\Delta_n + i\gamma_n - \delta_2) (1 + c_1 a_1 a_2 + c_2 a_2^2) \left(1 - \frac{\delta_1}{D_n^2} + \frac{\delta_1^2}{D_n^4}\right) \quad (4.26)$$

The part of the field dependence of the numerator that is common to both the real and imaginary parts of G comes from this product:

$$(1 + c_1 a_1 a_2 + c_2 a_2^2) \left(1 - \frac{\delta_1}{D_n^2} + \frac{\delta_1^2}{D_n^4}\right) = 1 + \left[c_1 a_1 a_2 - \frac{\delta_1}{D_n^2}\right] + \left[\frac{\delta_1^2}{D_n^4} - \frac{\delta_1}{D_n^2} c_1 a_1 a_2 + c_2 a_2^2\right] = 1 + A_1 y + A_2 y^2 \quad (4.27)$$

where we've kept on term second order in y . For only the real part, there is an additional term:

$$-\delta_2(1 + c_1 a_1 a_2 + c_2 a_2^2) \left(1 - \frac{\delta_1}{D_n^2} + \frac{\delta_1^2}{D_n^4}\right) = -\delta_2 + \left[\frac{\delta_1 \delta_2}{D_n^2} - c_1 \delta_2 a_1 a_2\right] = \omega_{\text{so}} (B_1 y + B_2 y^2) \quad (4.28)$$

Now we have:

$$G(y) = \frac{(-\Delta_n + i\gamma_n)(1 + A_1 y + A_2 y^2) + \omega_{\text{so}}(B_1 y + B_2 y^2)}{\Delta_n^2 + \gamma_n^2} \quad (4.29)$$

The second order expansion of the product of parameters are:

$$a_1 a_2 = -\beta_1 y + \beta_2 y^2 \quad (4.30)$$

$$a_2^2 = \beta_1^2 y^2 \quad (4.31)$$

$$\delta_2^2 = a^2 \omega_{\text{so}}^2 y^2 \quad (4.32)$$

$$\delta_1 = 2\Delta_n \delta_2 + \delta_2^2 = 2\Delta_n \omega_{\text{so}} (a y + b y^2) + a^2 \omega_{\text{so}}^2 y^2 \quad (4.33)$$

$$\delta_1^2 = 4a^2 \Delta_n^2 \omega_{\text{so}}^2 y^2 \quad (4.34)$$

$$\delta_1 \delta_2 = 2a^2 \Delta_n \omega_{\text{so}}^2 y^2 \quad (4.35)$$

$$\delta_2 a_1 a_2 = -a \beta_1 \omega_{\text{so}} y^2 \quad (4.36)$$

$$\delta_1 a_1 a_2 = -2a \beta_1 \Delta_n \omega_{\text{so}} y^2 \quad (4.37)$$

Plugging these in and collecting them by powers of y allows us to identify $A_1, A_2, B_1, & B_2$:

$$A_1 = -c_1 \beta_1 - \frac{2a \Delta_n \omega_{\text{so}}}{D_n^2} \quad (4.38)$$

$$A_2 = +c_1 \beta_2 + c_2 \beta_1^2 + \frac{2(ac_1 \beta_1 - b) \Delta_n \omega_{\text{so}} - a^2 \omega_{\text{so}}^2}{D_n^2} + \frac{4a^2 \Delta_n^2 \omega_{\text{so}}^2}{D_n^4} \quad (4.39)$$

$$B_1 = -a \quad (4.40)$$

$$B_2 = ac_1 \beta_1 - b + \frac{2a^2 \Delta_n \omega_{\text{so}}}{D_n^2} \quad (4.41)$$

where the values for the parameters for all the transitions are listed in Tab. (4.1). We'll define a lorentzian and dispersive line shape in the following way:

$$\mathcal{L}_n = \frac{\gamma_n}{D_n^2} = \frac{\gamma_n}{\Delta_n^2 + \gamma_n^2} \quad \mathcal{D}_n = \frac{-\Delta_n}{D_n^2} = \frac{-\Delta_n}{\Delta_n^2 + \gamma_n^2} \quad (4.42)$$

m	q	s	$m+q$	n	T	c_1	c_2	β_2	a	b	$-c_1\beta_1$	a^2	$(ac_1\beta_1 - b)$	$(c_1\beta_2 + c_2\beta_1^2)$
-	-	+	-3/2	2	3/4	0	0	0	+1	0	0	1	0	0
+	-	-	-1/2	1	1	$+\sqrt{2}$	-1/2	$-\sqrt{2}/9$	+4/3	+2/9	-2/3	16/9	+2/3	-1/3
+	-	+	-1/2	2	1/4	$-2\sqrt{2}$	+1	$-\sqrt{2}/9$	+5/3	-2/9	+4/3	25/9	-2	+2/3
-	0	-	-1/2	1	1/2	$-2\sqrt{2}$	+1	$-\sqrt{2}/9$	-2/3	+2/9	+4/3	4/9	+2/3	+2/3
-	0	+	-1/2	2	1/2	$+\sqrt{2}$	-1/2	$-\sqrt{2}/9$	-1/3	-2/9	-2/3	1/9	0	-1/3
+	0	-	+1/2	1	1/2	$+2\sqrt{2}$	+1	$+\sqrt{2}/9$	+2/3	+2/9	-4/3	4/9	+2/3	+2/3
+	0	+	+1/2	2	1/2	$-\sqrt{2}$	-1/2	$+\sqrt{2}/9$	+1/3	-2/9	+2/3	1/9	0	-1/3
-	+	-	+1/2	1	1	$-\sqrt{2}$	-1/2	$+\sqrt{2}/9$	-4/3	+2/9	+2/3	16/9	+2/3	-1/3
-	+	+	+1/2	2	1/4	$+2\sqrt{2}$	+1	$+\sqrt{2}/9$	-5/3	-2/9	-4/3	25/9	-2	+2/3
+	+	+	+3/2	2	3/4	0	0	0	-1	0	0	1	0	0

Table 4.1: Low Field Expansion Parameters. Dn transition due to r_q from $|S, m\rangle$ to $|P_s, m+q\rangle$. For all transitions, $\beta_0 = 1/9$ and $\beta_1 = \sqrt{2}/3$.

Using this notation, we rewrite $G(y)$ and the parameters within it:

$$G(y) = (\mathcal{D}_n + i\mathcal{L}_n)(1 + A_1y + A_2y^2) + \frac{\omega_{\text{so}}}{\gamma_n}\mathcal{L}_n(B_1y + B_2y^2) \quad (4.43)$$

$$A_1 = -c_1\beta_1 + 2a\omega_{\text{so}}\mathcal{D}_n \quad (4.44)$$

$$A_2 = +(c_1\beta_2 + c_2\beta_1^2) - 2(ac_1\beta_1 - b)\omega_{\text{so}}\mathcal{D}_n + a^2\omega_{\text{so}}^2\left(4\mathcal{D}_n^2 - \frac{\mathcal{L}_n}{\gamma_n}\right) \quad (4.45)$$

$$B_1 = -a \quad (4.46)$$

$$B_2 = (ac_1\beta_1 - b) - 2a^2\omega_{\text{so}}\mathcal{D}_n \quad (4.47)$$

The real part is written as:

$$\Re G = \mathcal{D}_n \left\{ 1 + [-c_1\beta_1 + 2a\omega_{\text{so}}\mathcal{D}_n]y + \left[(c_1\beta_2 + c_2\beta_1^2) - 2(ac_1\beta_1 - b)\omega_{\text{so}}\mathcal{D}_n + a^2\omega_{\text{so}}^2\left(4\mathcal{D}_n^2 - 3\frac{\mathcal{L}_n}{\gamma_n}\right) \right] y^2 \right\} \\ + \mathcal{L}_n \frac{\omega_{\text{so}}}{\gamma_n} \left\{ -ay + (ac_1\beta_1 - b)y^2 \right\} \quad (4.48)$$

The imaginary part is written as:

$$\Im G = \mathcal{L}_n \left\{ 1 + [-c_1\beta_1 + 2a\omega_{\text{so}}\mathcal{D}_n]y + \left[(c_1\beta_2 + c_2\beta_1^2) - 2(ac_1\beta_1 - b)\omega_{\text{so}}\mathcal{D}_n + a^2\omega_{\text{so}}^2\left(4\mathcal{D}_n^2 - \frac{\mathcal{L}_n}{\gamma_n}\right) \right] y^2 \right\} \quad (4.49)$$

4.2.3 Imaginary Part of the Polarizability: Absorption

The imaginary part of each term in the sum is written as:

$$\frac{nT(1 \pm P)}{2C}\mathcal{L}_n \left\{ 1 + [-c_1\beta_1 + 2a\omega_{\text{so}}\mathcal{D}_n]y + \left[(c_1\beta_2 + c_2\beta_1^2) - 2(ac_1\beta_1 - b)\omega_{\text{so}}\mathcal{D}_n + a^2\omega_{\text{so}}^2\left(4\mathcal{D}_n^2 - \frac{\mathcal{L}_n}{\gamma_n}\right) \right] y^2 \right\} \quad (4.50)$$

where as a reminder $1/C = 4\pi\epsilon_0 r_e c^2 f_1/\omega_1$, n refers to the Dn transition, P is the polarization of the ground state, and the other parameters are obtained from Tab. (4.1). Plugging in the parameters for the $q = -1$ component gives:

$$C\Im\alpha_- = \frac{3}{4}(1-P)\mathcal{L}_2 \left\{ 1 + [2\omega_{\text{so}}\mathcal{D}_2]y + \left[\omega_{\text{so}}^2\left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2}\right) \right] y^2 \right\} \\ + \frac{1}{6}(1+P)\mathcal{L}_1 \left\{ 3 + [-2 + 8\omega_{\text{so}}\mathcal{D}_1]y + \left[-1 - 4\omega_{\text{so}}\mathcal{D}_1 + \frac{16}{3}\omega_{\text{so}}^2\left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1}\right) \right] y^2 \right\} \\ + \frac{1}{12}(1+P)\mathcal{L}_2 \left\{ 3 + [4 + 10\omega_{\text{so}}\mathcal{D}_2]y + \left[2 + 12\omega_{\text{so}}\mathcal{D}_2 + \frac{25}{3}\omega_{\text{so}}^2\left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2}\right) \right] y^2 \right\} \quad (4.51)$$

Combining the D2 terms while separating the polarization dependent terms gives:

$$\begin{aligned}
C\mathfrak{S}\alpha_- &= \mathcal{L}_2 \left\{ 1 + \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[\frac{1}{6} + \omega_{\text{so}}\mathcal{D}_2 + \frac{13}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
&\quad - \frac{P}{2}\mathcal{L}_2 \left\{ 1 + \left[-\frac{2}{3} + \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
&\quad + \frac{(1+P)}{2}\mathcal{L}_1 \left\{ 1 + \left[-\frac{2}{3} + \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{16}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \quad (4.52)
\end{aligned}$$

Plugging in the parameters for the $q = 0$ component gives:

$$\begin{aligned}
C\mathfrak{S}\alpha_0 &= +\frac{1}{4}(1-P)\mathcal{L}_1 \left\{ 1 + \left[\frac{4}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
&\quad + \frac{1}{2}(1-P)\mathcal{L}_2 \left\{ 1 + \left[-\frac{2}{3} - \frac{2}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
&\quad + \frac{1}{4}(1+P)\mathcal{L}_1 \left\{ 1 + \left[-\frac{4}{3} + \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
&\quad + \frac{1}{2}(1+P)\mathcal{L}_2 \left\{ 1 + \left[\frac{2}{3} + \frac{2}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \quad (4.53)
\end{aligned}$$

Combining the D1 & D2 terms while separating the polarization dependent terms gives:

$$\begin{aligned}
C\mathfrak{S}\alpha_0 &= +\frac{1}{2}\mathcal{L}_1 \left\{ 1 + \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
&\quad + \mathcal{L}_2 \left\{ 1 + \left[-\frac{1}{3} + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
&\quad + P \{ \mathcal{L}_1 [-1 + \omega_{\text{so}}\mathcal{D}_1] + \mathcal{L}_2 [+1 + \omega_{\text{so}}\mathcal{D}_2] \} \frac{2y}{3} \quad (4.54)
\end{aligned}$$

Plugging in the parameters for the $q = +1$ component gives:

$$\begin{aligned}
C\mathfrak{S}\alpha_+ &= \frac{(1-P)}{2}\mathcal{L}_1 \left\{ 1 + \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{16}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
&\quad + \frac{1}{4}(1-P)\mathcal{L}_2 \left\{ 1 + \left[-\frac{4}{3} - \frac{10}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[\frac{2}{3} + 4\omega_{\text{so}}\mathcal{D}_2 + \frac{25}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
&\quad + \frac{3}{4}(1+P)\mathcal{L}_2 \left\{ 1 + [-2\omega_{\text{so}}\mathcal{D}_2] y + \left[\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \quad (4.55)
\end{aligned}$$

Combining the D2 terms while separating the polarization dependent terms gives:

$$\begin{aligned}
C\mathfrak{S}\alpha_+ &= \frac{(1-P)}{2}\mathcal{L}_1 \left\{ 1 + \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{16}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
&\quad + \mathcal{L}_2 \left\{ 1 + \left[-\frac{1}{3} - \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[\frac{1}{6} + \omega_{\text{so}}\mathcal{D}_2 + \frac{13}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
&\quad + \frac{P}{2}\mathcal{L}_2 \left\{ 1 + \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \quad (4.56)
\end{aligned}$$

Putting all three results together gives for $q = 0, \pm 1$:

$$C\mathfrak{S}\alpha_q = \frac{(1-qP)}{2}\mathcal{L}_1 \left\{ 1 + q \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[\frac{2}{3} - q^2 - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4+12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\}$$

$$\begin{aligned}
& +\mathcal{L}_2 \left\{ 1 - q \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{q^2}{2} + q^2\omega_{\text{so}}\mathcal{D}_2 + \frac{1+12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + \frac{qP}{2}\mathcal{L}_2 \left\{ 1 + q \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + (1 - q^2)P \{ \mathcal{L}_1 [-1 + \omega_{\text{so}}\mathcal{D}_1] + \mathcal{L}_2 [+1 + \omega_{\text{so}}\mathcal{D}_2] \} \frac{2y}{3}
\end{aligned} \tag{4.57}$$

4.2.4 Real Part of the Polarizability: Phase Shift

The real part of each term in the sum is written as the sum between one part that has an imaginary analogue:

$$\frac{nT(1 \pm P)}{2}\mathcal{D}_n \left[1 + [-c_1\beta_1 + 2a\omega_{\text{so}}\mathcal{D}_n] y + \left[(c_1\beta_2 + c_2\beta_1^2) - 2(ac_1\beta_1 - b)\omega_{\text{so}}\mathcal{D}_n + a^2\omega_{\text{so}}^2 \left(4\mathcal{D}_n^2 - 3\frac{\mathcal{L}_n}{\gamma_n} \right) \right] y^2 \right] \tag{4.58}$$

and an additional term that does not have an imaginary analogue:

$$\frac{nT(1 \pm P)}{2}\mathcal{L}_n \frac{\omega_{\text{so}}}{\gamma_n} \{ -ay + (ac_1\beta_1 - b)y^2 \} \tag{4.59}$$

where again $1/C = 4\pi\epsilon_0 r_e c^2 f_1/\omega_1$, n refers to the D_n transition, P is the polarization of the ground state, and the other parameters are obtained from Tab. (4.1) To be explicit, the three main differences between the calculation for the imaginary part (that we've already done) and this one for the real part are:

1. the overall \mathcal{L}_n outside the brackets becomes \mathcal{D}_n
2. the last term in the y^2 bracket goes from $-\mathcal{L}_n\gamma_n$ to $-3\mathcal{L}_n/\gamma_n$
3. there is an additional term proportional to $\mathcal{L}_n \frac{\omega_{\text{so}}}{\gamma_n}$ that we must work out as well

Using the results for the imaginary part, the first term (α_q^1) for the real part for the $q = 0, \pm 1$ component is:

$$\begin{aligned}
C\Re\alpha_q^1 &= \frac{(1 - qP)}{2}\mathcal{D}_1 \left\{ 1 + q \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[\frac{2}{3} - q^2 - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4+12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3\frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
& + \mathcal{D}_2 \left\{ 1 - q \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{q^2}{2} + q^2\omega_{\text{so}}\mathcal{D}_2 + \frac{1+12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + \frac{qP}{2}\mathcal{D}_2 \left\{ 1 + q \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + (1 - q^2)P \{ \mathcal{D}_1 [-1 + \omega_{\text{so}}\mathcal{D}_1] + \mathcal{D}_2 [+1 + \omega_{\text{so}}\mathcal{D}_2] \} \frac{2y}{3}
\end{aligned} \tag{4.60}$$

Now calculating the second term (α_q^2) for the real part for the $q = -1$ component:

$$C\Re\alpha_-^2 = \frac{3(1 - P)}{4}\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \{ -y \} + \frac{(1 + P)}{2}\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ -\frac{4}{3}y + \frac{2}{3}y^2 \right\} + \frac{(1 + P)}{4}\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ -\frac{5}{3}y - 2y^2 \right\} \tag{4.61}$$

Combining the D_2 terms while separating the polarization dependent terms gives:

$$C\Re\alpha_-^2 = (1 + P)\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ -\frac{2}{3}y + \frac{1}{3}y^2 \right\} + \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ -\frac{7}{6}y - \frac{1}{2}y^2 \right\} + P\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{1}{3}y - \frac{1}{2}y^2 \right\} \tag{4.62}$$

Now calculating the second term (α_q^2) for the real part for the $q = 0$ component:

$$\begin{aligned}
C\Re\alpha_0^2 &= \frac{(1 - P)}{4}\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{2}{3}y + \frac{2}{3}y^2 \right\} + \frac{(1 - P)}{2}\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{1}{3}y \right\} \\
& + \frac{(1 + P)}{4}\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ -\frac{2}{3}y + \frac{2}{3}y^2 \right\} + \frac{(1 + P)}{2}\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ -\frac{1}{3}y \right\}
\end{aligned} \tag{4.63}$$

Combining the D2 terms while separating the polarization dependent terms gives:

$$C\Re\alpha_0^2 = \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{1}{3}y^2 \right\} - P\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{1}{3}y \right\} - P\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{1}{3}y \right\} \quad (4.64)$$

Now calculating the second term (α_q^2) for the real part for the $q = +1$ component:

$$C\Re\alpha_+^2 = +\frac{(1-P)}{2}\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{4}{3}y + \frac{2}{3}y^2 \right\} + \frac{(1-P)}{4}\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{5}{3}y - 2y^2 \right\} + \frac{3(1+P)}{4}\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \{y\} \quad (4.65)$$

Combining the D2 terms while separating the polarization dependent terms gives:

$$C\Re\alpha_+^2 = (1-P)\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{2}{3}y + \frac{1}{3}y^2 \right\} + \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{7}{6}y - \frac{1}{2}y^2 \right\} + P\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{1}{3}y + \frac{1}{2}y^2 \right\} \quad (4.66)$$

Putting this altogether gives:

$$\begin{aligned} C\Re\alpha_q^2 &= (1-qP)\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ q\frac{2}{3}y + \frac{1}{3}y^2 \right\} + \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ q\frac{7}{6}y - q^2\frac{1}{2}y^2 \right\} \\ &\quad - (1-q^2)P\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{1}{3}y \right\} + P\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{2q^2-1}{3}y + q\frac{1}{2}y^2 \right\} \end{aligned} \quad (4.67)$$

Finally, combining both terms gives for the real part α_q where $q = 0, \pm 1$:

$$\begin{aligned} C\Re\alpha_q &= \frac{(1-qP)}{2}\mathcal{D}_1 \left\{ 1 + q \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[\frac{2}{3} - q^2 - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4+12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3\frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &\quad + \mathcal{D}_2 \left\{ 1 - q \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{q^2}{2} + q^2\omega_{\text{so}}\mathcal{D}_2 + \frac{1+12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &\quad + \frac{qP}{2}\mathcal{D}_2 \left\{ 1 + q \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &\quad + (1-q^2)P \left\{ \mathcal{D}_1 [-1 + \omega_{\text{so}}\mathcal{D}_1] + \mathcal{D}_2 [+1 + \omega_{\text{so}}\mathcal{D}_2] - \frac{1}{2}\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \right\} \frac{2y}{3} \\ &\quad + (1-qP)\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{2q}{3}y + \frac{1}{3}y^2 \right\} + \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{7q}{6}y - \frac{q^2}{2}y^2 \right\} + P\mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{2q^2-1}{3}y + \frac{q}{2}y^2 \right\} \end{aligned} \quad (4.68)$$

4.3 Atomic Polarization Vector

4.3.1 Light Propagation At a Skew Angle

It is useful to know how light is effected by the presence of a polarized alkali vapor when (1) optical pumping or (2) measuring alkali polarization and densities using Faraday Rotation. We'll assume that the polarized alkali vapor is located within a magnetic field that orients the alkali angular momentum. In other words, the magnetic field provides one axis of a coordinate system that naturally describes the alkali atoms. The light and the alkali atoms are connected through the atomic polarizability, which itself is related to the dielectric permittivity. We'll start with Maxwell's equations and end with a matrix eigenvalue equation. The solution to this equation will give the wave numbers and polarization vectors for the two eigenmodes of propagation through the vapor. An eigenmode of propagation has the property that its polarization vector does not change as it propagates through the alkali vapor.

In SI, Maxwell's equations are:

$$\begin{aligned} \vec{\nabla} \cdot \vec{D} &= \rho & \vec{\nabla} \times \vec{E} &= -\partial\vec{B}/\partial t \\ \vec{\nabla} \cdot \vec{B} &= 0 & \vec{\nabla} \times \vec{H} &= \vec{J} + \partial\vec{D}/\partial t \end{aligned} \quad (4.69)$$

and the constitutive relations for a linear medium between the electric vector \vec{E} & the electric displacement \vec{D} and between the magnetic induction \vec{B} & the magnetic vector \vec{H} are:

$$\vec{D} = \vec{\epsilon} \cdot \vec{E} \quad \vec{B} = \vec{\mu} \cdot \vec{H} \quad (4.70)$$

where $\overleftrightarrow{\epsilon}$ & $\overleftrightarrow{\mu}$ are the dielectric permittivity & the magnetic permeability tensors, respectively. In our case, there are no free charges ρ and currents \vec{J} . Since the light has optical frequencies, the magnetic permeability tensor $\overleftrightarrow{\mu}$ is very nearly equal to the scalar free space value μ_0 :

$$\begin{aligned}\vec{\nabla} \cdot \vec{D} &= 0 & \vec{\nabla} \times \vec{E} &= -\mu_0 \partial \vec{H} / \partial t \\ \vec{\nabla} \cdot \vec{H} &= 0 & \vec{\nabla} \times \vec{H} &= \partial \vec{D} / \partial t\end{aligned}\quad (4.71)$$

Representing the spatial and time dependence of \vec{E} , \vec{D} , \vec{B} , & \vec{H} in plane wave form, such as $\vec{E} \rightarrow \vec{E} \exp[i\vec{k} \cdot \vec{r} - i\omega t]$, results in:

$$\begin{aligned}\vec{k} \cdot \vec{D} &= 0 & \vec{k} \times \vec{E} &= \omega \mu_0 \vec{H} \\ \vec{k} \cdot \vec{H} &= 0 & \vec{k} \times \vec{H} &= -\omega \vec{D}\end{aligned}\quad (4.72)$$

where \vec{k} is the wave number and $\omega = 2\pi\nu$ is the frequency. Combining the two cross product equations results in:

$$\vec{k} \times (\vec{k} \times \vec{E}) = \vec{k} (\vec{k} \cdot \vec{E}) - k^2 \vec{E} = -\omega^2 \mu_0 \vec{D} \quad (4.73)$$

where we've used the identity $\vec{a} \times (\vec{b} \times \vec{c}) = \vec{b}(\vec{a} \cdot \vec{c}) - \vec{c}(\vec{a} \cdot \vec{b})$. Finally, using the constitutive relation for \vec{D} , factoring out \vec{E} , and moving things around gives:

$$\left(\begin{bmatrix} k^2 & 0 & 0 \\ 0 & k^2 & 0 \\ 0 & 0 & k^2 \end{bmatrix} - \begin{bmatrix} k_1^2 & k_1 k_2 & k_1 k_3 \\ k_2 k_1 & k_2^2 & k_2 k_3 \\ k_3 k_1 & k_3 k_2 & k_3^2 \end{bmatrix} - \omega^2 \mu_0 \overleftrightarrow{\epsilon} \right) \cdot \vec{E} = 0 \quad (4.74)$$

The derivation of this equation can also be found in chapter 15 of *Born & Wolf* [25] and also *Yariv & Yeh* [26].

4.3.2 Wave Number Eigenvalues

The following calculation is a detailed extension to the one found in [27]. There are in general three coordinate systems that one could use to solve for the possible eigenvalues for k :

1. the atomic basis, namely one that reflects the symmetry of the alkali vapor (\hat{r}_+^* ; \hat{r}_-^* ; $\hat{r}_0^* = \hat{B}_0$) which is determined by the magnetic field \vec{B}_0
2. the linear (\mathcal{P} ; \mathcal{S} ; $\mathcal{Z} = \hat{k}$) or circular (\mathcal{R} ; \mathcal{L} ; \mathcal{Z}) polarization basis of the light
3. the polarization eigenvector basis, namely the one for which the matrix multiplying \vec{E} is diagonal

Unfortunately, we usually do not know beforehand what the polarization eigenvector basis is. However, when the magnetic field and light propagation direction point in the same direction, all three coordinate systems happen to coincide. Therefore we'll take advantage of this fact and choose to work in the circular polarization basis of the light. Consequently, the wave number dyad is represented as:

$$\vec{k} \vec{k} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & k^2 \end{bmatrix} \quad (4.75)$$

where $k_1 = k_2 = 0$ and $\sqrt{k_1^2 + k_2^2 + k_3^2} = k^2$ due to the orthonormality of the circular polarization basis.

In the atomic basis (\hat{r}_+^* ; \hat{r}_-^* ; \hat{r}_0^*), the dielectric tensor is, by construction, diagonal and given as:

$$\overleftrightarrow{\epsilon} = \epsilon_0 \left(1 + \frac{[\text{A}]}{\epsilon_0} \begin{bmatrix} \alpha_+ & 0 & 0 \\ 0 & \alpha_- & 0 \\ 0 & 0 & \alpha_0 \end{bmatrix} \right) \quad (4.76)$$

where ε_0 is the dielectric permittivity of free space and $[A]$ is the alkali number density. When the magnetic field is zero, the polarizabilities are given by:

$$\alpha_q = \frac{\varepsilon_0 r_e c^2}{2\pi} \left[\underbrace{\frac{f_1/\nu_1}{\nu_1 - \nu - i\Gamma_1/2} (1 - qP_A)}_{\text{D1 transition}} + \underbrace{\frac{f_2/\nu_2}{\nu_2 - \nu - i\Gamma_2/2} \left(1 + \frac{qP_A}{2}\right)}_{\text{D2 transition}} \right] \quad (4.77)$$

where r_e is the classical electron radius, c is the speed of light in a vacuum, P_A is the alkali polarization, $q(= 0, \pm 1)$ is the amount of angular momentum transferred to an alkali atom, f_n is the oscillator strength, ν_n is the transition frequency, and Γ_n is the full width half maximum of the transition. The subscripts $n(= 1, 2)$ refer to the D1 and D2 transitions of the alkali atom.

We'll have to transform the polarizability tensor from the $(\hat{r}_+^*; \hat{r}_-^*; \hat{r}_0^*)$ basis to the $(\mathcal{R}; \mathcal{L}; \mathcal{Z})$ basis in the following way:

1. switch from the $(\hat{r}_+^*; \hat{r}_-^*; \hat{r}_0^*)$ basis to the $(\hat{x}; \hat{y}; \hat{z})$ basis relative to the atomic system
2. rotate by an angle θ from the $(\hat{x}; \hat{y}; \hat{z})$ basis relative to the atomic system to the $(\mathcal{P}; \mathcal{S}; \mathcal{Z})$ basis relative to the light polarization, where θ is the angle between the magnetic field and the light propagation direction as in $\hat{B}_0 \cdot \hat{k} = \cos(\theta)$
3. switch from the $(\mathcal{P}; \mathcal{S}; \mathcal{Z})$ basis to the $(\mathcal{R}; \mathcal{L}; \mathcal{Z})$ basis relative to the light polarization

We'll note the following relationships between the different bases relative to the light system:

$$\mathcal{R} = \frac{\mathcal{P} + i\mathcal{S}}{\sqrt{2}} \quad \mathcal{L} = \frac{\mathcal{P} - i\mathcal{S}}{\sqrt{2}} \quad (4.78)$$

between the different bases relative to the atomic system:

$$\vec{r} = r_+ \hat{r}_+^* + r_- \hat{r}_-^* + r_0 \hat{r}_0^* = x\hat{x} + y\hat{y} + z\hat{z} \quad (4.79)$$

$$r_+ = -\left(\frac{x + iy}{\sqrt{2}}\right) \quad r_- = \frac{x - iy}{\sqrt{2}} \quad r_0 = z \quad (4.80)$$

and finally between the atomic and light systems:

$$\hat{x} = \mathcal{P} \cos(\theta) - \mathcal{Z} \sin(\theta) \quad \hat{z} = \mathcal{P} \sin(\theta) + \mathcal{Z} \cos(\theta) \quad (4.81)$$

Switching the basis of the polarizability tensor from the circular basis to linear basis relative to the atomic system gives:

$$\overleftrightarrow{\alpha} = \frac{1}{\sqrt{2}} \begin{bmatrix} -1 & +1 & 0 \\ -i & -i & 0 \\ 0 & 0 & +1 \end{bmatrix} \begin{bmatrix} \alpha_+ & 0 & 0 \\ 0 & \alpha_- & 0 \\ 0 & 0 & \alpha_0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} -1 & +i & 0 \\ +1 & +i & 0 \\ 0 & 0 & +1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} \sigma & -i\delta & 0 \\ i\delta & \sigma & 0 \\ 0 & 0 & 2\alpha_0 \end{bmatrix} \quad (4.82)$$

where σ & δ are the sum & difference of α_+ & α_- :

$$\sigma = \alpha_+ + \alpha_- = 2\alpha_0 \quad \delta = \alpha_+ - \alpha_- \quad (4.83)$$

To simplify things, we'll break the the resulting matrix up into the following:

$$\overleftrightarrow{\alpha} = \frac{1}{2} \begin{bmatrix} \sigma & -i\delta & 0 \\ i\delta & \sigma & 0 \\ 0 & 0 & 2\alpha_0 \end{bmatrix} = \frac{\sigma}{2} + i\frac{\delta}{2} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (4.84)$$

Now we rotate by θ from the linear basis of atomic system to linear polarization basis of the light:

$$\begin{bmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0 & 1 & 0 \\ -\sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \cos(\theta) & 0 & -\sin(\theta) \\ 0 & 1 & 0 \\ \sin(\theta) & 0 & \cos(\theta) \end{bmatrix} = \begin{bmatrix} 0 & -\cos(\theta) & 0 \\ \cos(\theta) & 0 & -\sin(\theta) \\ 0 & \sin(\theta) & 0 \end{bmatrix} \quad (4.85)$$

Finally we'll switch from the linear polarization basis of the light to the circular one:

$$\frac{1}{\sqrt{2}} \begin{bmatrix} +1 & -i & 0 \\ +1 & +i & 0 \\ 0 & 0 & +1 \end{bmatrix} \begin{bmatrix} 0 & -\cos(\theta) & 0 \\ \cos(\theta) & 0 & -\sin(\theta) \\ 0 & \sin(\theta) & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} +1 & +1 & 0 \\ +i & -i & 0 \\ 0 & 0 & +1 \end{bmatrix} \quad (4.86)$$

which gives:

$$\begin{bmatrix} -i \cos(\theta) & 0 & -\frac{i}{2} \sin(\theta) \\ 0 & +i \cos(\theta) & +\frac{i}{2} \sin(\theta) \\ +\frac{i}{2} \sin(\theta) & -\frac{i}{2} \sin(\theta) & 0 \end{bmatrix} \quad (4.87)$$

Therefore, the polarizability in the circular polarization basis of the is:

$$\overleftrightarrow{\alpha} = \frac{1}{2} \begin{bmatrix} \sigma + \delta \cos(\theta) & 0 & +\frac{\delta}{2} \sin(\theta) \\ 0 & \sigma - \delta \cos(\theta) & -\frac{\delta}{2} \sin(\theta) \\ -\frac{\delta}{2} \sin(\theta) & +\frac{\delta}{2} \sin(\theta) & \sigma \end{bmatrix} = \begin{bmatrix} \alpha_{\mathcal{R}} & 0 & +\frac{\delta}{4} \sin(\theta) \\ 0 & \alpha_{\mathcal{L}} & -\frac{\delta}{4} \sin(\theta) \\ -\frac{\delta}{4} \sin(\theta) & +\frac{\delta}{4} \delta \sin(\theta) & \alpha_0 \end{bmatrix} \quad (4.88)$$

and consequently the matrix equation is written as

$$\begin{bmatrix} k^2 - k_{\mathcal{R}}^2 & 0 & -\Delta_k^2 \\ 0 & k^2 - k_{\mathcal{L}}^2 & +\Delta_k^2 \\ +\Delta_k^2 & -\Delta_k^2 & -k_0^2 \end{bmatrix} \cdot \vec{E} = 0 \quad (4.89)$$

where we have defined the following quantities:

$$k_{\mathcal{Q}}^2 = \frac{\omega^2}{c^2} \left(1 + \frac{[A]}{\varepsilon_0} \alpha_{\mathcal{Q}} \right) \quad \Delta_k^2 = \frac{\omega^2}{c^2} \frac{[A]}{\varepsilon_0} \left(\frac{\alpha_+ - \alpha_-}{4} \right) \sin(\theta) \quad (4.90)$$

$$\alpha_{\mathcal{Q}} = \frac{\varepsilon_0 r_e c^2}{2\pi} \left[\frac{f_1/\nu_1}{\nu_1 - \nu - i\Gamma_1/2} (1 - qP_A \cos(\theta)) + \frac{f_2/\nu_2}{\nu_2 - \nu - i\Gamma_2/2} \left(1 + \frac{qP_A \cos(\theta)}{2} \right) \right] \quad (4.91)$$

where $q = +1, 0, -1$ for $\mathcal{Q} = \mathcal{R}, 0, \mathcal{L}$ respectively. This equation is solved by setting the determinant of the matrix to zero:

$$\begin{vmatrix} k^2 - k_{\mathcal{R}}^2 & 0 & -\Delta_k^2 \\ 0 & k^2 - k_{\mathcal{L}}^2 & +\Delta_k^2 \\ +\Delta_k^2 & -\Delta_k^2 & -k_0^2 \end{vmatrix} = (k^2 - k_{\mathcal{R}}^2) [-(k^2 - k_{\mathcal{L}}^2) k_0^2 + \Delta_k^4] + \Delta_k^4 (k^2 - k_{\mathcal{L}}^2) = 0 \quad (4.92)$$

This can be rearranged to:

$$k^4 + k^2 [-k_{\mathcal{L}}^2 - k_{\mathcal{R}}^2 - 2\Delta_k^4/k_0^2] + [k_{\mathcal{R}}^2 k_{\mathcal{L}}^2 + (k_{\mathcal{R}}^2 + k_{\mathcal{L}}^2) \Delta_k^4/k_0^2] = 0 \quad (4.93)$$

and is then solved using the quadratic equation:

$$k^2 = \frac{1}{2} \left[k_{\mathcal{R}}^2 + k_{\mathcal{L}}^2 + 2\Delta_k^4/k_0^2 \pm \sqrt{(k_{\mathcal{R}}^2 - k_{\mathcal{L}}^2)^2 + 4\Delta_k^8/k_0^4} \right] \quad (4.94)$$

The two eigenvalues for k^2 are given by the two solutions above. However, a more illuminating form for k^2 can be obtained if we compare the size of Δ_k^2 against two different scales:

$$\frac{\Delta_k^2}{k_0^2} = \frac{[A] (\alpha_+ - \alpha_-) \sin(\theta)}{4\varepsilon_0 \left(1 + \frac{[A]}{\varepsilon_0} \alpha_0 \right)} \approx 10^{-3} \left(\frac{\sin(\theta)}{4} \right) \quad \frac{\Delta_k^2}{k_{\mathcal{R}}^2 - k_{\mathcal{L}}^2} = \frac{\tan(\theta)}{4} \quad (4.95)$$

where we have used the fact that the maximum absolute value of the polarizability occurs at resonance for the D2 transition $\nu = \nu_2$ which corresponds to:

$$\left[\frac{[A]}{\varepsilon_0} \alpha_0 \right]_{\max} = \left[\frac{[A]}{\varepsilon_0} \left(\frac{\alpha_+ - \alpha_-}{P_A} \right) \right]_{\max} = \frac{[A] r_e c \lambda_2 f_2}{\pi \Gamma_2} = 10^{-3} \times \left(\frac{[A]}{10^{15} \text{ cm}^{-3}} \right) \left(\frac{\lambda_2}{780 \text{ nm}} \right) \left(\frac{140 \text{ GHz}}{\Gamma_2} \right) \quad (4.96)$$

and we have put in typical values for the alkali density and absorption line width. Therefore, the angle for which the two terms under the square root are equal, for $P_A = 1$, is about $\theta = 89.993$. In almost all cases, the first term dominates over the second term under the square root and we can write the two solutions as:

$$k^2 = (k_{\mathcal{R}}^2 \text{ or } k_{\mathcal{L}}^2) + \Delta_k^4/k_0^2 \quad (4.97)$$

4.3.3 Light Polarization Eigenvectors

The polarization eigenvectors that correspond to these wave number eigenvalues are found by solving the following system of equations:

$$\begin{aligned} (k^2 - k_{\mathcal{R}}^2) E_1 - \Delta_k^2 E_3 &= 0 \\ (k^2 - k_{\mathcal{L}}^2) E_2 + \Delta_k^2 E_3 &= 0 \\ \Delta_k^2 E_1 - \Delta_k^2 E_2 - k_0^2 E_3 &= 0 \end{aligned} \quad (4.98)$$

which can be rearranged to give the following useful ratios among the components of the eigenvectors:

$$(k^2 - k_{\mathcal{R}}^2) E_1 = - (k^2 - k_{\mathcal{L}}^2) E_2 \quad E_3 = \frac{\Delta_k^2}{k_0^2} (E_1 - E_2) \quad (4.99)$$

Finally, the two eigenvectors in the circular polarization basis of the light (\mathcal{R} ; \mathcal{L} ; \mathcal{Z}) to lowest order in Δ_k^2 are:

$$k_{\mathcal{R}} : (1 ; 0 ; 0) + \frac{\Delta_k^2}{k_0^2} \left(0 ; -\frac{\tan(\theta)}{4} ; +1 \right) \quad (4.100)$$

$$k_{\mathcal{L}} : (0 ; 1 ; 0) + \frac{\Delta_k^2}{k_0^2} \left(+\frac{\tan(\theta)}{4} ; 0 ; -1 \right) \quad (4.101)$$

This means that polarization eigenvector basis:

1. is very well approximated by the circular polarization basis of the light
2. has a small admixture of linear polarization
3. is slightly parallel to the propagation direction

4.3.4 Generalization to Atomic Polarization Vector

We've found that when we have a skew angle θ , the polarization P in the atomic polarizability is replaced by $P \cos(\theta)$. This is very suggestive, and following the argument of Dehmelt [28], we'll replace $P \cos(\theta)$ with $\hat{k} \cdot \vec{P}$ where \hat{k} is the beam propagation direction and \vec{P} is the polarization vector. The quantum mechanical form of this polarization vector is given by $\vec{P} = 2 \langle \vec{S} \rangle$ where \vec{S} is the vector spin-1/2 operator. Therefore, all instances of P should be replaced by $\hat{k} \cdot \vec{P}$:

$$P \rightarrow 2 (k_x \langle S_x \rangle + k_y \langle S_y \rangle + k_z \langle S_z \rangle) \quad k_x^2 + k_y^2 + k_z^2 = 1 \quad (4.102)$$

When the beam is parallel to the magnetic field, then $k_z = 1$ and $P \rightarrow 2 \langle S_z \rangle$. Since S_z is parallel to the magnetic field by definition, its expectation value is since the difference in populations or P , as expected. On the other hand, when the beam is perpendicular to the magnetic field, say $k_x = 1$, then $P \rightarrow 2 \langle S_x \rangle$. The expectation value of S_x involves coherences. If there is no external RF field, then the coherences are oscillating at the Larmor frequency. If there is an external RF field, then the coherences will be oscillating at the frequency of the RF field. In either case, the expectation value of S_x will be oscillatory and as a consequence so will the polarizability.

A more rigorous derivation of this generalization involving group theoretical methods can be found in *Happer & Mathur* [29]. They derive an irreducible tensor decomposition of the atomic polarizability (in the linear polarization basis):

$$\overleftrightarrow{\alpha} = \alpha_S \overleftrightarrow{1} + \alpha_V (\langle \vec{\mu} \rangle \times) + \alpha_T \left\langle \overleftrightarrow{Q} \right\rangle \quad (4.103)$$

where $\alpha_{S,V,T}$ are the scalar, vector, & tensor polarizabilities, $\vec{\mu}$ is the magnetic dipole operator, and \overleftrightarrow{Q} is the electric quadrupole operator. Dropping the electric quadrupole part, we can write atomic polarizability in matrix form:

$$\overleftrightarrow{\alpha} = \begin{bmatrix} \alpha_S & 0 & 0 \\ 0 & \alpha_S & 0 \\ 0 & 0 & \alpha_S \end{bmatrix} + \frac{\alpha_V g_S \mu_B}{2} \begin{bmatrix} 0 & -P_z & P_y \\ P_z & 0 & -P_x \\ -P_y & P_x & 0 \end{bmatrix} \quad (4.104)$$

where $\vec{\mu} = g_S \mu_B \vec{S}$, $P_n = 2 \langle S_n \rangle$, and we used the matrix form of the cross product. This looks suspiciously like Eqn. (4.84):

$$\vec{\alpha} = \frac{1}{2} \begin{bmatrix} \sigma & -i\delta & 0 \\ i\delta & \sigma & 0 \\ 0 & 0 & 2\alpha_0 \end{bmatrix} = \frac{\sigma}{2} + i\frac{\delta}{2} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (4.105)$$

where we can equate $\sigma/2 = \alpha_0 = \alpha_S$, $i\delta/2 = \alpha_V g_S \mu_B P_z/2$, $P_x = P_y = 0$. We'll now proceed with the rest of the analysis from Sec.(4.3.2), but now with $P_x \neq 0$ and $P_y \neq 0$. As a reminder, we're starting in the linear atomic basis. We rotate by θ from the linear basis of atomic system to linear polarization basis of the light:

$$\begin{bmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0 & 1 & 0 \\ -\sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \begin{bmatrix} 0 & -P_z & P_y \\ P_z & 0 & -P_x \\ -P_y & P_x & 0 \end{bmatrix} \begin{bmatrix} \cos(\theta) & 0 & -\sin(\theta) \\ 0 & 1 & 0 \\ \sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \quad (4.106)$$

where we get:

$$P_z M_z + P_x M_x + P_y M_y = \begin{bmatrix} 0 & -P_z \cos(\theta) + P_x \sin(\theta) & P_y \\ +P_z \cos(\theta) - P_x \sin(\theta) & 0 & -P_z \sin(\theta) - P_x \cos(\theta) \\ -P_y & P_z \sin(\theta) + P_x \cos(\theta) & 0 \end{bmatrix} \quad (4.107)$$

Finally we'll switch from the linear polarization basis of the light to the circular one. We already know how to transform $P_z M_z$:

$$P_z M'_z = \frac{1}{\sqrt{2}} \begin{bmatrix} +1 & -i & 0 \\ +1 & +i & 0 \\ 0 & 0 & +1 \end{bmatrix} P_z \begin{bmatrix} 0 & -\cos(\theta) & 0 \\ \cos(\theta) & 0 & -\sin(\theta) \\ 0 & \sin(\theta) & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} +1 & +1 & 0 \\ +i & -i & 0 \\ 0 & 0 & +1 \end{bmatrix} \quad (4.108)$$

which gives:

$$P_z M'_z = \begin{bmatrix} -iP_z \cos(\theta) & 0 & -\frac{i}{2}P_z \sin(\theta) \\ 0 & +iP_z \cos(\theta) & +\frac{i}{2}P_z \sin(\theta) \\ +\frac{i}{2}P_z \sin(\theta) & -\frac{i}{2}P_z \sin(\theta) & 0 \end{bmatrix} \quad (4.109)$$

If we make the substitutions $P_z \cos(\theta) \rightarrow -P_x \sin(\theta)$ and $P_z \sin(\theta) \rightarrow P_x \cos(\theta)$, then if can immediately transform M_x to M'_x to give:

$$P_x M'_x = \begin{bmatrix} +iP_x \sin(\theta) & 0 & -\frac{i}{2}P_x \cos(\theta) \\ 0 & -iP_x \sin(\theta) & +\frac{i}{2}P_x \cos(\theta) \\ +\frac{i}{2}P_x \cos(\theta) & -\frac{i}{2}P_x \cos(\theta) & 0 \end{bmatrix} \quad (4.110)$$

Finally, we need to transform $P_y M_y$ in the following way:

$$P_y M'_y = \frac{1}{\sqrt{2}} \begin{bmatrix} +1 & -i & 0 \\ +1 & +i & 0 \\ 0 & 0 & +1 \end{bmatrix} P_y \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} +1 & +1 & 0 \\ +i & -i & 0 \\ 0 & 0 & +1 \end{bmatrix} \quad (4.111)$$

which gives:

$$P_y M'_y = \begin{bmatrix} 0 & 0 & P_y/2 \\ 0 & 0 & P_y/2 \\ -P_y/2 & -P_y/2 & 0 \end{bmatrix} \quad (4.112)$$

Putting this altogether gives:

$$P_z M'_z + P_x M'_x + P_y M'_y = -i \begin{bmatrix} +\hat{k} \cdot \vec{P} & 0 & +p_{xz}/2 + iP_y/2 \\ 0 & -\hat{k} \cdot \vec{P} & -p_{xz}/2 + iP_y/2 \\ -p_{xz}/2 - iP_y/2 & +p_{xz}/2 - iP_y/2 & 0 \end{bmatrix} \quad (4.113)$$

where $P_z \cos(\theta) - P_x \sin(\theta) = \hat{k} \cdot \vec{P}$ and $p_{xz} = P_z \sin(\theta) + P_x \cos(\theta)$. Therefore, the polarizability in the circular polarization basis is:

$$\vec{\alpha} = \frac{1}{2} \begin{bmatrix} \sigma + \delta' \hat{k} \cdot \vec{P} & 0 & +\delta'(p_{xz} + iP_y)/2 \\ 0 & \sigma - \delta' \hat{k} \cdot \vec{P} & -\delta'(p_{xz} - iP_y)/2 \\ -\delta'(p_{xz} + iP_y)/2 & +\delta'(p_{xz} - iP_y)/2 & \sigma \end{bmatrix} \quad (4.114)$$

where $\delta' = \delta/P$ and compared to Eqn. (4.88):

$$\leftrightarrow \frac{1}{2} \begin{bmatrix} \sigma + \delta \cos(\theta) & 0 & +\frac{\delta}{2} \sin(\theta) \\ 0 & \sigma - \delta \cos(\theta) & -\frac{\delta}{2} \sin(\theta) \\ -\frac{\delta}{2} \sin(\theta) & +\frac{\delta}{2} \sin(\theta) & \sigma \end{bmatrix} \quad (4.115)$$

we see that (1) $\delta \cos(\theta)$ has been replaced by $\delta' \hat{k} \cdot \vec{P}$ and (2) the off diagonal elements $\delta \sin(\theta)/2$ have been replaced by $\delta'(p_{xz} \pm iP_y)$. Analogous to before, we'll define the following quantities:

$$k_Q^2 = \frac{\omega^2}{c^2} \left(1 + \frac{[A]}{\varepsilon_0} \alpha_Q \right) \quad \alpha_Q = \frac{\varepsilon_0 r_e c^2}{2\pi} \left[\frac{f_1/\nu_1}{\nu_1 - \nu - i\Gamma_1/2} \left(1 - q \hat{k} \cdot \vec{P}_A \right) + \frac{f_2/\nu_2}{\nu_2 - \nu - i\Gamma_2/2} \left(1 + \frac{q \hat{k} \cdot \vec{P}_A}{2} \right) \right] \quad (4.116)$$

where $q = +1, 0, -1$ for $Q = \mathcal{R}, 0, \mathcal{L}$ respectively. Just as before, the eigenvalues are essentially $k_{\mathcal{R}}$ and $k_{\mathcal{L}}$ with very small corrections at the level of $\delta'^2(p_{xz} \pm iP_y)^2/(16k_0^2)$. Corrections due to a non-zero field slightly modify these very small corrections and therefore can safely be ignored as well.

4.3.5 Components Without An RF Field (Calculation of $\langle S_z \rangle$)

The components of the atomic polarization vector \vec{P} are just the expectation values of the spin-1/2 operators $S_x, S_y, \& S_z$. We'll work in the $|F, m\rangle$ basis To calculate the expectation values of S_z, S_x & S_y , we'll first calculate it for S_q ($S_0 = S_z$; $S_{\pm} = S_x \pm iS_y$) using:

$$\langle S_q \rangle = \sum_{F, F', m} \langle F', m | \rho | F, m \pm 1 \rangle \langle F, m + q | S_q | F', m \rangle \quad (4.117)$$

The coherences are simply:

$$\langle F', m | \rho | F, m + q \rangle = \rho_{F' m F m + q}(0) \exp[-i\omega_{F' m F m + q} t] \quad (4.118)$$

For a large collection of atoms at equilibrium, the spins have all dephased and $\rho_{F' m F m + q}(0)$ is equal to zero. Therefore, all the coherences are zero. Consequently, the only nonzero terms are ones that involve populations:

$$\langle S_z \rangle = \sum_{F, m} \rho_m \langle F, m | S_z | F, m \rangle \quad (4.119)$$

Since we originally defined $P = 2 \langle S_z \rangle$, we should obtain $\langle S_z \rangle = P_z/2$. To evaluate the S_z matrix element, we'll have to expand $|F, m\rangle$ in the $|I, 1/2\rangle, m_I, \pm 1/2\rangle$ basis:

$$\begin{aligned} \langle S_z \rangle &= \sum_{F, m, m_S, m'_S} \frac{\exp(\beta m)}{Z_I Z_{1/2}} \times \\ &\quad \left\langle F, m \left| \left(I, \frac{1}{2} \right), m - m'_S, m'_S \right\rangle \langle m - m'_S, m'_S | S_z | m - m_S, m_S \rangle \left\langle \left(I, \frac{1}{2} \right), m - m_S, m_S \left| F, m \right\rangle \right. \end{aligned} \quad (4.120)$$

$$= \sum_{F, m, m_S} \frac{\exp(\beta m)}{Z_I Z_{1/2}} m_S \left[\left\langle F, m \left| \left(I, \frac{1}{2} \right), m - m_S, m_S \right\rangle \right]^2 \quad (4.121)$$

$$(4.122)$$

Since there are two manifolds $F = I \pm 1/2$, we'll split the sum into two pieces:

$$\begin{aligned} \langle S_z \rangle &= \sum_{m=-I-1/2}^{m=+I+1/2} \sum_{m_S=-1/2}^{+1/2} \frac{\exp(\beta m)}{Z_I Z_{1/2}} m_S \left[\left\langle I + 1/2, m \left| \left(I, \frac{1}{2} \right), m - m_S, m_S \right\rangle \right]^2 \\ &+ \sum_{m=-I+1/2}^{m=+I-1/2} \sum_{m_S=-1/2}^{+1/2} \frac{\exp(\beta m)}{Z_I Z_{1/2}} m_S \left[\left\langle I - 1/2, m \left| \left(I, \frac{1}{2} \right), m - m_S, m_S \right\rangle \right]^2 \end{aligned} \quad (4.123)$$

$$(4.124)$$

Using the Clebsch-Gordon formulas from Sec. (C.2):

$$\begin{aligned}
\langle S_z \rangle &= \sum_{m=-I-1/2}^{m=+I+1/2} \sum_{m_S=-1/2}^{+1/2} \frac{\exp(\beta m)}{Z_I Z_{1/2}} m_S \left[\frac{I+1/2+2m_S m}{[I]} \right] \\
&+ \sum_{m=-I+1/2}^{m=+I-1/2} \sum_{m_S=-1/2}^{+1/2} \frac{\exp(\beta m)}{Z_I Z_{1/2}} m_S \left[\frac{I+1/2-2m_S m}{[I]} \right] \\
&= \sum_{m=-I-1/2}^{m=+I+1/2} \sum_{m_S=-1/2}^{+1/2} \frac{\exp(\beta m)}{Z_I Z_{1/2}} \left[\frac{+2m_S^2 m}{[I]} \right] + \sum_{m=-I+1/2}^{m=+I-1/2} \sum_{m_S=-1/2}^{+1/2} \frac{\exp(\beta m)}{Z_I Z_{1/2}} \left[\frac{-2m_S^2 m}{[I]} \right] \\
&= \sum_{m_S=-1/2}^{+1/2} \left(\frac{\exp(+\beta[I]/2)}{Z_I Z_{1/2}} \left[\frac{+2m_S^2 [I]/2}{[I]} \right] + \frac{\exp(-\beta[I]/2)}{Z_I Z_{1/2}} \left[\frac{-2m_S^2 [I]/2}{[I]} \right] \right)
\end{aligned} \tag{4.125}$$

where the symmetric sum over $m_S = \pm 1/2$ cancels the $m_S(I+1/2)/[I]$ terms and the $2m_S^2 m/[I]$ term from one manifold cancels the one from the other manifold, except for the edge states $m = I \pm 1/2$:

$$\begin{aligned}
\langle S_z \rangle &= \frac{2 \exp(+\beta[I]/2)}{4Z_I Z_{1/2}} - \frac{2 \exp(-\beta[I]/2)}{4Z_I Z_{1/2}} = \frac{\sinh(\beta[I]/2)}{Z_I Z_{1/2}} = \frac{\sinh(\beta/2) \sqrt{1-P_z^2}}{2} \\
&= \left(\sqrt{\frac{1+P_z}{1-P_z}} - \sqrt{\frac{1-P_z}{1+P_z}} \right) \frac{\sqrt{1-P_z^2}}{4} = \left(\frac{(1+P_z) - (1-P_z)}{\sqrt{1-P_z^2}} \right) \frac{\sqrt{1-P_z^2}}{4} = \frac{P_z}{2}
\end{aligned} \tag{4.126}$$

where we've used Eqns. (3.265) & (3.266) (with $P \rightarrow P_z$) and as expected $P_z = 2 \langle S_z \rangle$.

4.3.6 Components With An RF Field (Calculation of $\langle S_x \rangle$ & $\langle S_y \rangle$)

In this section, we'll assume that there is an RF Field with frequency ω creating coherences only within a manifold. In other words, there are no RF fields that induce $F = I + 1/2 \leftrightarrow F' = I - 1/2$ transitions. Therefore, the expectation value for S_z is the same as the last section. To calculate the expectation values of S_x and S_y , we'll first calculate $S_{\pm} = S_x \pm iS_y$ using Eqn. (3.55) in the form of:

$$\begin{aligned}
\langle S_{\pm} \rangle &= \sum_m \left\{ \frac{\Omega(\rho_m - \rho_{m \mp 1}) (u_{\pm}^{\mp})^* |\langle F, m | \mathcal{U}_{\pm} | F, m \mp 1 \rangle|^2}{\pm \omega - \omega_{FmFm \mp 1} - i\gamma_{FmFm \mp 1}} \times \exp(\pm i\omega t) \right. \\
&+ \left. \frac{\Omega(\rho_m - \rho_{m \mp 1}) (u_{\pm}^{\pm})^* |\langle F', m | \mathcal{U}_{\pm} | F', m \mp 1 \rangle|^2}{\mp \omega - \omega_{F'mF'm \mp 1} - i\gamma_{F'mF'm \mp 1}} \times \exp(\mp i\omega t) \right\}
\end{aligned} \tag{4.127}$$

where we've split the sum over the two manifolds ($F = I + 1/2$ & $F' = I - 1/2$) and the population of each state depends only on m . As a reminder, \pm is the sign of $\omega_{Fm+qFm} = \omega_{Fm+q} - \omega_{Fm}$. Finally, for the $F = I + 1/2$ manifold, the energy of the m state is higher than the energy of the $m - 1$ state, whereas for the $F' = I - 1/2$ manifold, the opposite is true. Therefore the frequency of the transition $m \leftrightarrow m - 1$ is positive for the $F = I + 1/2$ manifold, whereas its negative for the F' manifold. Since $S_x = (S_+ + S_-)/2$, we can write its expectation value as:

$$\begin{aligned}
\langle S_x \rangle &= \sum_m \left\{ \frac{\Omega(\rho_m - \rho_{m-1}) (u_+^-)^* |\langle F, m | S_+ | F, m-1 \rangle|^2}{+\omega - \omega_{FmFm-1} - i\gamma_{FmFm-1}} \times \frac{\exp(+i\omega t)}{2} \right. \\
&+ \frac{\Omega(\rho_m - \rho_{m+1}) (u_-^+)^* |\langle F, m | S_- | F, m+1 \rangle|^2}{-\omega - \omega_{FmFm+1} - i\gamma_{FmFm+1}} \times \frac{\exp(-i\omega t)}{2} \\
&+ \left. \frac{\Omega(\rho_m - \rho_{m-1}) (u_+^+)^* |\langle F', m | S_+ | F', m-1 \rangle|^2}{-\omega - \omega_{F'mF'm-1} - i\gamma_{F'mF'm-1}} \times \frac{\exp(-i\omega t)}{2} \right\}
\end{aligned}$$

$$+ \frac{\Omega(\rho_m - \rho_{m+1})(u_-^-)^* |\langle F', m | S_- | F', m+1 \rangle|^2}{+\omega - \omega_{F'mF'm+1} - i\gamma_{F'mF'm+1}} \times \frac{\exp(+i\omega t)}{2} \Big\} \quad (4.128)$$

where $\Omega = g_S \mu_B B_{\text{rf}} / \hbar$, $u_q^- = \epsilon_q^* \cdot \hat{B}_{\text{rf}}$, and $u_q^+ = \epsilon_q^* \cdot \hat{B}_{\text{rf}}^*$. As mentioned before, we'll label the transition by the higher m involved. Relabeling the terms in the sum and moving a few minus signs around gives:

$$\begin{aligned} \langle S_x \rangle = & \sum_m \left\{ \frac{\Omega(\rho_m - \rho_{m-1})(u_+^-)^* |\langle F, m | S_+ | F, m-1 \rangle|^2}{+\omega - \omega_{FmFm-1} - i\gamma_{FmFm-1}} \times \frac{\exp(+i\omega t)}{2} \right. \\ & + \frac{\Omega(\rho_m - \rho_{m-1})(u_-^+)^* |\langle F, m-1 | S_- | F, m \rangle|^2}{+\omega - \omega_{FmFm-1} + i\gamma_{Fm-1Fm}} \times \frac{\exp(-i\omega t)}{2} \\ & - \frac{\Omega(\rho_m - \rho_{m-1})(u_+^+)^* |\langle F', m | S_+ | F', m-1 \rangle|^2}{+\omega - \omega_{F'm-1F'm} + i\gamma_{F'mF'm-1}} \times \frac{\exp(-i\omega t)}{2} \\ & \left. - \frac{\Omega(\rho_m - \rho_{m-1})(u_-^-)^* |\langle F', m-1 | S_- | F', m \rangle|^2}{+\omega - \omega_{F'm-1F'm} - i\gamma_{F'm-1F'm}} \times \frac{\exp(+i\omega t)}{2} \right\} \quad (4.129) \end{aligned}$$

We've already calculated that:

$$\rho_m - \rho_{m-1} = Q_{I\bar{m}} P_z \quad (4.130)$$

$$|\langle F, m | S_{\pm} | F, m \mp 1 \rangle|^2 = \frac{F(F+1) - m(m \mp 1)}{[I]} \quad (4.131)$$

So we just need to work out what this term looks like:

$$\frac{u^* \exp(+i\omega t)/2}{\omega - \omega_0 - i\gamma} + \frac{u \exp(-i\omega t)/2}{\omega - \omega_0 + i\gamma} = \Re \left\{ \frac{u \exp(-i\omega t)}{\omega - \omega_0 + i\gamma} \right\} = \Re \{ u [\cos(\omega t) - i \sin(\omega t)] [\mathcal{D} - i\mathcal{L}] \} \quad (4.132)$$

where the two terms are just complex conjugates of each other, which makes their sum just the real part of either term and we've made the substitutions:

$$\mathcal{D} = \frac{\omega - \omega_0}{(\omega - \omega_0)^2 + \gamma^2} \quad \mathcal{L} = \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2} \quad (4.133)$$

Expanding this out and grouping terms by phase:

$$\Re \{ u [\cos(\omega t) - i \sin(\omega t)] [\mathcal{D} - i\mathcal{L}] \} = [\mathcal{D}\Re\{u\} + \mathcal{L}\Im\{u\}] \cos(\omega t) + [\mathcal{D}\Im\{u\} - \mathcal{L}\Re\{u\}] \sin(\omega t) \quad (4.134)$$

Using this, we can anticipate the final form of the expectation value of S_x :

$$\langle S_x \rangle = P_z [\langle S_x \rangle_c \cos(\omega t) + \langle S_x \rangle_s \sin(\omega t)] \quad (4.135)$$

where $c(s)$ refers to the cosine (sine) component, \pm refers to the manifold, and we get:

$$\langle S_x \rangle_c = \frac{\Omega}{[I]} \sum_{(\pm), m} (\pm) Q_{I\bar{m}} [(I+1/2)(I+1/2 \pm 1) - m(m-1)] [\mathcal{D}_m^{\pm} \Re\{u_{\pm}^-\} + \mathcal{L}_m^{\pm} \Im\{u_{\pm}^-\}] \quad (4.136)$$

$$\langle S_x \rangle_s = \frac{\Omega}{[I]} \sum_{(\pm), m} (\pm) Q_{I\bar{m}} [(I+1/2)(I+1/2 \pm 1) - m(m-1)] [\mathcal{D}_m^{\pm} \Im\{u_{\pm}^-\} - \mathcal{L}_m^{\pm} \Re\{u_{\pm}^-\}] \quad (4.137)$$

where I is the nuclear spin, \pm refers to the manifold, we sum over both m and \pm and:

$$\mathcal{D}_m^+ = \frac{\omega - \omega_{FmFm-1}}{(\omega - \omega_{FmFm-1})^2 + \gamma_{FmFm-1}^2} \quad (4.138)$$

$$\mathcal{L}_m^+ = \frac{\gamma_{FmFm-1}}{(\omega - \omega_{FmFm-1})^2 + \gamma_{FmFm-1}^2} \quad (4.139)$$

$$\mathcal{D}_m^- = \frac{\omega - \omega_{F'm-1F'm}}{(\omega - \omega_{F'm-1F'm})^2 + \gamma_{F'm-1F'm}^2} \quad (4.140)$$

$$\mathcal{L}_m^- = \frac{\gamma_{F'm-1F'm}}{(\omega - \omega_{F'm-1F'm})^2 + \gamma_{F'm-1F'm}^2} \quad (4.141)$$

where $F = I + 1/2$ and $F' = I - 1/2$.

For $S_y = (S_+ - S_-)/(2i)$, we get terms that look like:

$$\frac{u^* \exp(+i\omega t)/(2i)}{\omega - \omega_0 - i\gamma} - \frac{u \exp(-i\omega t)/(2i)}{\omega - \omega_0 + i\gamma} = -\Im \left\{ \frac{u \exp(-i\omega t)}{\omega - \omega_0 + i\gamma} \right\} = -\Im \{ u [\cos(\omega t) - i \sin(\omega t)] [\mathcal{D} - i\mathcal{L}] \} \quad (4.142)$$

Expanding this out and grouping terms by phase:

$$-\Im \{ u [\cos(\omega t) - i \sin(\omega t)] [\mathcal{D} - i\mathcal{L}] \} = [\mathcal{D}\Re\{u\} + \mathcal{L}\Im\{u\}] \sin(\omega t) - [\mathcal{D}\Im\{u\} - \mathcal{L}\Re\{u\}] \cos(\omega t) \quad (4.143)$$

This is the same as for S_x except we make the substitutions $\cos \rightarrow \sin$ and $\sin \rightarrow -\cos$:

$$\langle S_y \rangle = P_z [\langle S_y \rangle_c \cos(\omega t) + \langle S_y \rangle_s \sin(\omega t)] \quad (4.144)$$

$$\langle S_y \rangle_c = \frac{\Omega}{[I]} \sum_{(\pm), m} (\mp) Q_{I\bar{m}} [(I + 1/2)(I + 1/2 \pm 1) - m(m - 1)] [\mathcal{D}_m^\pm \Im\{u_\pm\} - \mathcal{L}_m^\pm \Re\{u_\pm\}] \quad (4.145)$$

$$\langle S_y \rangle_s = \frac{\Omega}{[I]} \sum_{(\pm), m} (\pm) Q_{I\bar{m}} [(I + 1/2)(I + 1/2 \pm 1) - m(m - 1)] [\mathcal{D}_m^\pm \Re\{u_\pm\} + \mathcal{L}_m^\pm \Im\{u_\pm\}] \quad (4.146)$$

The expectation values contain both lorentzian (\mathcal{L}) and dispersive (\mathcal{D}) line shapes. They both contain in-phase and out-of-phase terms. Finally, the two manifolds appear with opposite signs.

4.4 Synthesis

We're now in a position to write the wave vector k_q in terms of the polarizability:

$$k_q = \frac{\omega}{c} n_q = \frac{\omega}{c} \sqrt{\frac{\epsilon_q \mu_q}{\epsilon_0 \mu_0}} = \frac{\omega}{c} \sqrt{1 + \frac{[A]\alpha_q}{\epsilon_0}} = \frac{\omega}{c} \left(1 + \frac{[A]\alpha_q}{2\epsilon_0} - \frac{[A]^2 \alpha_q^2}{8\epsilon_0^2} + \dots \right) \quad (4.147)$$

Expanding k_q in terms of its real and imaginary parts gives, up to second order:

$$k_q = \frac{\omega}{c} \left(1 + \frac{[A]}{2\epsilon_0} (\Re\alpha_q + i\Im\alpha_q) - \frac{[A]^2}{8\epsilon_0^2} \{ (\Re\alpha_q)^2 - (\Im\alpha_q)^2 + 2i(\Re\alpha_q)(\Im\alpha_q) \} \right) \quad (4.148)$$

Under our typical densities, the second order term is quite small and keep only up to first order:

$$k_q = \frac{\omega}{c} + [A] 2\pi r_e c f_1 \frac{\omega}{\omega_1} \left(\frac{\Re\alpha_q + i\Im\alpha_q}{4\pi\epsilon_0 r_e c^2 f_1 / \omega_1} \right) = \frac{\omega}{c} + [A] r_e c f_1 \left(\frac{\omega}{\omega_1} \right) (2\pi C \Re\alpha_q + i 2\pi C \Im\alpha_q) \quad (4.149)$$

where $1/C = 4\pi\epsilon_0 r_e c^2 f_1 / \omega_1$. Making the substitution $P \rightarrow \hat{k} \cdot \vec{P}_A$, the imaginary part of the polarizability is for $q = 0, \pm 1$:

$$\begin{aligned} C\Im\alpha_q &= \frac{(1 - q\hat{k} \cdot \vec{P}_A)}{2} \mathcal{L}_1 \left\{ 1 + q \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[\frac{2}{3} - q^2 - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4 + 12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &+ \mathcal{L}_2 \left\{ 1 - q \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{q^2}{2} + q^2\omega_{\text{so}}\mathcal{D}_2 + \frac{1 + 12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ \frac{q\hat{k} \cdot \vec{P}_A}{2} \mathcal{L}_2 \left\{ 1 + q \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ (1 - q^2)\hat{k} \cdot \vec{P}_A \{ \mathcal{L}_1 [-1 + \omega_{\text{so}}\mathcal{D}_1] + \mathcal{L}_2 [+1 + \omega_{\text{so}}\mathcal{D}_2] \} \frac{2y}{3} \end{aligned} \quad (4.150)$$

and similarly for the real part:

$$C\Re\alpha_q = \frac{(1 - q\hat{k} \cdot \vec{P}_A)}{2} \mathcal{D}_1 \left\{ 1 + q \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[\frac{2}{3} - q^2 - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4 + 12q^2}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3\frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\}$$

$$\begin{aligned}
& +\mathcal{D}_2 \left\{ 1 - q \left[\frac{1}{3} + \frac{7}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{q^2}{2} + q^2 \omega_{\text{so}} \mathcal{D}_2 + \frac{1 + 12q^2}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3 \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + \frac{q \hat{k} \cdot \vec{P}_A}{2} \mathcal{D}_2 \left\{ 1 + q \left[\frac{2}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}} \mathcal{D}_2 + \frac{1}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3 \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + (1 - q^2) \hat{k} \cdot \vec{P}_A \left\{ \mathcal{D}_1 [-1 + \omega_{\text{so}} \mathcal{D}_1] + \mathcal{D}_2 [+1 + \omega_{\text{so}} \mathcal{D}_2] - \frac{1}{2} \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \right\} \frac{2y}{3} \\
& + (1 - q \hat{k} \cdot \vec{P}_A) \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{2q}{3} y + \frac{1}{3} y^2 \right\} + \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{7q}{6} y - \frac{q^2}{2} y^2 \right\} + \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{2q^2 - 1}{3} y + \frac{q}{2} y^2 \right\}
\end{aligned} \tag{4.151}$$

and finally :

$$\hat{k} \cdot \vec{P}_A = P_A [k_z + (k_x \langle S_x \rangle_c + k_y \langle S_y \rangle_c) \cos(\omega_{\text{rf}} t) + (k_x \langle S_x \rangle_s + k_y \langle S_y \rangle_s) \sin(\omega_{\text{rf}} t)] \tag{4.152}$$

where $P_z = P_A$ and ω_{rf} is the frequency of the RF field.

Chapter 5

Experimental Applications

5.1 Accessing Observables Using Polarized Light

5.1.1 Modulating Polarized Light Using a PEM

The effect of the atomic interaction on the light is expressed by the complex index of refraction through the wave vector \vec{k} . The direction of \vec{k} is always in the direction that the light is propagating. On the other hand, the magnitude of \vec{k} depends on the details of the atomic system and the polarization vector of the light. Our general experiment will consist of polarized traveling through a PEM, then the alkali vapor, and finally a beam splitting polarizing cube for detection. We'll start with a arbitrarily polarized plane wave:

$$\vec{E} = |E\rangle e^{i\vec{k}\cdot\vec{r}-i\omega t} \quad (5.1)$$

$$|E\rangle = E_0 e^{i\phi_p} \left[\left(\sqrt{1-P} \frac{e^{+i\theta}}{2} + \sqrt{1+P} \frac{e^{-i\theta}}{2} \right) |P\rangle + \left(\sqrt{1-P} \frac{e^{+i\theta}}{2i} - \sqrt{1+P} \frac{e^{-i\theta}}{2i} \right) |S\rangle \right] \quad (5.2)$$

Going through a photoelastic modulator:

$$|E\rangle = E_0 e^{i\phi_p} \left[\left(\sqrt{1-P} \frac{e^{+i\theta_+}}{2} + \sqrt{1+P} \frac{e^{-i\theta_-}}{2} \right) |P\rangle + \left(\sqrt{1-P} \frac{e^{+i\theta_-}}{2i} - \sqrt{1+P} \frac{e^{-i\theta_+}}{2i} \right) |S\rangle \right] \quad (5.3)$$

$$\theta_{\pm} = \theta \pm \frac{\beta(t)}{2} \quad (5.4)$$

Going back into the circular polarization basis, the right (+) and left (-) components are:

$$|E\rangle_{\pm} = +\frac{E_0}{2\sqrt{2}} e^{i(\phi_p)} \left[\{e^{+i\theta_-} \mp e^{+i\theta_+}\} \sqrt{1-P} - \{e^{-i\theta_+} \pm e^{-i\theta_-}\} \sqrt{1+P} \right] \quad (5.5)$$

Going through the atomic vapor, each polarization component q of the light propagates with wave vector \vec{k}_q :

$$\vec{E} = \sum_q |E\rangle_q \hat{\epsilon}_q e^{i(\vec{k}_q\cdot\vec{r}-\omega t)} \quad (5.6)$$

After traversing a distance of l in the atomic vapor and reentering a uniform and isotropic medium with wave vector \vec{k} , we get:

$$\vec{E} = e^{i(\vec{k}\cdot\vec{r}-\omega t)} \sum_q |E\rangle_q \hat{\epsilon}_q e^{ik_q l} \quad (5.7)$$

The time averaged intensity of the light is:

$$I = \sqrt{\frac{\epsilon}{\mu}} \frac{\vec{E}^* \cdot \vec{E}}{2} = \sqrt{\frac{\epsilon}{\mu}} \sum_q \frac{\langle E | E \rangle_q}{2} e^{i(k_q - k_q^*)l} = \sqrt{\frac{\epsilon}{\mu}} \sum_q \frac{\langle E | E \rangle_q}{2} e^{-2l\Im k_q} \quad (5.8)$$

The effect of the atomic vapor can be written in (a very suggestive) matrix form in the linear polarization basis in the light coordinate system:

$$|E\rangle_{\text{aft}} = \hat{M} |E\rangle_{\text{bef}} \quad (5.9)$$

$$\hat{M} = e^{i(k_+ + k_-)l/2} \begin{bmatrix} \cos\left(\frac{k_+ - k_-}{2}l\right) & \sin\left(\frac{k_+ - k_-}{2}l\right) \\ -\sin\left(\frac{k_+ - k_-}{2}l\right) & \cos\left(\frac{k_+ - k_-}{2}l\right) \end{bmatrix} \quad (5.10)$$

$$|E\rangle_{\text{bef}} = \frac{E_0 e^{i\phi_p}}{2} \begin{bmatrix} \sqrt{1-P}e^{+i\theta_+} + \sqrt{1+P}e^{-i\theta_-} \\ -i(\sqrt{1-P}e^{+i\theta_-} - \sqrt{1+P}e^{-i\theta_+}) \end{bmatrix} \quad (5.11)$$

The atomic vapor has the effect of creating an overall complex phase of $i(k_+ + k_-)l/2$ and a complex rotation through an angle $(k_+ - k_-)l/2$. Now we'll send the light through a half waveplate whose axis is at an angle ϕ_h :

$$\hat{W}_{\frac{1}{2}} \hat{M}_0 = i \begin{bmatrix} +\cos\left(\frac{k_+ - k_-}{2}l + 2\phi_h\right) & +\sin\left(\frac{k_+ - k_-}{2}l + 2\phi_h\right) \\ +\sin\left(\frac{k_+ - k_-}{2}l + 2\phi_h\right) & -\cos\left(\frac{k_+ - k_-}{2}l + 2\phi_h\right) \end{bmatrix} \quad (5.12)$$

The final polarization vector can be written as:

$$|E\rangle_{\text{f}} = i \frac{E_0 e^{i\phi'_p}}{2} \begin{bmatrix} \sqrt{1-P}e^{+i\theta} \left(\cos(\psi)e^{+i\frac{\beta}{2}} - i \sin(\psi)e^{-i\frac{\beta}{2}} \right) + \sqrt{1+P}e^{-i\theta} \left(\cos(\psi)e^{+i\frac{\beta}{2}} + i \sin(\psi)e^{-i\frac{\beta}{2}} \right) \\ i\sqrt{1-P}e^{+i\theta} \left(\cos(\psi)e^{-i\frac{\beta}{2}} - i \sin(\psi)e^{+i\frac{\beta}{2}} \right) - i\sqrt{1+P}e^{-i\theta} \left(\cos(\psi)e^{-i\frac{\beta}{2}} + i \sin(\psi)e^{+i\frac{\beta}{2}} \right) \end{bmatrix} \quad (5.13)$$

$$\phi'_p = \phi_p + (k_+ + k_-) \frac{l}{2} \quad (5.14)$$

$$\psi = (k_+ - k_-) \frac{l}{2} + 2\phi_h \quad (5.15)$$

Noting that ψ is complex, the intensities of the two components are:

$$\zeta = \sqrt{\frac{\epsilon}{\mu}} \frac{E_0^2}{4} e^{-l\Im\{k_+ + k_-\}} \quad (5.16)$$

$$\frac{I_{\mathcal{P}}}{\zeta} = |\cos(\psi)|^2 + |\sin(\psi)|^2 + iP \left(\cos(\psi^*) \sin(\psi) e^{-i\beta} - \cos(\psi) \sin(\psi^*) e^{+i\beta} \right) + \sqrt{1-P^2} \times \Re \left\{ e^{+2i\theta} \left[|\cos(\psi)|^2 - |\sin(\psi)|^2 - i \cos(\psi^*) \sin(\psi) e^{-i\beta} - i \cos(\psi) \sin(\psi^*) e^{+i\beta} \right] \right\} \quad (5.17)$$

$$\frac{I_{\mathcal{S}}}{\zeta} = |\cos(\psi)|^2 + |\sin(\psi)|^2 + iP \left(\cos(\psi^*) \sin(\psi) e^{+i\beta} - \cos(\psi) \sin(\psi^*) e^{-i\beta} \right) - \sqrt{1-P^2} \times \Re \left\{ e^{+2i\theta} \left[|\cos(\psi)|^2 - |\sin(\psi)|^2 - i \cos(\psi^*) \sin(\psi) e^{+i\beta} - i \cos(\psi) \sin(\psi^*) e^{-i\beta} \right] \right\} \quad (5.18)$$

Using the following relations:

$$|\cos(\psi)|^2 = \cos(\psi) \cos(\psi^*) = \frac{1}{2} [\cosh(2\Im\psi) + \cos(2\Re\psi)] \quad (5.19)$$

$$|\sin(\psi)|^2 = \sin(\psi) \sin(\psi^*) = \frac{1}{2} [\cosh(2\Im\psi) - \cos(2\Re\psi)] \quad (5.20)$$

$$\sin(\psi) \cos(\psi^*) = \frac{1}{2} [+i \sinh(2\Im\psi) + \sin(2\Re\psi)] \quad (5.21)$$

$$\sin(\psi^*) \cos(\psi) = \frac{1}{2} [-i \sinh(2\Im\psi) + \sin(2\Re\psi)] \quad (5.22)$$

finally gives:

$$I_{\mathcal{P},\mathcal{S}} = \frac{I_{\sigma} \pm I_{\delta}}{2} \quad (5.23)$$

$$I_{\sigma} = 2\zeta \left[\cosh(2\Im\psi) + \sinh(2\Im\psi) \left(\sqrt{1-P^2} \sin(2\theta) \sin(\beta) - \cos(\beta) \right) \right] \quad (5.24)$$

$$I_{\delta} = 2\zeta \left[P \sin(\beta) \sin(2\Re\psi) + \sqrt{1-P^2} (\cos(2\theta) \cos(2\Re\psi) + \sin(2\theta) \sin(2\Re\psi) \cos(\beta)) \right] \quad (5.25)$$

Using the following expansions for the β terms:

$$\beta(t) = \beta_0 \cos(\Omega_{\text{mod}} t) \quad (5.26)$$

$$\sin(\beta_0 \cos(\Omega_{\text{mod}} t)) = 2J_1(\beta_0) \cos(\Omega_{\text{mod}} t) - \dots \quad (5.27)$$

$$\cos(\beta_0 \cos(\Omega_{\text{mod}} t)) = J_0(\beta_0) - 2J_2(\beta_0) \cos(2\Omega_{\text{mod}} t) + \dots \quad (5.28)$$

we can extract the DC, the RMS AC1, and the RMS AC2 components of the sum (σ) and difference (δ) signals:

$$I_\sigma(\text{DC}) = 2\zeta [\cosh(2\Im\psi) - J_0(\beta_0) \sinh(2\Im\psi)] \quad (5.29)$$

$$I_\sigma(\text{AC1}) = 2\zeta \sqrt{2} J_1(\beta_0) \sinh(2\Im\psi) \sqrt{1-P^2} \sin(2\theta) \quad (5.30)$$

$$I_\sigma(\text{AC2}) = 2\zeta \sqrt{2} J_2(\beta_0) \sinh(2\Im\psi) \quad (5.31)$$

$$I_\delta(\text{DC}) = 2\zeta \sqrt{1-P^2} [\cos(2\theta) \cos(2\Re\psi) + J_0(\beta_0) \sin(2\theta) \sin(2\Re\psi)] \quad (5.32)$$

$$I_\delta(\text{AC1}) = 2\zeta \sqrt{2} J_1(\beta_0) P \sin(2\Re\psi) \quad (5.33)$$

$$I_\delta(\text{AC2}) = 2\zeta \sqrt{2} J_2(\beta_0) \sqrt{1-P^2} \sin(2\theta) \sin(2\Re\psi) \quad (5.34)$$

$$2\zeta = \sqrt{\frac{\epsilon}{\mu} \frac{E_0^2}{2}} e^{-l\Im\{k_+ + k_-\}} \quad (5.35)$$

$$\psi = (k_+ - k_-) \frac{l}{2} + 2\phi_h \quad (5.36)$$

where:

1. J_n is a Bessel function of the first kind or order n
2. $\beta_0 = 2\pi\beta_{\text{set}} \left(\frac{\lambda_{\text{set}}}{\lambda_{\text{light}}} \right)$ is the PEM retardation. If there is no PEM, then we can simply set $\beta_0 = 0$.
3. ϕ_h is the angle of the half waveplate axis with respect to the PEM axis
4. P is the degree of circular polarization of the light before the PEM
5. θ is the angle of linear polarization component of the light with respect to the PEM axis before the PEM
6. \Re and \Im refer to the real and imaginary parts of a complex number

The AC components can be picked out using a Lock-In Amplifier referenced to the PEM frequency (Ω_{mod}). The DC components can be picked out using a low pass filter with a time constant that is several times longer than the PEM period $1/\Omega_{\text{mod}}$. For the case where there is no atomic vapor ($l = 0$):

$$I_\sigma(\text{DC}) = \sqrt{\frac{\epsilon}{\mu} \frac{E_0^2}{2}} \quad (5.37)$$

$$I_\sigma(\text{AC1}) = 0 \quad (5.38)$$

$$I_\sigma(\text{AC2}) = 0 \quad (5.39)$$

$$I_\delta(\text{DC}) = I_\sigma(\text{DC}) \sqrt{1-P^2} [\cos(2\theta) \cos(4\phi_h) + J_0(\beta_0) \sin(2\theta) \sin(4\phi_h)] \quad (5.40)$$

$$I_\delta(\text{AC1}) = I_\sigma(\text{DC}) \sqrt{2} J_1(\beta_0) P \sin(4\phi_h) \quad (5.41)$$

$$I_\delta(\text{AC2}) = I_\sigma(\text{DC}) \sqrt{2} J_2(\beta_0) \sqrt{1-P^2} \sin(2\theta) \sin(4\phi_h) \quad (5.42)$$

This gives a simple method for measuring the degree of circular polarization (Sec. (2.6.2)) using a rotatable half-waveplate (RHWP). As the RHWP is rotated, the signal $I_\delta(\text{AC1})/I_\sigma$ will oscillate between a maximum and minimum four times through one complete rotation. The normalized amplitude of this sinusoidal oscillation is $\sqrt{2} J_1(\beta_0) P$. If there is no PEM, then $J_0(0) = 1$ and $I_\delta(\text{DC})/I_\sigma$ will oscillate in the same way, this time with an amplitude of $\sqrt{1-P^2}$.

5.1.2 The Imaginary Part of the Polarizability Sum

The imaginary sum is given by:

$$\Im(k_+ + k_-) = \frac{[A]2\pi r_e c f_1 \omega}{\omega_1} C\Im(\alpha_+ + \alpha_-) \quad (5.43)$$

The sum of the imaginary parts of the polarizability is given by:

$$\begin{aligned} C\Im(\alpha_+ + \alpha_-) &= \frac{(1 - \hat{k} \cdot \vec{P}_A)}{2} \mathcal{L}_1 \left\{ 1 + \left[\frac{2}{3} - \frac{8}{3} \omega_{\text{so}} \mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_1 + \frac{4+12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &+ \mathcal{L}_2 \left\{ 1 - \left[\frac{1}{3} + \frac{7}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{2} + \omega_{\text{so}} \mathcal{D}_2 + \frac{1+12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ \frac{\hat{k} \cdot \vec{P}_A}{2} \mathcal{L}_2 \left\{ 1 + \left[\frac{2}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}} \mathcal{D}_2 + \frac{1}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ (1-1) \hat{k} \cdot \vec{P}_A \{ \mathcal{L}_1 [-1 + \omega_{\text{so}} \mathcal{D}_1] + \mathcal{L}_2 [+1 + \omega_{\text{so}} \mathcal{D}_2] \} \frac{2y}{3} \\ &+ \frac{(1 + \hat{k} \cdot \vec{P}_A)}{2} \mathcal{L}_1 \left\{ 1 - \left[\frac{2}{3} - \frac{8}{3} \omega_{\text{so}} \mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_1 + \frac{4+12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &+ \mathcal{L}_2 \left\{ 1 + \left[\frac{1}{3} + \frac{7}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{2} + \omega_{\text{so}} \mathcal{D}_2 + \frac{1+12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ \frac{-\hat{k} \cdot \vec{P}_A}{2} \mathcal{L}_2 \left\{ 1 - \left[\frac{2}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}} \mathcal{D}_2 + \frac{1}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ (1-1) \hat{k} \cdot \vec{P}_A \{ \mathcal{L}_1 [-1 + \omega_{\text{so}} \mathcal{D}_1] + \mathcal{L}_2 [+1 + \omega_{\text{so}} \mathcal{D}_2] \} \frac{2y}{3} \\ &= +\mathcal{L}_1 \left\{ 1 + \left[-\frac{1}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_1 + \frac{16}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &+ 2\mathcal{L}_2 \left\{ 1 + \left[\frac{1}{6} + \omega_{\text{so}} \mathcal{D}_2 + \frac{13}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &- \hat{k} \cdot \vec{P}_A \mathcal{L}_1 \left[\frac{2}{3} - \frac{8}{3} \omega_{\text{so}} \mathcal{D}_1 \right] y + \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \left[\frac{2}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y \end{aligned} \quad (5.44)$$

5.1.3 The Imaginary Part of the Polarizability Difference

The imaginary difference is given by:

$$2\Im\psi = 2\Im(k_+ - k_-) \frac{l}{2} = \frac{l[A]2\pi r_e c f_1 \omega}{\omega_1} C\Im(\alpha_+ - \alpha_-) \quad (5.45)$$

The difference of the imaginary parts of the polarizability is given by:

$$\begin{aligned} C\Im(\alpha_+ - \alpha_-) &= \frac{(1 - \hat{k} \cdot \vec{P}_A)}{2} \mathcal{L}_1 \left\{ 1 + \left[\frac{2}{3} - \frac{8}{3} \omega_{\text{so}} \mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_1 + \frac{4+12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &+ \mathcal{L}_2 \left\{ 1 - \left[\frac{1}{3} + \frac{7}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{2} + \omega_{\text{so}} \mathcal{D}_2 + \frac{1+12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ \frac{\hat{k} \cdot \vec{P}_A}{2} \mathcal{L}_2 \left\{ 1 + \left[\frac{2}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}} \mathcal{D}_2 + \frac{1}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ (1-1) \hat{k} \cdot \vec{P}_A \{ \mathcal{L}_1 [-1 + \omega_{\text{so}} \mathcal{D}_1] + \mathcal{L}_2 [+1 + \omega_{\text{so}} \mathcal{D}_2] \} \frac{2y}{3} \\ &- \frac{(1 + \hat{k} \cdot \vec{P}_A)}{2} \mathcal{L}_1 \left\{ 1 - \left[\frac{2}{3} - \frac{8}{3} \omega_{\text{so}} \mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_1 + \frac{4+12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \end{aligned}$$

$$\begin{aligned}
& -\mathcal{L}_2 \left\{ 1 + \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{2} + \omega_{\text{so}}\mathcal{D}_2 + \frac{1+12}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + \frac{\hat{k} \cdot \vec{P}_A}{2} \mathcal{L}_2 \left\{ 1 - \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& - (1-1)\hat{k} \cdot \vec{P}_A \{ \mathcal{L}_1 [-1 + \omega_{\text{so}}\mathcal{D}_1] + \mathcal{L}_2 [+1 + \omega_{\text{so}}\mathcal{D}_2] \} \frac{2y}{3} \\
= & + \mathcal{L}_1 \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y - \hat{k} \cdot \vec{P}_A \mathcal{L}_1 \left\{ 1 + \left[-\frac{1}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{16}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
& - 2\mathcal{L}_2 \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \left\{ 1 + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \quad (5.46)
\end{aligned}$$

5.1.4 The Real Part of the Polarizability Sum

The real sum is given by:

$$\Re(k_+ + k_-) = \frac{[A]2\pi r_e c f_1 \omega}{\omega_1} C\Re(\alpha_+ + \alpha_-) \quad (5.47)$$

The sum of the real parts of the polarizability is given by:

$$\begin{aligned}
C\Re(\alpha_+ + \alpha_-) &= \frac{(1 - \hat{k} \cdot \vec{P}_A)}{2} \mathcal{D}_1 \left\{ 1 + \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4+12}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3\frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
& + \mathcal{D}_2 \left\{ 1 - \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{2} + \omega_{\text{so}}\mathcal{D}_2 + \frac{1+12}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + \frac{\hat{k} \cdot \vec{P}_A}{2} \mathcal{D}_2 \left\{ 1 + \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + (1-1)\hat{k} \cdot \vec{P}_A \left\{ \mathcal{D}_1 [-1 + \omega_{\text{so}}\mathcal{D}_1] + \mathcal{D}_2 [+1 + \omega_{\text{so}}\mathcal{D}_2] - \frac{1}{2}\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \right\} \frac{2y}{3} \\
& + (1 - \hat{k} \cdot \vec{P}_A) \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{2}{3}y + \frac{1}{3}y^2 \right\} + \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{7}{6}y - \frac{1}{2}y^2 \right\} + \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{2-1}{3}y + \frac{1}{2}y^2 \right\} \\
& + \frac{(1 + \hat{k} \cdot \vec{P}_A)}{2} \mathcal{D}_1 \left\{ 1 - \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{4+12}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3\frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\
& + \mathcal{D}_2 \left\{ 1 + \left[\frac{1}{3} + \frac{7}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{2} + \omega_{\text{so}}\mathcal{D}_2 + \frac{1+12}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + \frac{-\hat{k} \cdot \vec{P}_A}{2} \mathcal{D}_2 \left\{ 1 - \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}}\mathcal{D}_2 + \frac{1}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\
& + (1-1)\hat{k} \cdot \vec{P}_A \left\{ \mathcal{D}_1 [-1 + \omega_{\text{so}}\mathcal{D}_1] + \mathcal{D}_2 [+1 + \omega_{\text{so}}\mathcal{D}_2] - \frac{1}{2}\mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \right\} \frac{2y}{3} \\
& + (1 + \hat{k} \cdot \vec{P}_A) \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ -\frac{2}{3}y + \frac{1}{3}y^2 \right\} + \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ -\frac{7}{6}y - \frac{1}{2}y^2 \right\} + \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{1}{3}y - \frac{1}{2}y^2 \right\} \\
= & + \mathcal{D}_1 \left\{ 1 + \left[-\frac{1}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_1 + \frac{16}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3\frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} - \hat{k} \cdot \vec{P}_A \mathcal{D}_1 \left[\frac{2}{3} - \frac{8}{3}\omega_{\text{so}}\mathcal{D}_1 \right] y \\
& + 2\mathcal{D}_2 \left\{ 1 + \left[\frac{1}{6} + \omega_{\text{so}}\mathcal{D}_2 + \frac{13}{9}\omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3\frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} + \hat{k} \cdot \vec{P}_A \mathcal{D}_2 \left[\frac{2}{3} - \frac{4}{3}\omega_{\text{so}}\mathcal{D}_2 \right] y \\
& + \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{2}{3}y^2 \right\} - \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} y^2 + \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \frac{2}{3}y - \hat{k} \cdot \vec{P}_A \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{4}{3}y \right\} \quad (5.48)
\end{aligned}$$

5.1.5 The Real Part of the Polarizability Difference

The real difference is given by:

$$2\Re\psi = 2\Re(k_+ - k_-) \frac{l}{2} + 4\phi_h = \frac{l[A]2\pi r_e c f_1 \omega}{\omega_1} C\Re(\alpha_+ - \alpha_-) + 4\phi_h \quad (5.49)$$

The difference of the real parts of the polarizability is given by:

$$\begin{aligned} C\Re(\alpha_+ - \alpha_-) &= \frac{(1 - \hat{k} \cdot \vec{P}_A)}{2} \mathcal{D}_1 \left\{ 1 + \left[\frac{2}{3} - \frac{8}{3} \omega_{\text{so}} \mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_1 + \frac{4 + 12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3 \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &+ \mathcal{D}_2 \left\{ 1 - \left[\frac{1}{3} + \frac{7}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{2} + \omega_{\text{so}} \mathcal{D}_2 + \frac{1 + 12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3 \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ \frac{\hat{k} \cdot \vec{P}_A}{2} \mathcal{D}_2 \left\{ 1 + \left[\frac{2}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}} \mathcal{D}_2 + \frac{1}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3 \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ (1 - 1) \hat{k} \cdot \vec{P}_A \left\{ \mathcal{D}_1 [-1 + \omega_{\text{so}} \mathcal{D}_1] + \mathcal{D}_2 [+1 + \omega_{\text{so}} \mathcal{D}_2] - \frac{1}{2} \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \right\} \frac{2y}{3} \\ &+ (1 - \hat{k} \cdot \vec{P}_A) \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{2}{3} y + \frac{1}{3} y^2 \right\} + \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{7}{6} y - \frac{1}{2} y^2 \right\} + \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{2 - 1}{3} y + \frac{1}{2} y^2 \right\} \\ &- \frac{(1 + \hat{k} \cdot \vec{P}_A)}{2} \mathcal{D}_1 \left\{ 1 - \left[\frac{2}{3} - \frac{8}{3} \omega_{\text{so}} \mathcal{D}_1 \right] y + \left[-\frac{1}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_1 + \frac{4 + 12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3 \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &- \mathcal{D}_2 \left\{ 1 + \left[\frac{1}{3} + \frac{7}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} + \frac{1}{2} + \omega_{\text{so}} \mathcal{D}_2 + \frac{1 + 12}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3 \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &- \frac{-\hat{k} \cdot \vec{P}_A}{2} \mathcal{D}_2 \left\{ 1 - \left[\frac{2}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \left[-\frac{1}{3} - 2\omega_{\text{so}} \mathcal{D}_2 + \frac{1}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3 \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &- (1 - 1) \hat{k} \cdot \vec{P}_A \left\{ \mathcal{D}_1 [-1 + \omega_{\text{so}} \mathcal{D}_1] + \mathcal{D}_2 [+1 + \omega_{\text{so}} \mathcal{D}_2] - \frac{1}{2} \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \right\} \frac{2y}{3} \\ &- (1 + \hat{k} \cdot \vec{P}_A) \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ -\frac{2}{3} y + \frac{1}{3} y^2 \right\} - \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ -\frac{7}{6} y - \frac{1}{2} y^2 \right\} - \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{1}{3} y - \frac{1}{2} y^2 \right\} \\ &= +\mathcal{D}_1 \left[\frac{2}{3} - \frac{8}{3} \omega_{\text{so}} \mathcal{D}_1 \right] y - \hat{k} \cdot \vec{P}_A \mathcal{D}_1 \left\{ 1 + \left[-\frac{1}{3} - \frac{4}{3} \omega_{\text{so}} \mathcal{D}_1 + \frac{16}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_1^2 - 3 \frac{\mathcal{L}_1}{\gamma_1} \right) \right] y^2 \right\} \\ &- 2\mathcal{D}_2 \left[\frac{1}{3} + \frac{7}{3} \omega_{\text{so}} \mathcal{D}_2 \right] y + \hat{k} \cdot \vec{P}_A \mathcal{D}_2 \left\{ 1 + \left[-\frac{1}{3} - 2\omega_{\text{so}} \mathcal{D}_2 + \frac{1}{9} \omega_{\text{so}}^2 \left(4\mathcal{D}_2^2 - 3 \frac{\mathcal{L}_2}{\gamma_2} \right) \right] y^2 \right\} \\ &+ \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} \left\{ \frac{7}{3} y \right\} + \hat{k} \cdot \vec{P}_A \mathcal{L}_2 \frac{\omega_{\text{so}}}{\gamma_2} y^2 + \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{4}{3} y \right\} - \hat{k} \cdot \vec{P}_A \mathcal{L}_1 \frac{\omega_{\text{so}}}{\gamma_1} \left\{ \frac{2}{3} y^2 \right\} \quad (5.50) \end{aligned}$$

5.2 D1 & D2 Absorption Spectroscopy

5.2.1 Experimental Signal: The Absorption Cross Section

For absorption measurements:

1. The intensity of the probe beam is kept very small so that there is essentially no optical pumping. Therefore the alkali polarization is thermal and essentially zero, $P_A = 0$.
2. The alkali vapor is subject only to the earth's magnetic field. This is less than a gauss, so we take the field to be zero, $B = y = 0$.
3. A PEM will not be used, therefore, $\beta_0 = 0$ and $J_n(0) = \delta_{n0}$.
4. There is no analyzer half-wave plate, $\phi_h = 0$.
5. Only the total (sum) intensity before and after the alkali vapor is measured.

The transmitted intensity is therefore given by:

$$I_t = 2\zeta [\cosh(2\Im\psi) - \sinh(2\Re\psi)] \quad 2\zeta = I_0 e^{-l\Im\{k_+ + k_-\}} \quad \psi = \Im(k_+ - k_-) \frac{l}{2} \quad (5.51)$$

where I_0 is the intensity of the probe beam before the alkali vapor and the imaginary sum & difference of the polarizabilities are given by:

$$\Im(\alpha_+ - \alpha_-) = 0 \quad \Im(\alpha_+ + \alpha_-) = \mathcal{L}_1 + 2\mathcal{L}_2 \quad (5.52)$$

We'll now introduce the absorption cross section:

$$\sigma(\nu) = \frac{\Im(k_+ + k_-)}{[A]\ell} = 2\pi r_e c \left[\left(\frac{\omega}{\omega_1} \right) f_1 \mathcal{L}_1 + \left(\frac{\omega}{\omega_2} \right) f_2 \mathcal{L}_2 \right] \quad (5.53)$$

We'll make the approximations $\omega \approx \omega_1$ & $\omega \approx \omega_2$ and the substitutions $\nu = \omega/(2\pi)$ & $\Gamma/2 = \gamma/(2\pi)$ to get:

$$\sigma(\nu) = r_e c \left[\frac{f_1 \Gamma_1/2}{(\nu - \nu_1)^2 + \Gamma_1^2/4} + \frac{f_2 \Gamma_2/2}{(\nu - \nu_2)^2 + \Gamma_2^2/4} \right] \quad (5.54)$$

where ν is the laser frequency, r_e is the classical electron radius, c is the speed of light in a vacuum, $f_{1(2)}$ is the D1(2) oscillator strength, $\nu_{1(2)}$ is the D1(2) transition frequency, and $\Gamma_{1(2)}$ is the full width at half maximum pressure broadening D1(2) line width.

The probe beam from the Ti:Sapphire (aka Single Frequency aka Ring) laser has a frequency dependent intensity which is modulated by an optical chopper at a frequency ω_{mod} :

$$I_0(\nu, t) = I_0(\nu) \left[\frac{1}{2} + \frac{2}{\pi} \sum_{k=1}^{\infty} \frac{\sin((2k-1)\omega_{\text{mod}}t)}{2k-1} \right] \quad (5.55)$$

where we've explicitly written the Fourier decomposition of the square wave produced by the chopper. The reference and transmitted intensities are converted into AC voltages (due to the chopper) by the photodiodes, amplified by the "photodiode box," converted into DC signals by the Lock-In amplifiers (referenced to ω_{mod}), and finally digitized by the "autoscan interface box:"

$$N_{\text{ref}}(\nu) = G_{\text{PD1}} G_{\text{PD1-box}} G_{\text{lockin-1}} G_{\text{ADC}} I_0(\nu) \quad (5.56)$$

$$N_{\text{trans}}(\nu) = G_{\text{PD2}} G_{\text{PD2-box}} G_{\text{lockin-2}} G_{\text{ADC}} I_t(\nu) \quad (5.57)$$

where N is the number of bits from 0 to 4095 that the data channel reads. The raw data recorded in the ".SCN" file are the frequencies and the values of N_{ref} and N_{trans} in binary format. Before analysis, they have to be converted into ASCII format using a LabVIEW vi called "readscn.vi." We ultimately want to fit to $\sigma(\nu)$. Therefore the analysis program first makes the following transformation:

$$x = \nu \quad y = \log \left(\frac{N_{\text{trans}}}{N_{\text{ref}}} \right) = -[A]\sigma(x)l + \log \left(\frac{G_{\text{PD2}} G_{\text{PD2-box}} G_{\text{lockin-2}}}{G_{\text{PD1}} G_{\text{PD1-box}} G_{\text{lockin-1}}} \right) \quad (5.58)$$

5.2.2 Corrections to the Line Shape

Introduction

Eqn. (5.54) implies that the line shape is a sum of pure lorentzian curves. However, it neglects:

1. An oscillatory background due to imperfect cancellation of the interference pattern produced by the cover of the photodiodes.
2. Natural line width
3. Doppler broadening
4. Finite hyperfine splittings of the ground and excited states.

5. Natural isotopic composition of the alkali vapor
6. Possible “leakage” of the wings of nearby absorption lines

Since we claim that the PB method is accurate at the 1 percent level (or even less), we’ll discuss the above points more carefully.

When trying to determine how small of an effect is small enough to ignore, it’s important to keep in mind the relative scales of the line shape. The FWHM of the absorption curve is about 20 GHz/amagat; so, an 8 amagat cell has about a 160 GHz FWHM. The frequency resolution (frequency jitter/noise and line width) of the Ti:Sapphire is about 1 MHz. Data is acquired in about 1 GHz intervals. The accuracy of the Autoscan Wavemeter is in principle easily sub-GHz. However, in practice, the frequency can be shifted by as much as 20 GHz with the shift being independent of frequency. The quantities of interest are *insensitive* to the absolute frequency. This is because we only use the width of the line (and not the shift of the line) to determine the noble gas density. In addition, the alkali density is derived from the “size” of the dip and not from the “location.” As a final note, it’s important to mention that the data acquisition time interval and lock-in time constant are chosen carefully to minimize lock-in time averaging signal shaping effects (minimum time between points > five lock-in time constants).

Natural Line width

The natural line width is given by the spontaneous emission rate. For both lines of potassium and rubidium, the excited state lifetimes are all about $\tau \approx 30$ ns. Therefore the natural line width is about $\gamma_{\text{nat}} = \tau^{-1} \approx 0.03$ GHz. This is negligible.

Doppler Broadening

Doppler broadening of a spectral line is due to the Doppler shift. The Doppler width is obtained from the width of the velocity distribution of the gas molecules or atoms. In our case, this is the Maxwell velocity distribution, which is Gaussian. The FWHM as a fraction of the transition frequency is given by the formula (Demtroder, page 68, eq 3.43c):

$$\frac{\delta\nu_D}{\nu_0} = 7.16 \times 10^{-7} \sqrt{\frac{T \text{ (in Kelvin)}}{M \text{ (in grams per mole)}}} \quad (5.59)$$

For the D2 lines of Potassium and Rubidium at 150 C, the doppler widths are 0.91 GHz and 0.60 GHz respectively. These widths are less than one percent of the pressure broadened widths and are therefore negligible(?). For much lower pressure broadened widths, this is not negligible and the data must be fit to a Voigt profile, which is a convolution of a lorentzian line shape (pressure broadening) with a Gaussian line shape (Doppler broadening). An alternative is to simulate the effect and determine a Doppler correction factor.

Effect of Buffer Gas Collisions

When the collision between the alkali metal atom and perturbing atom occurs instantaneously ($T_d = 0$), then the absorption line shape is written as:

$$L(\Delta) = \frac{1}{2\pi} \frac{\gamma}{\Delta^2 + \gamma^2/4} \quad (5.60)$$

$$\Delta \equiv \omega - \omega_0 - \delta\omega(T) \quad (5.61)$$

$$\gamma = \gamma_{\text{nat}} + \langle\sigma v\rangle_{\text{pb}}(T)[N] \quad (5.62)$$

where γ is the FWHM broadening rate, Δ is the detuning from resonance ($\omega_0 + \delta\omega$), $\delta\omega$ is the temperature dependent resonance detuning shift due to collisions, γ_{nat} is the natural line width, $\langle\sigma v\rangle_{\text{pb}}(T)$ is the temperature dependent velocity averaged collisional cross section, and $[N]$ is the perturber density. This is called

the impact approximation. Generalizing to finite collision times ($T_d \neq 0$) results in a detuning dependent broadening rate:

$$L(\Delta) = \frac{1}{2\pi} \frac{\gamma(x(T))}{\Delta^2 + \gamma(0)^2/4} \quad (5.63)$$

$$x(T) \equiv \Delta(T)T_d(T) \quad (5.64)$$

The exact form of $\gamma(x)$ depends on the interatomic potentials between the alkali atom and the perturber atom. If a van der Waals potential of the form:

$$\hbar(V_{\text{excited}} - V_{\text{ground}}) = \hbar\Delta V(R) = -\frac{C_6}{R^6} \quad (5.65)$$

is assumed to be the interatomic potential (where R is the interatomic separation) and working the low perturber density regime ($T_d\gamma \ll 1$), then Walkup et al [30] showed that the broadening rate could be written as:

$$\gamma(x) = \gamma_{\text{nat}} + \langle\sigma v\rangle_{\text{pb}}(x(T))[N] \quad (5.66)$$

$$\langle\sigma v\rangle_{\text{pb}}(x(T)) = 8\pi R_{\text{th}}^2(T)v_{\text{th}}(T)f(x(T)) \quad (5.67)$$

$$v_{\text{th}}(T) = \sqrt{\frac{2kT}{\mu}} \quad (5.68)$$

$$R_{\text{th}}(T) = \sqrt[5]{|C_6|v_{\text{th}}^{-1}} \quad (5.69)$$

$$T_d(T) \equiv \frac{R_{\text{th}}}{v_{\text{th}}} = \sqrt[5]{|C_6|v_{\text{th}}^{-6}} \quad (5.70)$$

where v_{th} is the most probable thermal velocity in the center of mass system, μ is the reduced mass, R_{th} is the effective collision radius, T_d is the temperature dependent effective collision duration time, and $f(x, T)$ is a dimensionless function that contains the detuning dependence.

Walkup et al calculated $f(x, T)$ in three regimes:

$$f(x, T) \approx \left\{ \begin{array}{ll} \frac{\pi}{6}\sqrt{x} & x < -2.4 \\ 0.3380 - 0.2245x & -1.5 < x < 0.5 \\ 0.8464\sqrt{x} \exp[-2.1341x^{\frac{5}{9}}] & x > 2.4 \end{array} \right\} \quad (5.71)$$

Near resonance, $x \approx 0$, the FWHM in the numerator should be replaced with:

$$\Gamma_n \rightarrow \Gamma_n \left[1 - \left(\frac{0.2245}{0.3380} \right) T_d^n 2\pi(\nu - \nu_n) \right] \quad (5.72)$$

where n refers to the Dn transition & T_d^n is the effective collision time.

Finite Hyperfine Splitting, Isotopic Composition, and Wing Leakage

Table A.6 lists the hyperfine splittings of all the alkali metal isotopes (AIV₇₇ = Arimondo et al, RMP, 49, p31-75 (1977)). The natural abundance of each of these isotopes is listed in table A.5 (NIST_x = NIST websites). The hyperfine interaction between the nuclear spin and electron angular momentum causes an additional small splitting of the spectral line. This splitting, if not accounted for, would appear as a slight additional broadening. All the excited state hyperfine splittings are less than 0.5 GHz and therefore will be neglected. The ground state hyperfine splitting for both isotopes of Rb are larger than 3 GHz, see table A.6. The energy shifts due to the hyperfine splitting of ground state are given by:

$$\frac{\Delta E_F}{h} = \Delta\nu_F = \Delta x_F = \frac{A}{2} \left[F(F+1) - I(I+1) - \frac{3}{4} \right] \quad (5.73)$$

where I is the nuclear spin of the isotope and $F = I \pm \frac{1}{2}$.

This is large enough to worry about for Rb and therefore each line of Rb should be fit to a set of *four* Lorentzians, two for the hyperfine splitting and one for each isotope:

$$\begin{aligned}
y = & 0.7217c_0 \left(\left[\frac{7}{12} \right] \frac{[1 + 0.664 \times 2\pi c_1 (x - c_2 + 1.264887)]}{(x - c_2 + 1.264887)^2 + \frac{c_3^2}{4}} \right. \\
& \left. + \left[\frac{5}{12} \right] \frac{[1 + 0.664 \times 2\pi c_1 (x - c_2 - 1.770844)]}{(x - c_2 - 1.770844)^2 + \frac{c_3^2}{4}} \right) \\
& + 0.2783c_0 \left(\left[\frac{5}{8} \right] \frac{[1 + 0.664 \times 2\pi c_1 (x - c_2 + 2.563005)]}{(x - c_2 + 2.563005)^2 + \frac{c_3^2}{4}} \right. \\
& \left. + \left[\frac{3}{8} \right] \frac{[1 + 0.664 \times 2\pi c_1 (x - c_2 - 4.271676)]}{(x - c_2 - 4.271676)^2 + \frac{c_3^2}{4}} \right) + c_4 \tag{5.74}
\end{aligned}$$

where x , the laser frequency, is in units of GHz and the parameters c_0, c_1, c_2, c_3 & c_4 are:

$$\int_0^\infty \sigma(\nu) d\nu = \sigma_0 = \pi r_e c f \tag{5.75}$$

$$c_0 = -\frac{[A]l\sigma_0\Gamma}{2\pi} \quad (\text{GHz}^2) \tag{5.76}$$

$$c_1 = T_d \quad (\text{GHz}^{-1}) \tag{5.77}$$

$$c_2 = \nu_0 \quad (\text{GHz}) \tag{5.78}$$

$$c_3 = \Gamma \quad (\text{GHz}) \tag{5.79}$$

$$c_4 = \log \left(\frac{G_{\text{PD2}} G_{\text{PD2-box}} G_{\text{lockin-2}}}{G_{\text{PD1}} G_{\text{PD1-box}} G_{\text{lockin-1}}} \right) \quad (\text{unitless}) \tag{5.80}$$

Only one isotope of K has a hyperfine splitting of greater than 1 GHz. However, that isotope (^{40}K) is naturally abundant only at the ppm level, which is negligible. The more abundant isotopes of K have negligible (< 1 GHz) hyperfine splittings. The potassium D1 and D2 lines are very close (≈ 1700 GHz) compared to the expected widths (≈ 160 GHz). Note that this is not a problem for Rb, because the D1 and D2 lines are well separated (≈ 7100 GHz) compared to their widths (≈ 160 GHz). Although the D1 line for K and the D2 line for Rb are well separated (≈ 5000 GHz) compared to their widths (≈ 160 GHz), the relative size of the “peaks” is expected to be about 10 to 1 favoring K. This may mean that the K D1 line leaks into the Rb D2 line. We’ll have to see what the data looks like, but if this is the case, then we’ll need to fit the K D1, K D2, and Rb D2 lines altogether. If that is not the case, then the Rb D2 can be fit separately but the K D1 and D2 lines still should be fit together (neglecting the small hyperfine splitting for K):

$$y = \underbrace{\frac{c_0 [1 + 0.664 \times 2\pi c_1 (x - c_2)]}{(x - c_2)^2 + \frac{c_3^2}{4}}}_{\text{D1}} + \underbrace{\frac{c_5 [1 + 0.664 \times 2\pi c_6 (x - c_7 - 1730.32)]}{(x - c_7 - 1730.32)^2 + \frac{c_8^2}{4}}}_{\text{D2}} + c_4 \tag{5.81}$$

where, for K, (c_0, c_1, c_2, c_3) refer to the D1 transition and analogously (c_5, c_6, c_7, c_8) refer to the D2 transition.

5.2.3 ^3He Density: Pressure Broadening

The density of the buffer gas is proportional to the FWHM (full-width half maximum) of the line shape and for Rubidium [31]:

$$c_3 = \Gamma = \langle \sigma v \rangle_{\text{Rb-}^3\text{He}} [^3\text{He}] + \langle \sigma v \rangle_{\text{Rb-N}_2} [\text{N}_2] \tag{5.82}$$

$$\langle \sigma v \rangle_{\text{Rb-D1-}^3\text{He}} = 18.7 \left(\frac{T}{353 \text{ K}} \right)^{0.05, 0.11} \frac{\text{GHz}}{\text{amagat}} \tag{5.83}$$

$$\langle \sigma v \rangle_{\text{Rb-D}_1\text{-N}_2} = 17.8 \left(\frac{T}{353 \text{ K}} \right)^{0.30} \frac{\text{GHz}}{\text{amagat}} \quad (5.84)$$

$$\langle \sigma v \rangle_{\text{Rb-D}_2\text{-}^3\text{He}} = 20.8 \left(\frac{T}{353 \text{ K}} \right)^{0.53,0.34} \frac{\text{GHz}}{\text{amagat}} \quad (5.85)$$

$$\langle \sigma v \rangle_{\text{Rb-D}_2\text{-N}_2} = 18.1 \left(\frac{T}{353 \text{ K}} \right)^{0.30} \frac{\text{GHz}}{\text{amagat}} \quad (5.86)$$

To get the correct helium density, one has to know the temperature of the cell and the nitrogen density (gotten from filling data). (Reference: Romalis, Miron, and Cates, PRA Vol 56 Num 6 p4569 (1997)) For Potassium, we've cross calibrated the number for Helium-3, but assumed the same for Nitrogen:

$$\langle \sigma v \rangle_{\text{K-D}_1\text{-}^3\text{He}} = 14.4 \left(\frac{T}{353 \text{ K}} \right)^{0.41} \frac{\text{GHz}}{\text{amagat}} \quad (5.87)$$

$$\langle \sigma v \rangle_{\text{Rb-D}_1\text{-N}_2} = 17.8 \left(\frac{T}{353 \text{ K}} \right)^{0.30} \frac{\text{GHz}}{\text{amagat}} \quad (5.88)$$

$$\langle \sigma v \rangle_{\text{K-D}_2\text{-}^3\text{He}} = 20.15 \left(\frac{T}{353 \text{ K}} \right)^{0.23} \frac{\text{GHz}}{\text{amagat}} \quad (5.89)$$

$$\langle \sigma v \rangle_{\text{Rb-D}_2\text{-N}_2} = 18.1 \left(\frac{T}{353 \text{ K}} \right)^{0.30} \frac{\text{GHz}}{\text{amagat}} \quad (5.90)$$

5.2.4 Alkali Density: Total Absorption

The alkali density is proportional to the size of the the ‘‘absorption dip’’ of the line shape:

$$[A] = -c_0 \frac{2\pi}{l\sigma_0\Gamma} = -c_0 \frac{2\pi}{l\pi r_e c f c_3} = -\frac{c_0}{c_3} \frac{2}{l r_e c f} \quad (5.91)$$

where l is the path length through the cell, $r_e = 2.817940325 \times 10^{-15}$ m (classical electron radius), c is the speed of light, and f is the oscillator strength of the transition. For both rubidium and potassium, $f = 1/3$ for the D1 transition and $f = 2/3$ for the D2 transition.

In principle, one can also get the alkali density by integrating over the line shape:

$$\int_{c_2-\Delta x}^{c_2+\Delta x} y(x) dx = \int_{c_2-\Delta x}^{c_2+\Delta x} \frac{c_0}{(x-c_2)^2 + \frac{c_3^2}{4}} + \frac{c_0 0.664 \times 2\pi c_1 (x-c_2)}{(x-c_2)^2 + \frac{c_3^2}{4}} + c_4 dx \quad (5.92)$$

$$\lim_{\Delta x \rightarrow \infty} \int_{c_2-\Delta x}^{c_2+\Delta x} \frac{c_0}{(x-c_2)^2 + \frac{c_3^2}{4}} dx = 2\pi \frac{c_0}{c_3} \quad (5.93)$$

$$\int_{c_2-\Delta x}^{c_2+\Delta x} \frac{x-c_2}{(x-c_2)^2 + \frac{c_3^2}{4}} dx = 0 \text{ (by symmetry)} \quad (5.94)$$

$$\int_{c_2-\Delta x}^{c_2+\Delta x} c_4 dx = 2c_4\Delta x \quad (5.95)$$

where the alkali density is gotten from:

$$p \equiv \int_{c_2-\Delta x}^{c_2+\Delta x} y(x) dx \approx 2\pi \frac{c_0}{c_3} + 2c_4\Delta x \quad (5.96)$$

$$[A] \approx -\frac{(p - 2c_4\Delta x)}{l\pi r_e c f} \quad (5.97)$$

To do this, one must be very certain that the background integrates to zero ($c_4 \approx 0$) or to some well known value.

5.3 Paramagnetic Faraday Rotation

5.3.1 Experimental Signal: The Rotation Angle

To measure the Faraday rotation induced by the alkali vapor:

1. The detector is a rotatable half-wave plate mounted in front a beam splitting polarizing cube. The intensity of each beam from the cube is measured by a photodiode.
2. The rotation angle is encoded in the difference of the intensities.
3. The intensity of the beam must be normalized because there the intensity has a strong wavelength dependence. This is due to both the probe laser itself and the absorption by the alkali vapor itself. This can be obtained from the sum of the intensities.
4. Any remaining normalization factors can be obtained by rotating the HWP.

The sum and difference intensities are given by:

$$I_{\sigma}(\text{DC}) = 2\zeta [\cosh(2\Im\psi) - J_0(\beta_0) \sinh(2\Im\psi)] \quad (5.98)$$

$$I_{\delta}(\text{DC}) = 2\zeta \sqrt{1 - P^2} [\cos(2\theta) \cos(2\Re\psi) + J_0(\beta_0) \sin(2\theta) \sin(2\Re\psi)] \quad (5.99)$$

$$I_{\delta}(\text{AC1}) = 2\zeta \sqrt{2} J_1(\beta_0) P \sin(2\Re\psi) \quad (5.100)$$

$$2\zeta = \sqrt{\frac{\epsilon}{\mu}} \frac{E_0^2}{2} e^{-l\Im\{k_+ + k_-\}} \quad (5.101)$$

$$\psi = (k_+ - k_-) \frac{l}{2} + 2\phi_h \quad (5.102)$$

From these equations, we see for the case where a PEM isn't used ($\beta_0 = 0$):

$$\frac{I_{\delta}(\text{DC})}{I_{\sigma}(\text{DC})} = \underbrace{\left[\frac{\sqrt{1 - P^2}}{\cosh(2\Im\psi) - \sinh(2\Im\psi)} \right]}_{\text{normalization}} \cos(2\theta - 2\Re\psi) \quad (5.103)$$

With no PEM, we're interested in the DC difference over the DC sum and the probe beam must be linearly polarized, $P = 0$. When we do use a PEM and a Lock-In Amplifier for the difference signal (referenced to the PEM frequency):

$$\frac{I_{\delta}(\text{AC1})}{I_{\sigma}(\text{DC})} = \underbrace{\left[\frac{\sqrt{2} J_1(\beta_0) P}{\cosh(2\Im\psi) - J_0(\beta_0) \sinh(2\Im\psi)} \right]}_{\text{normalization}} \sin(2\Re\psi) \quad (5.104)$$

With a PEM, we're interested in the AC difference over the DC sum and the probe beam must be circularly polarized, $P = \pm 1$. Both rotation formulas contain the term $\Re\psi$. The Faraday rotation angle is defined by $\phi = \Re\psi - 2\phi_h = \Re(k_+ - k_-) \frac{l}{2}$. This implies that:

1. the electric field polarization vector rotates by an angle of ϕ due to the atomic vapor
2. the observable quantity is 2ϕ from the reference axis
3. Faraday rotation (ϕ) can be canceled by a half waveplate with an angle of $-\phi/2$ between the its axis and the reference axis

We'll now calculate the Faraday rotation angle ϕ starting with:

$$\phi = \Re\psi - 2\phi_h = \Re(k_+ - k_-) \frac{l}{2} = \frac{l[A]\pi r_e c f_1 \omega}{\omega_1} C \Re(\alpha_+ - \alpha_-) \quad (5.105)$$

Since we're making these measurements at very low field ≤ 40 gauss, we'll only keep terms up to first order in field, y , which gives for the difference of the real parts of the polarizability:

$$\begin{aligned} C\Re(\alpha_+ - \alpha_-) &= -\frac{y\omega_{\text{so}}}{3} \left[7 \left(2\mathcal{D}_2^2 - \frac{\mathcal{L}_2}{\gamma_2} \right) + 4 \left(2\mathcal{D}_1^2 - \frac{\mathcal{L}_1}{\gamma_1} \right) - 2 \left(\frac{\mathcal{D}_1 - \mathcal{D}_2}{\omega_{\text{so}}} \right) \right] \\ &\quad + \hat{k} \cdot \vec{P}_A [\mathcal{D}_2 - \mathcal{D}_1] \end{aligned} \quad (5.106)$$

There is a natural separation between the rotation due to the magnetic field (y) and the alkali polarization (P_A). Traditionally, Faraday rotation refers to the part due to the field only and the constant of proportionality is called the Verdet constant. The rotation due to the alkali polarization is called paramagnetic Faraday rotation and under our conditions will be the dominant term. Making the approximation $\omega \approx \omega_1$, making the substitution $y\omega_{\text{so}} = \mu_B B/\hbar$, using $\Delta_n = 2\pi(\nu - \nu_n)$ where ν is the probe laser frequency, using $\gamma_n = 2\pi\Gamma_n/2$ where Γ_n is the pressure broadened FWHM, and noting the following:

$$2\pi\mathcal{L}_n = \frac{\Gamma_n/2}{(\nu - \nu_n)^2 + \Gamma_n^2/4} \quad 2\pi\mathcal{D}_n = \frac{(\nu_n - \nu)}{(\nu - \nu_n)^2 + \Gamma_n^2/4} \quad (5.107)$$

we can write down the rotation formulas:

$$\begin{aligned} \phi_B &= -l[A]B \left(\frac{r_e c f_1 \mu_B}{6h} \right) \left[7 \left\{ \frac{(\nu - \nu_2)^2 - \Gamma_2^2/4}{[(\nu - \nu_2)^2 + \Gamma_2^2/4]^2} \right\} + 4 \left\{ \frac{(\nu - \nu_1)^2 - \Gamma_1^2/4}{[(\nu - \nu_1)^2 + \Gamma_1^2/4]^2} \right\} \right. \\ &\quad \left. - \left(\frac{2}{\nu_1 - \nu_2} \right) \left\{ \frac{(\nu - \nu_1)}{(\nu - \nu_1)^2 + \Gamma_1^2/4} - \frac{(\nu - \nu_2)}{(\nu - \nu_2)^2 + \Gamma_2^2/4} \right\} \right] \end{aligned} \quad (5.108)$$

$$\phi_P = l[A]P_A \cos(\theta) \left(\frac{r_e c f_1}{2} \right) \left[\frac{(\nu - \nu_1)}{(\nu - \nu_1)^2 + \Gamma_1^2/4} - \frac{(\nu - \nu_2)}{(\nu - \nu_2)^2 + \Gamma_2^2/4} \right] \quad (5.109)$$

When the probe laser frequency is far from resonance $(\nu - \nu_n) \gg \Gamma_n/2$ for both Dn transitions, then these formulas can be simplified even further to [32]:

$$\phi_B = -l[A]B \left(\frac{r_e c f_1 \mu_B}{6h} \right) \left[\frac{7}{(\nu - \nu_2)^2} + \frac{4}{(\nu - \nu_1)^2} - \frac{2}{(\nu - \nu_1)(\nu - \nu_2)} \right] \quad (5.110)$$

$$\phi_P = - \left(\frac{r_e c f_1 \nu_{\text{so}}}{2} \right) \left[\frac{l[A]P_A \cos(\theta)}{(\nu - \nu_1)(\nu - \nu_2)} \right] \quad (5.111)$$

where ν_{so} is the spin-orbit splitting in frequency. The scales for these two rotations are given by:

$$\left(\frac{180 \text{ deg}}{\pi} \right) \left(\frac{r_e c f_1 \mu_B}{6h} \right) = \frac{(3.76 \text{ millidegrees}) (1000 \text{ GHz})^2}{(1 \text{ cm}) (10^{14} \text{ cm}^{-3}) (1 \text{ gauss})} \quad (5.112)$$

$$\left(\frac{180 \text{ deg}}{\pi} \right) \left[\frac{r_e c f_1 \nu_{\text{so}}}{2} \right]_{\text{Rb}} = \frac{(57.5 \text{ degrees}) (1000 \text{ GHz})^2}{(1 \text{ cm}) (10^{14} \text{ cm}^{-3})} \quad (5.113)$$

$$\left(\frac{180 \text{ deg}}{\pi} \right) \left[\frac{r_e c f_1 \nu_{\text{so}}}{2} \right]_{\text{K}} = \frac{(14.0 \text{ degrees}) (1000 \text{ GHz})^2}{(1 \text{ cm}) (10^{14} \text{ cm}^{-3})} \quad (5.114)$$

$$(5.115)$$

5.3.2 Alkali Number Density

The alkali number densities are obtained by simply fitting the paramagnetic Faraday rotation angle vs frequency:

$$y = lP_A \cos(\theta) \left(\frac{r_e c f_1}{2} \right) \{ [\text{K}]F_{\text{K}} + [\text{Rb}]F_{\text{Rb}} \} \quad (5.116)$$

where the function F_X is given by:

$$F_X = \left(\frac{(x - \nu_1)}{(x - \nu_1)^2 + \Gamma_1^2/4} - \frac{(x - \nu_2)}{(x - \nu_2)^2 + \Gamma_2^2/4} \right) \quad (5.117)$$

To extract the alkali densities, you must know:

1. the alkali polarization, which is assumed to be the same for K and Rb
2. the laser beam path length through the cell
3. the skew angle which is usually a small correction
4. the absolute calibration of the angle obtained from the normalization with the RHWP

5.4 Probing EPR RF Transitions

5.4.1 Experimental Signal: Relative Change in the Alkali Polarization

The EPR transitions are driven using a small RF coil producing an RF field perpendicular to the main holding field. When the RF coil frequency is held constant, the holding field is swept changing the transition frequencies. To obtain an alkali EPR RF spectrum, we need some observable that indicates that an RF transition is being driven. When the alkali atoms are polarized due to optical pumping, then driving an RF transition is depolarizing. As the magnetic field is swept, the alkali polarization is lowered when the transition frequency matches the RF coil frequency. These dips or peaks in the alkali polarization correspond to a particular EPR RF transition that can be identified provided we know magnitude of the magnetic field.

The alkali polarization is given by:

$$P_A(z) = \frac{R(z)}{R(z) + \gamma + \gamma_{\text{rf}}(z)} \quad (5.118)$$

where $R(z)$ is the position dependent optical pumping rate, γ is the spin relaxation rate, and $\gamma_{\text{rf}}(z)$ is the position dependent effective relaxation rate due to the RF coil.

There are two different ways that we can measure the relative alkali polarization:

1. the paramagnetic Faraday rotation angle
2. the intensity of the D2 fluorescence emitted by the alkali vapor during optical pumping

When the Faraday rotation angle is canceled out by the RHWP, the difference signal will be zero. Therefore, small changes in the alkali polarization will result in a small changes in the rotation angle. Under the “small” condition, the change in the difference signal will be proportional to the change in rotation angle $I_\delta \propto \sin(\Delta\phi) \approx \Delta\phi$. Therefore the zeroed difference signal is directly a probe of the relative change in the alkali polarization:

$$\Delta\phi \propto \Delta P_A = P_A - P_A^0 = \frac{R}{R + \gamma + \gamma_{\text{rf}}} - \frac{R}{R + \gamma} \approx \frac{R}{R + \gamma} \left[1 - \frac{\gamma_{\text{rf}}}{R + \gamma} \right] - \frac{R}{R + \gamma} = -P_A^0 \left[\frac{\gamma_{\text{rf}}}{R + \gamma} \right] \quad (5.119)$$

where P_A^0 is the alkali polarization when the RF coil is off or the RF coil frequency is off resonance.

Although the presence of N_2 molecules greatly suppresses the number of radiative decays, a few percent of the transitions back to the ground state still occur radiatively. The amount of D1 and D2 fluorescence is essentially the same because of collisional mixing of the excited states. However, a filter is placed in front of a photodiode to allow transmission of only the D2 fluorescence. This is because the large D1 background from the pump laser light could potentially saturate the photodiode.

Therefore, the signal detected in the photodiode consists mainly of D2 fluorescence. A strong DC component is present due to the D2 light reaching the photodiode from parts of the cell that are minimally effected by the EPR excitation coil and due to the fact that the EPR excitation is very small and therefore the alkali polarization is not changing much. More important is the AC component that is at the modulation frequency of the EPR excitation coil. For the alkali polarization measurement, the amplitude of the RF coil is modulated; whereas, for the He-3 polarization measurement, the frequency of the RF coil is modulated. Either way, a lock-in amplifier is used to detect this small AC signal. The intensity of the D2 fluorescence detected by a photodiode observing the cell can be estimated by:

$$I_{\text{D2}} \approx h\nu_2 \left(\frac{\Delta\Omega}{A_{\text{pd}}} \right) \left(\frac{1}{1 + \Gamma_{\text{non}}\tau_{\text{spon}}} \right) V[A] \langle R \rangle (1 - \langle P_A \rangle) \quad (5.120)$$

where Γ_{non} is the non-radiative quenching rate, τ_{spon}^{-1} is the spontaneous emission rate, V is the volume of the pumping chamber, $\Delta\Omega$ is the solid angle subtended by the photodiode, A_{pd} is the area of the photodiode, and the brackets $\langle \rangle$ refer to a volume average over the whole pumping chamber. Rewriting $\langle R \rangle (1 - \langle P_A \rangle)$ as $\langle P_A \rangle (\gamma + \gamma_{\text{rf}})$ can be used to give the change in the D2 intensity due to the RF coils:

$$\Delta I_{\text{D2}} \approx h\nu_2 \left(\frac{\Delta\Omega}{A_{\text{pd}}} \right) \left(\frac{1}{1 + \Gamma_{\text{non}}\tau_{\text{spon}}} \right) V[A] \langle P_A^0 \rangle \gamma_{\text{rf}} \quad (5.121)$$

where the D2 fluorescence intensity depends on $\langle \gamma_{\text{rf}} \rangle$ the volume averaged effective relaxation rate due to the RF coil. In both cases, the observable is proportional to the effective relaxation rate due to the RF coil.

5.4.2 Effective Relaxation Rate Due to EPR RF Transitions

We've already calculated the change in populations due to a dipole interaction, see Sec. (3.2.3). For an RF field in the x direction, where the holding field is in the z direction, the change in population is given by:

$$\dot{\rho}_{Fm} = 2\Omega_{\text{rf}}^2 \left\{ \frac{\gamma_m (\rho_{Fm+1} - \rho_{Fm}) |u_+^-|^2 |\langle F, m+1 | S_+ | F, m \rangle|^2}{(\omega - \omega_{Fm+1Fm})^2 + \gamma_m^2} + \frac{\gamma_m (\rho_{Fm-1} - \rho_{Fm}) |u_-^+|^2 |\langle F, m-1 | S_- | F, m \rangle|^2}{(-\omega - \omega_{Fm-1Fm})^2 + \gamma_m^2} \right\} \quad (5.122)$$

The effective relaxation rate is given by the amount of change in $\langle S_z \rangle$ times the transition rate. The change in $\langle S_z \rangle$ for every $m \leftrightarrow m-1$ transition is $1/[I]$. There the effective relaxation rate is given as:

$$\frac{dP_A}{dt} = \frac{d2 \langle S_z \rangle}{dt} = \frac{4\Omega_{\text{rf}}^2}{[I]} \sum_{F,m} \frac{\gamma_m (\rho_{Fm-1} - \rho_{Fm}) |u_-^+|^2 |\langle F, m-1 | S_- | F, m \rangle|^2}{(-\omega - \omega_{Fm-1Fm})^2 + \gamma_m^2} \quad (5.123)$$

where we've labeled the transitions with the higher m value, ω is the RF coil frequency, and we've summed over all $m \leftrightarrow m-1$ transitions in both manifolds $F = I \pm 1/2$. Since $S_x = (S_+ + S_-)/2$, $|u_\pm^\pm|^2 = 1/4$ and plugging in values for the matrix element & population difference, we find:

$$\frac{dP_A}{dt} = -P_A \frac{\Omega_{\text{rf}}^2}{[I]^2} \sum_{\pm, m} Q_{I\bar{m}} ((I+1/2)(I+1/2 \pm 1) - m(m-1)) \mathcal{L}_m^\pm = -\gamma_{\text{rf}} P_A \quad (5.124)$$

where \mathcal{L}_m^\pm is the lorentzian line shape associated with the $m \leftrightarrow m-1$ transition in the $F = I \pm 1/2$ manifold:

$$\mathcal{L}_m^\pm = \frac{\gamma_m}{(\omega - \omega_{FmFm-1})^2 + \gamma_m^2} \quad (5.125)$$

where ω_{FmFm-1} is the transitions frequency. The effective spin relaxation rate is given by the sum:

$$\gamma_{\text{rf}} = \frac{\Omega_{\text{rf}}^2}{[I]^2} \sum_{\pm, m} Q_{I\bar{m}} ((I+1/2)(I+1/2 \pm 1) - m(m-1)) \mathcal{L}_m^\pm \quad (5.126)$$

5.4.3 Alkali Polarization: Ratio of Areas

The observable (rotation angle or D2 light intensity) is proportional to the effective spin relaxation rate which is given by the sum:

$$\frac{\Omega_{\text{rf}}^2}{[I]^2} \sum_{\pm, m} Q_{I\bar{m}} ((I+1/2)(I+1/2 \pm 1) - m(m-1)) \mathcal{L}_m^\pm \quad (5.127)$$

When the field is high enough, the transitions frequency are spaced far enough apart, relative to the width γ_m , that only one term dominated the effective relaxation rate. In other words, the peaks corresponding to

the different transitions are well resolved. In practice, we can make adjacent transitions ($m \leftrightarrow m - 1$ and $m - 1 \leftrightarrow m - 2$) well resolved, but the twin transitions ($F = I + 1/2, m \leftrightarrow m - 1$ and $F = I - 1/2, m \leftrightarrow m - 1$) are unresolved.

The area under each peak is given by [24, 32]:

$$A_{Fm} = A_0 f_I [A] \left[\frac{B_{\text{rf}}}{2I + 1} \right]^2 [F(F + 1) - m(m - 1)] \frac{\exp(\beta \bar{m})}{Z_I} \quad (5.128)$$

where F labels the manifold, m refers to the $m \leftrightarrow m - 1$ transition, A_0 is area factor common to all transitions, f_I is the isotopic fraction of the alkali species, I is the nuclear spin of that species, β is the spin temperature, and $\bar{m} = m - 1/2$ is the mean m of the transition.

The ratio of the area of two peaks for the same alkali species is given by:

$$r = \frac{A_{Fm} + A_{F'm}}{A_{Fm'} + A_{F'm'}} = \left[\frac{F(F + 1) - m(m - 1) + F(F - 1) - m(m - 1)}{F(F + 1) - m'(m' - 1) + F(F - 1) - m'(m' - 1)} \right] \exp(\beta[m - m']) \quad (5.129)$$

where $F = I + 1/2$, $F' = I - 1/2$, and $\exp(\beta) = (1 + P_A)/(1 - P_A)$. We add the areas of the twin transitions together because we are assuming that they are unresolved. In addition, there is no $m = F \leftrightarrow F - 1$ transition for the F' manifold. Note however that $F(F - 1) - F(F - 1) = 0$ so the formula still holds. For the case $m - m' = 1$, we find:

$$r = \left[\frac{F(F + 1) - m(m - 1) + F(F - 1) - m(m - 1)}{F(F + 1) - (m - 1)(m - 2) + F(F - 1) - (m - 1)(m - 2)} \right] \left(\frac{1 + P_A}{1 - P_A} \right) \quad (5.130)$$

which can be solved for P_A to give:

$$P_A = \frac{[F^2 - (m - 1)(m - 2)] r - [F^2 - m(m - 1)]}{[F^2 - (m - 1)(m - 2)] r + [F^2 - m(m - 1)]} \quad (5.131)$$

When the twin transitions are unresolved and we take ratios involving the end transitions, then for a nuclear spin $I = 3/2$ isotope like K-39 or Rb-87:

$$P_A = \frac{2r - 1}{2r + 1} \quad r = \frac{A_{22}}{A_{21} + A_{11}} \quad (5.132)$$

$$P_A = \frac{r - 2}{r + 2} \quad r = \frac{A_{20} + A_{10}}{A_{2-1}} \quad (5.133)$$

whereas for a nuclear spin $I = 5/2$ isotope like Rb-85:

$$P_A = \frac{7r - 3}{7r + 3} \quad r = \frac{A_{33}}{A_{32} + A_{22}} \quad (5.134)$$

$$P_A = \frac{3r - 7}{3r + 7} \quad r = \frac{A_{3-1} + A_{2-1}}{A_{3-2}} \quad (5.135)$$

5.4.4 Alkali Density Ratio: Ratio of Areas

If we look at the same transition for two different alkali species with the same nuclear spin, then the ratio of areas gives the ratio of densities:

$$r = \frac{A_{Fm}^i + A_{F'm}^i}{A_{Fm}^k + A_{F'm}^k} = \frac{f_i[A_i]}{f_k[A_k]} \quad (5.136)$$

where $f_{i,(k)}$ is the natural isotopic fraction of alkali species i (k). For example, K-39, Rb-87, K-41, and Na-23 all have $I = 3/2$. Therefore the ratio of K-39 to Rb-87 for the same transition would give:

$$r = \frac{(0.93258)[\text{K}]}{(0.2783)[\text{Rb}]} = 3.35 \cdot D \quad (5.137)$$

where D is the ratio of K to Rb. On the other hand, we can take the ratio of K-39 to K-41 for the same transition:

$$r = \frac{(0.93258)[\text{K}]}{(0.06730)[\text{K}]} = 13.9 \quad (5.138)$$

If natural abundance K is being used, then the ratio should be equal to 13.9. This is a powerful cross check of the method.

5.4.5 ^3He Polarization: EPR Frequency Shifts

Introduction

It is sometimes profitable to measure the longitudinal nuclear spin polarization of ^3He . The method described here takes advantage of the vaporized alkali metal already present in a glass target cell. Long range and short range interactions with polarized ^3He gas result in an “effective” magnetic field felt by the alkali metal atoms. A precisely detectable Zeeman shift in the alkali EPR frequency that is proportional to the ^3He polarization and density is produced. The EPR frequency is located by exciting the EPR transition and observing the resulting change in either the D2 fluorescence intensity or the Faraday rotation angle. A PI feedback loop is used to lock to the EPR frequency while the direction of the ^3He spins is reversed via AFP with respect to any baseline magnetic fields. This isolates the ^3He contribution to the EPR frequency and consequently the ^3He polarization can be extracted. It is appropriate and obligatory to list the following references in chronological order in which this technique was developed, refined, and “calibrated:” [33, 34, 35, 36, 37].

At “low” field, the Zeeman splitting among the hyperfine states of an alkali metal is approximately linear in field. “Low” field is judged by the strength of the Zeeman interaction relative to the hyperfine interaction. For ^{39}K and ^{85}Rb , low field therefore is defined to be much less than 165 gauss and 1080 gauss respectively. An approximately linear energy splitting results in transition frequencies that are also approximately linear in field. Traditionally, the target cells are located in a magnetic holding field that is on the order of 10’s of gauss. The holding field is produced from an external source such as an electromagnet.

The alkali metal atoms experience a small additional “effective” field due to the presence of polarized ^3He gas. Under typical operating conditions, about 1/6 of this “effective” field is due to the classical magnetic field produced by the bulk magnetization of the polarized ^3He gas. The rest of the “effective” field comes from the very short but frequent spin-exchange collisions that occur between the alkali metal atoms and the ^3He atoms. During these spin-exchange collisions, the alkali valence electron is essentially located within the ^3He nucleus thus facilitating a hyperfine-like Fermi contact interaction between their spins. These two sources of an additional “effective” field are distinguished in at least three important ways:

1. The size of the classical magnetic field is dependent on the geometry of the target cell; whereas the spin-exchange “effective” field is not.
2. The size of the classical magnetic field is independent of the alkali metal being perturbed; whereas the size of the spin-exchange “effective” field *does* depend on the alkali metal.
3. The classical magnetic field can be, in principle, detected by a sufficiently sensitive external magnetic field probe; whereas the spin-exchange “effective” field can not be.

Because the spin-exchange “effective” field is difficult to calculate precisely from theory, it is usually clumped together with the classical magnetic field and parametrized by a unitless temperature dependent quantity called κ_0 , which must be measured empirically.

The “effective” field produced by the ^3He is on the order of 10’s of milligauss, which causes a frequency shift on the order of 10’s of kHz. The EPR transition is probed by sending a frequency modulated excitation into a coil located near the pumping chamber of the target cell. This excitation induces EPR transitions in the alkali metal atoms and therefore depolarizes them. Because of the rapid and efficient spin-exchange between alkali metal atoms, the equilibrium polarization of a volume of alkali vapor near the EPR excitation coil tracks the frequency modulation of the excitation. When the excitation is off resonance, the alkali polarization is high. When the excitation is on resonance, the alkali polarization is lowered. This results in a modulation of the alkali polarization which in turn results in a modulation of the intensity of the D2 fluorescence or the Faraday rotation angle. Because of the frequency modulation of the EPR excitation, the

line shape that is produced when the lock-in response is plotted against the central frequency of the EPR excitation is the derivative of a lorentzian-like line shape.

This “FM sweep” line shape directly determines the behavior of the feedback loop used to lock to the EPR transition. Modulation and lock-in parameters must be adjusted to produce an optimal “FM sweep” line shape. The gains of the PI feedback box are then chosen based on the “feedback slope” extracted from the “FM sweep” line shape. The “feedback slope” is typically in units of μV per kHz and provides a conversion between the central excitation frequency detuning from EPR frequency and the voltage response of the excitation/sensing electronics. The analog voltage signal from the lock-in is then processed by a PI feedback box and converted into a frequency correction that is applied to the central frequency of the VCO that is generating the EPR excitation.

Once the EPR frequency is locked to by the excitation/sensing electronics, the excitation frequency is recorded by a counter as a function of time. The ^3He spins are then flipped twice relative to the holding field using NMR frequency sweep AFP. Enough counter data is taken with the ^3He in either state to result in a high precision determination of the EPR frequencies of the alkali atoms. The difference in these EPR frequencies is, to first order, proportional to the “effective” field and therefore polarization of the ^3He .

Extracting the Helium Polarization

When we start the measurement, the field seen by the alkali atoms is $B_1 = B_0 + B_{\text{He}}$, which corresponds to an EPR frequency of ν_1 . After we’ve measured ν_1 we flips the He-3 spins using frequency sweep adiabatic fast passage (AFP). We measure the EPR frequency again and obtain ν_2 which corresponds to a field of $B_2 = B_0 - B_{\text{He}}$. Finally we flip the He-3 spins back to their original orientation and get a third frequency ν_3 . We’ll assume for now that the He-3 polarization does not change during the measurement. The difference in fields $(B_1 - B_2)/2 = \Delta B/2 = B_{\text{He}}$ isolates the contribution from the He-3.

There are two ways to calculate ΔB from the frequencies ν_1 and ν_2 . We’ll assume that the end transition is being probed and consequently the end frequency is being measured. In method 1, we use the following equation to “invert” the frequency to get the field:

$$B(\nu) = \left(\frac{[I]h\nu}{g_I\mu_N} \right) \frac{\epsilon(1-f)}{1 - [I] \left\{ f(1-\epsilon) + \frac{\epsilon}{2} \right\} + \sqrt{(1 - [I]\frac{\epsilon}{2})^2 - 2f[I] \left(1 - \epsilon + [I]\frac{\epsilon-f}{2} \right)}} \quad (5.139)$$

where $s = \pm 1$ is the sign of the edge state involved in the transition and:

$$[I] = 2I + 1 \quad f = s\nu/\nu_{hf_s} \quad \epsilon = 1 - a = \frac{2g_I\mu_N}{g_I\mu_N - g_S\mu_B} = g_I \frac{\mu_N}{\mu_B} \left[\frac{-2}{g_S} \right] \left(1 - \frac{g_I\mu_N}{g_S\mu_B} \right)^{-1} \quad (5.140)$$

Therefore $\Delta B = B(\nu_1) - B(\nu_2)$. This method only works if we’re probing the end transition because the analytical form for B is only valid for end transitions. In method 2, we make the following approximation:

$$\Delta B = (\nu_1 - \nu_2) \times \left(\frac{d\nu}{dB} \right)^{-1} \quad (5.141)$$

where the derivative of the frequency with respect to the field is given by Eqns. (1.292) or (1.293). This method can be used for any transition.

Once we have ΔB , we can find the He-3 polarization from the effective field due to the He-3 using:

$$\Delta B/2 = B_{\text{He}} = \frac{2\mu_0}{3} (\kappa_0 - 1 + \kappa_{\text{geo}}) [\text{He}] g_{\text{He}} \mu_N \frac{P_{\text{He}}}{2} \quad (5.142)$$

where μ_0 is the magnetic permeability of free space, κ_0 is the empirical shift constant, κ_{geo} is a geometric factor, $[\text{He}]$ is the He-3 number density, g_{He} is the He-3 g -factor, μ_N is the nuclear magneton, $P_{\text{He}} = 2 \langle S_z \rangle$ is the He-3 polarization. The values for κ_0 are given by [36, 37]:

$$\text{Rb} : \kappa_0 = 6.39 + 0.00924 \cdot (T - 200 \text{ }^\circ\text{C}) \quad (5.143)$$

$$\text{K} : \kappa_0 = 5.99 + 0.0086 \cdot (T - 200 \text{ }^\circ\text{C}) \quad (5.144)$$

$$\text{Na} : \kappa_0 = 4.84 + 0.00914 \cdot (T - 200 \text{ }^\circ\text{C}) \quad (5.145)$$

The geometric factor κ_{geo} is the ratio of the classical magnetic field produced by the He-3 for the cell geometry averaged over the alkali sampling volume (ASV) to the classical magnetic field produced by a uniformly polarized spherical He-3 sample with the same density and polarization:

$$\kappa_{\text{geo}} = \frac{\frac{1}{V_{\text{ASV}}} \int_{\text{ASV}} \hat{z} \cdot \vec{B}_c dV}{\hat{z} \cdot \vec{B}_{\text{sphere}}} \quad \vec{B}_{\text{sphere}} = \frac{2\mu_0}{3} [\text{He}] g_{\text{He}} \mu_N \frac{P_{\text{He}}}{2} \hat{z} \quad (5.146)$$

where \hat{z} is the direction of the holding field. The classical field \vec{B}_c can be calculated using the method of magnetic scalar potentials (See section 5.9 of Jackson, 3rd Edition):

$$\vec{B}_c = \mu_0 (\vec{H}_c + \vec{M}_c) \quad \vec{H}_c = -\vec{\nabla} \Phi_M \quad \vec{M}_c = [\text{He}] \frac{g_{\text{He}} \mu_N}{2} \vec{P}_c(\vec{r}) \quad (5.147)$$

where $\vec{P}_c(\vec{r})$ is the possibly position dependent He polarization vector. For a uniformly polarized region bounded by a surface S , the magnetic scalar potential is given by:

$$\Phi_M(\vec{r}) = \frac{1}{4\pi} \int_S \frac{\hat{n}' \cdot \vec{M}_c(\vec{r}')}{|\vec{r} - \vec{r}'|} dA' \quad (5.148)$$

where \hat{n}' is the normal unit vector pointing out of S at a position \vec{r}' on the surface S . For a region far from the polarized He-3, the magnetic scalar potential is given by:

$$\Phi_M(\vec{r}) = \frac{V \vec{M}_c \times \vec{r}}{4\pi r^3} \quad (5.149)$$

where V is the total volume of the region containing the polarized He-3. The value of κ_{geo} for a few different geometries are given here:

1. $\kappa_{\text{geo}} = 1$ for a uniformly polarized sphere
2. $\kappa_{\text{geo}} = 3/2$ for an infinitely long cylinder polarized along its axis
3. $\kappa_{\text{geo}} = 3/4$ for an infinitely long cylinder polarized perpendicular to its axis

Bibliography

- [1] Norman F. Ramsey. *Molecular Beams*. Oxford University Press, London, 1964.
- [2] G. K. Woodgate. *Elementary Atomic Structure*. Oxford University Press, Oxford, 2nd edition, 2002.
- [3] Christopher J. Foot. *Atomic Physics*. Oxford University Press, Oxford, 2005.
- [4] H. N. Russell and F. A. Saunders. New Regularities in the Spectra of the Alkaline Earths. *Astrophysical Journal*, 61:38–69, 1925.
- [5] Murray R. Spiegel. *Mathematical Handbook of Formulas and Tables*. Schaum's Outline Series. McGraw-Hill, New York, 1993.
- [6] G. Breit and I. I. Rabi. Measurement of Nuclear Spin. *Physical Review*, 38(11):2082–2083, Dec 1931.
- [7] H. Kopfermann. *Nuclear Moments*. Academic Press, New York, 1958.
- [8] William H. Press, Brian P. Flannery, Saul A. Teukolsky, and William T. Vetterling. *Numerical Recipes in C: The Art of Scientific Computing*. Cambridge University Press, Cambridge, 1st edition, 1988.
- [9] R. Clark Jones. A New Calculus for the Treatment of Optical Systems, I. Description and Discussion of the Calculus. *Journal of the Optical Society of America*, 31(7):488–493, 1941.
- [10] Henry Hurwitz Jr. and R. Clark Jones. A New Calculus for the Treatment of Optical Systems, II. Proof of Three General Equivalence Theorems. *Journal of the Optical Society of America*, 31(7):493–495, 1941.
- [11] R. Clark Jones. A New Calculus for the Treatment of Optical Systems, III. The Sohncke Theory of Optical Activity. *Journal of the Optical Society of America*, 31(7):500–503, 1941.
- [12] Frank S. Crawford Jr. *Waves*. McGraw-Hill, New York, 1968.
- [13] Milton Abramowitz and Irene A. Stegun. *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*. Dover Publications, New York, 1965.
- [14] U. Fano. Description of States in Quantum Mechanics by Density Matrix and Operator Techniques. *Reviews of Modern Physics*, 29(1):74–93, Jan 1957.
- [15] I. I. Rabi, N. F. Ramsey, and J. Schwinger. Use of Rotating Coordinates in Magnetic Resonance Problems. *Reviews of Modern Physics*, 26(2):167–171, Apr 1954.
- [16] Albert Messiah. *Quantum Mechanics, Vols. I & II*. John Wiley & Sons, New York, 1966.
- [17] Carl Eckart. The Application of Group theory to the Quantum Dynamics of Monatomic Systems. *Reviews of Modern Physics*, 2(3):305–380, Jul 1930.
- [18] Eugene P. Wigner. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. Academic Press, New York, 1959.
- [19] Alan Corney. *Atomic and Laser Spectroscopy*. Clarendon Press, Oxford, 1977.

- [20] E.U. Condon and G.H. Shortley. *The Theory of Atomic Spectra*. Cambridge University Press, London, 1967.
- [21] A. R. Young, S. Appelt, A. Ben-Amar Baranga, C. Erickson, and W. Happer. Three-dimensional imaging of spin polarization of alkali-metal vapor in optical pumping cells. *Applied Physics Letters*, 70(23):3081–3083, 1997.
- [22] S. Appelt, A. Ben-Amar Baranga, C. J. Erickson, M. V. Romalis, A. R. Young, and W. Happer. ”theory of spin-exchange optical pumping of ^3He and ^{129}Xe ”. *Physical Review A*, 58(2):1412–1439, Aug 1998.
- [23] L. Wilmer Anderson, Francis M. Pipkin, and James C. Baird. N14-N15 Hyperfine Anomaly. *Physical Review*, 116(1):87–98, Oct 1959.
- [24] A. Ben-Amar Baranga, S. Appelt, C. J. Erickson, A. R. Young, and W. Happer. Alkali-metal-atom polarization imaging in high-pressure optical-pumping cells. *Physical Review A*, 58(3):2282–2294, Sep 1998.
- [25] Max Born and Emil Wolf. *Principles of Optics*. Cambridge University Press, Cambridge, 7th (expanded) edition, 1999.
- [26] Amnon Yariv and Pochi Yeh. *Optical Waves in Crystals: Propagation and Control of Laser Radiation*. John Wiley & Sons, Hoboken, 2003.
- [27] B. Chann, E. Babcock, L. W. Anderson, and T. G. Walker. Skew light propagation in optically thick optical pumping cells. *Physical Review A*, 66(3):033406, Sep 2002.
- [28] H. G. Dehmelt. Modulation of a Light Beam by Precessing Absorbing Atoms. *Physical Review*, 105(6):1924–1925, Mar 1957.
- [29] W. Happer and B. S. Mathur. Effective Operator Formalism in Optical Pumping. *Physical Review*, 163(1):12–25, Nov 1967.
- [30] R. Walkup, B. Stewart, and D. E. Pritchard. Collisional line broadening due to van der Waals potentials. *Physical Review A*, 29(1):169–173, Jan 1984.
- [31] M. V. Romalis, E. Miron, and G. D. Cates. Pressure broadening of Rb $D1$ and $D2$ lines by ^3He , ^4He , N_2 , and Xe: Line cores and near wings. *Physical Review A*, 56(6):4569–4578, Dec 1997.
- [32] B. Chann, E. Babcock, L. W. Anderson, and T. G. Walker. Measurements of ^3He spin-exchange rates. *Physical Review A*, 66(3):032703, Sep 2002.
- [33] S. R. Schaefer, G. D. Cates, Ting-Ray Chien, D. Gonatas, W. Happer, and T. G. Walker. Frequency shifts of the magnetic-resonance spectrum of mixtures of nuclear spin-polarized noble gases and vapors of spin-polarized alkali-metal atoms. *Physical Review A*, 39(11):5613–5623, Jun 1989.
- [34] N. R. Newbury, A. S. Barton, P. Bogorad, G. D. Cates, M. Gatzke, H. Mabuchi, and B. Saam. Polarization-dependent frequency shifts from Rb- ^3He collisions. *Physical Review A*, 48(1):558–568, Jul 1993.
- [35] A. S. Barton, N. R. Newbury, G. D. Cates, B. Driehuys, H. Middleton, and B. Saam. Self-calibrating measurement of polarization-dependent frequency shifts from Rb- ^3He collisions. *Physical Review A*, 49(4):2766–2770, Apr 1994.
- [36] M. V. Romalis and G. D. Cates. Accurate ^3He polarimetry using the Rb Zeeman frequency shift due to the Rb- ^3He spin-exchange collisions. *Physical Review A*, 58(4):3004–3011, Oct 1998.
- [37] Earl Babcock, Ian A. Nelson, Steve Kadlecsek, and Thad G. Walker. ^3He polarization-dependent EPR frequency shifts of alkali-metal- ^3He pairs. *Physical Review A*, 71(1):013414, Jan 2005.
- [38] M.E. Rose. *Elementary Theory of Angular Momentum*. John Wiley & Sons, New York, 1957.

Appendix A

Physical Constants and Alkali Data

These are tables of physical constants and data relevant to various alkali metals. All units are in SI unless otherwise noted. Sources are the following:

- CODATA Mohr, Peter J. and Barry N. Taylor. *Rev. Mod. Phys.* 77, p1 (2005).
- NIST_a <http://physics.nist.gov/cuu/Constants/index.html>
- NIST_b <http://physics.nist.gov/PhysRefData/ASD/index.html>
- NIST_c <http://physics.nist.gov/PhysRefData/IonEnergy/tblNew.html>
- NIST_d <http://www.physics.nist.gov/PhysRefData/Elements/cover.html>
- NIST_e <http://physics.nist.gov/PhysRefData/Handbook/periodictable.htm>
- RS₈₅ Radzig, A.A. and B.M. Smirnov. *Reference Data on Atoms, Molecules, and Ions*. Berlin: Springer-Verlag, 1985.
- AIV₇₇ Arimondo, E., M. Inguscio, and P. Violino. *Rev. Mod. Phys.* 49, pp31-75 (1977).

For each value, only the most significant digits are kept. The uncertainty on each value is in general ± 9 on the last digit, but is usually ± 2 . Values which are referenced to an equation denoted by () are calculated with other values found in the tables. The fields for which the Zeeman interaction becomes on order of the fine and hyperfine interactions are calculated only to three significant digits for illustrative purposes. Some useful relationships:

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{mc}{\hbar} r_e \quad (\text{A.1})$$

$$r_e = \frac{e^2}{4\pi\epsilon_0 mc^2} = \frac{\hbar}{mc} \alpha \quad (\text{A.2})$$

Symbol	Value	Units	Description
c	299 792 458	$\text{m} \cdot \text{s}^{-1}$	definition of the speed of light
ϵ_0	$8.854\,187\,817 \times 10^{-12}$	$\text{C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$	permittivity of free space
μ_0	$4\pi \times 10^{-7}$	$\text{N} \cdot \text{A}^{-2}$	permeability of free space
e	$1.602\,176\,5 \times 10^{-19}$	C	electron charge magnitude
m	$9.109\,383 \times 10^{-31}$	kg	electron mass
g_S	-2.002 319 304 372	unitless	electron g -factor
r_e	$2.817\,940\,325 \times 10^{-15}$	m	classical electron radius
μ_B	$9.274\,000\,95 \times 10^{-24}$	$\text{J} \cdot \text{T}^{-1}$	Bohr magneton
μ_N	$5.050\,783\,4 \times 10^{-27}$	$\text{J} \cdot \text{T}^{-1}$	Nuclear magneton
h	$6.626\,069 \times 10^{-34}$	$\text{J} \cdot \text{s}$	Planck constant
α^{-1}	137.035 999	unitless	fine structure constant
amu	$1.660\,538\,9 \times 10^{-27}$	kg	12·(atomic mass unit) = mass ^{12}C

Table A.1: Fundamental Physical Constants [CODATA 2002]. These values are found at [NIST_a].

Element	D1					D2				
	$\lambda(\text{nm, air})$	$\tau(\text{ns})$	f	$\tau(\text{ns})$	f	$\lambda(\text{nm, air})$	$\tau(\text{ns})$	f	$\tau(\text{ns})$	f
Lithium	670.791	26.9	0.251	27.3	0.247	670.776	26.9	0.502	27.9	0.494
Sodium	589.592 4	16.2	0.322	16.4	0.318	588.995 0	16.1	0.647	16.3	0.637
Potassium	769.896	26.2	0.340	27	0.35	766.490	25.8	0.682	27	0.70
Rubidium	794.760 3	27.7	0.342	28.5	0.32	780.026 8	26.2	0.695	26.5	0.67
Cesium	894.347	34.8	0.344	31	0.39	852.113	30.53	0.7131	31	0.81
Reference	NIST _b			RS ₈₅		NIST _b			RS ₈₅	

Table A.2: Alkali atom D1 and D2 transition wavelengths (λ), lifetimes (τ), and oscillator strengths (f).

	D1			D2			ν_{so}
	λ_1 (air)	λ_1 (vac)	ν_1	λ_2 (air)	λ_2 (vac)	ν_2	
Li	670.791	670.976	446 800.6	670.776	670.961	446 810.6	10.0
Na	589.592 4	589.755 8	508 333.2	588.995 0	589.158 2	508 848.8	515.6
K	769.896	770.108	389 286.3	766.490	766.701	391 016.1	1 729.9
Rb	794.760 3	794.978 9	377 107.4	780.026 8	780.241 4	384 230.4	7 123.0
Cs	894.347	894.593	335 116.0	852.113	852.347	351 725.8	16 609.8

Table A.3: Alkali atom D1 & D2 air & vacuum transition wavelengths (λ) in nm, transition frequencies (ν) in GHz, and spin-orbit splitting (ν_{so}) in GHz. Wavelength data from NIST_b.

Element	Ground State	$S_{1/2}$ g_J/g_S	$P_{1/2}$ g_J	$P_{3/2}$ g_J	ν_{so} (GHz)	Field for $y = 1$ (Tesla)
Lithium	2	1.000 003 4	-0.667	-1.335	9.994 18	0.712
Sodium	3	1.000 000 9	-0.665 8	-1.334 2	515.730	36.7
Potassium	4	1.000 018 44			1 730.32	123
Rubidium	5	1.000 005 9			7 124.94	508
Cesium	6	1.000 104 474	-0.665 90	-1.334 0	16 614.2	1180
Theory (if $g_S = -2$)		1.000 000 000	-0.665 894 -2/3	-1.334 106 -4/3		
Reference	NIST _c	AIV ₇₇			(1.57)	(1.59)

Table A.4: Alkali atom ground state and first excited states fine structure..

Isotope	Mass (amu)	Natural Abundance	Nuclear Spin, I	Magnetic Moment (μ_N)	g-factor $g_I(\mu_N)$
Lithium	6.941				
^6Li	6.015 122 3	0.075 9	1	+0.822 056	+0.822 056
^7Li	7.016 004 0	0.924 1	3/2	+3.256 44	+2.170 96
Sodium	22.989 770				
^{23}Na	22.989 769 7	1.0	3/2	+2.217 52	+1.478 35
Potassium	39.098 3				
^{39}K	38.963 706 9	0.932 58	3/2	+0.391 46	+0.260 97
^{40}K	39.963 998 7	0.000 117	4	-1.298	-0.324 5
^{41}K	40.961 826 0	0.067 30	3/2	+0.214 87	+0.143 25
Rubidium	85.467 8				
^{85}Rb	84.911 789	0.721 7	5/2	+1.353 02	+0.541 208
^{87}Rb	86.909 184	0.278 3	3/2	+2.751 2	+1.834 1
Cesium	132.905 45				
^{133}Cs	132.905 447	1.0	7/2	+2.579	+0.736 9
Reference	NIST _d		NIST _e		(1.5)

Table A.5: Alkali atom isotopic and nuclear data.

Iso.	$S_{1/2}$			$P_{1/2}$			$P_{3/2}$	
	A (MHz)	ν_{hfs} (MHz)	$x = 1$ (gauss)	A (MHz)	ν_{hfs} (MHz)	$x = 1$ (gauss)	A (MHz)	B (MHz)
${}^6\text{Li}$	152.136 841	228.205 261	81.4	17.38	26.06	27.9	-1.155	-0.1
${}^7\text{Li}$	401.752 043 3	803.504 086 6	287	45.92	91.83	98.4	-3.055	-0.22
${}^{23}\text{Na}$	885.813 064 4	1 771.626 128	632	94.3	188.6	202	18.69	2.9
${}^{39}\text{K}$	230.859 860 1	461.719 720 2	165	28.85	57.7	61.8	6.06	2.8
${}^{40}\text{K}$	-285.731	-1 142.92	-405				-7.59	-3.5
${}^{41}\text{K}$	127.006 935 2	254.013 870 4	90.6				3.40	3.3
${}^{85}\text{Rb}$	1 011.910 813	3 035.732 439	1 080	120.72	362.16	388	25.01	25.88
${}^{87}\text{Rb}$	3 417.341 306 4	6 834.682 612 8	2 440	406.2	812.4	870	84.845	12.52
${}^{133}\text{Cs}$	2 298.157 942 5	9 192.631 770	3 280	291.9	1 167	1 250	50.34	-0.4
Ref.	AIV ₇₇	(1.208)	(1.210)	"	"	"	AIV ₇₇	

Table A.6: Alkali atom ground State and first excited states hyperfine structure.

Appendix B

Irreducible Spherical Vector Basis

A vector is decomposed in the following way:

$$\vec{r} = \sum_{q=1}^3 r_q \hat{\varepsilon}_q^* \quad (\text{B.1})$$

In the rectangular basis, the components r_q and unit vectors ε_q are real and have the following interpretations:

$$r_q^* = r_q \leftrightarrow \hat{\varepsilon}_q^* = \hat{\varepsilon}_q \quad (\text{B.2})$$

$$r_1 = r_1^* = x \leftrightarrow \hat{\varepsilon}_1 = \hat{\varepsilon}_1^* = \hat{x} \quad (\text{B.3})$$

$$r_2 = r_2^* = y \leftrightarrow \hat{\varepsilon}_2 = \hat{\varepsilon}_2^* = \hat{y} \quad (\text{B.4})$$

$$r_3 = r_3^* = z \leftrightarrow \hat{\varepsilon}_3 = \hat{\varepsilon}_3^* = \hat{z} \quad (\text{B.5})$$

Orthogonality of the unit vectors is defined the following way:

$$\hat{\varepsilon}_p \cdot \hat{\varepsilon}_q = \hat{\varepsilon}_p^* \cdot \hat{\varepsilon}_q = \delta_p^q \quad (\text{B.6})$$

which immediately implies the dot product between two vectors and the modulus square of a vector:

$$\vec{r} \cdot \vec{s} = \sum_{p,q=1}^3 r_p s_q \hat{\varepsilon}_p \cdot \hat{\varepsilon}_q = \sum_{p,q=1}^3 r_p s_q \delta_p^q = \sum_{q=1}^3 r_q s_q \quad (\text{B.7})$$

$$|\vec{r}|^2 = \vec{r}^* \cdot \vec{r} = \sum_{q=1}^3 r_q^* r_q = x^2 + y^2 + z^2 \quad (\text{B.8})$$

The vector, all dot products, and the modulus squared are all real.

Alternatively, the same vector can be expanded in the spherical basis [38] where the components r_q and unit vectors ε_q are in general complex and have the following interpretations:

$$r_q^* = (-1)^q r_{-q} \leftrightarrow \hat{\varepsilon}_q^* = (-1)^q \hat{\varepsilon}_{-q} \quad (\text{B.9})$$

$$r_{-1} = -r_{+1}^* = + \left(\frac{x - iy}{\sqrt{2}} \right) \leftrightarrow \hat{\varepsilon}_{-1} = -\hat{\varepsilon}_{+1}^* = + \left(\frac{\hat{x} - i\hat{y}}{\sqrt{2}} \right) \quad (\text{B.10})$$

$$r_0 = r_0^* = z \leftrightarrow \hat{\varepsilon}_0 = \hat{\varepsilon}_0^* = \hat{z} \quad (\text{B.11})$$

$$r_{+1} = -r_{-1}^* = - \left(\frac{x + iy}{\sqrt{2}} \right) \leftrightarrow \hat{\varepsilon}_{+1} = -\hat{\varepsilon}_{-1}^* = - \left(\frac{\hat{x} + i\hat{y}}{\sqrt{2}} \right) \quad (\text{B.12})$$

Orthogonality of the unit vectors is defined the following way:

$$\hat{\varepsilon}_p^* \cdot \hat{\varepsilon}_q = \delta_p^q \quad \rightarrow \quad \hat{\varepsilon}_p \cdot \hat{\varepsilon}_q = (-1)^q \delta_p^{-q} \quad (\text{B.13})$$

which immediately implies the dot product between two vectors and the modulus square of a vector:

$$\vec{r} \cdot \vec{s} = \sum_{p,q=1}^3 (-1)^{p+q} r_p s_q \hat{e}_{-p} \cdot \hat{e}_{-q} = \sum_{p,q=1}^3 (-1)^{p+q} r_p s_q \delta_{-p}^q = \sum_{q=1}^3 r_q^* s_q \quad (\text{B.14})$$

$$\begin{aligned} |\vec{r}|^2 = \vec{r}^* \cdot \vec{r} &= \sum_{p,q=1}^3 (-1)^{p+q} r_p^* r_q \hat{e}_{-p}^* \cdot \hat{e}_{-q} \\ &= \sum_{p,q=1}^3 (-1)^{p+q} r_p^* r_q \delta_{-p}^{-q} = \sum_{p,q=1}^3 (-1)^{2q} r_q^* r_q = \sum_{p,q=1}^3 (-1)^q r_{-q} r_q = r_0^2 - 2r_{-1}r_{+1} \quad (\text{B.15}) \end{aligned}$$

Note that the irreducible spherical vector basis is just the irreducible spherical tensor basis of rank one.
#check#comment more on this at some point

Appendix C

Clebsch-Gordon Coefficients

C.1 General Formula

Adapted from equation (17.27) in Wigner's *Group Theory* [18] into equation 14³(5) in *Condon & Shortley* [20]:

$$\begin{aligned} \langle (J_1, J_2) m_1, m_2 | J, m \rangle &= \sqrt{\frac{(J + J_1 - J_2)! (J - J_1 + J_2)! (J_1 + J_2 - J)! (J + m)! (J - m)! (2J + 1)}{(J + J_1 + J_2 + 1)! (J_1 - m_1)! (J_1 + m_1)! (J_2 - m_2)! (J_2 + m_2)!}} \\ &\times \delta_m^{(m_1 + m_2)} \sum_{\kappa = \kappa_1}^{\kappa_2} \frac{(-1)^{\kappa + J_2 + m_2} (J + J_2 + m_1 - \kappa)! (J_1 - m_1 + \kappa)!}{(J - J_1 + J_2 - \kappa)! (J + m - \kappa)! \kappa! (\kappa + J_1 - J_2 - m)!} \end{aligned} \quad (\text{C.1})$$

$$\kappa_a = \max [0, J_2 - J_1 + m] \quad (\text{C.2})$$

$$\kappa_b = \min [J + m, J_2 - J_1 + J] \quad (\text{C.3})$$

$$\kappa_1 = \min [\kappa_a, \kappa_b] \quad (\text{C.4})$$

$$\kappa_2 = \max [\kappa_a, \kappa_b] \quad (\text{C.5})$$

where κ is summed over all non-negative integers between κ_1 and κ_2 . Note the usual rules:

$$\langle (J_1, J_2) m_1, m_2 | J, m \rangle = (-1)^{J - J_1 - J_2} \langle (J_2, J_1) m_2, m_1 | J, m \rangle \quad (\text{C.6})$$

$$J_1, J_2, J \geq 0 \quad J = |J_1 - J_2| \dots (J_1 + J_2) \quad (\text{C.7})$$

$$m_1 = -J_1 \dots + J_1 \quad m_2 = -J_2 \dots + J_2 \quad m = m_1 + m_2 = -J \dots + J \quad (\text{C.8})$$

The following formulas for $J = 1/2, 1$ and $J = 3/2$ were derived by E.P. Wigner and F. Seitz and are catalogued in CU in tables 1³, 2³, & 3³.

C.2 For the case $\vec{J}_1 + \frac{1}{2}$

$$\begin{aligned} \left\langle \left(J_1, \frac{1}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 + \frac{1}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J - \frac{1}{2}, \frac{1}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= \sqrt{\frac{J_1 \pm m + \frac{1}{2}}{[J_1]}} = \sqrt{\frac{J_1 \pm m_1 + 1}{[J_1]}} = \sqrt{\frac{J \pm m}{2J}} \end{aligned} \quad (\text{C.9})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{1}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 - \frac{1}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J + \frac{1}{2}, \frac{1}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= \mp \sqrt{\frac{J_1 \mp m + \frac{1}{2}}{[J_1]}} = \mp \sqrt{\frac{J_1 \mp m_1}{[J_1]}} = \mp \sqrt{\frac{J \mp m + 1}{2(J + 1)}} \end{aligned} \quad (\text{C.10})$$

C.3 For the case $\vec{J}_1 + \vec{1}$

C.3.1 With $m = m_1 \pm 1$:

$$\begin{aligned} \langle (J_1, 1), m_1, \pm 1 | J_1 + 1, m_1 \pm 1 \rangle &= \langle (J - 1, 1), m \mp 1, \pm 1 | J, m \rangle \\ &= \sqrt{\frac{(J_1 \pm m)(J_1 \pm m + 1)}{2[J_1](J_1 + 1)}} \end{aligned} \quad (\text{C.11})$$

$$= \sqrt{\frac{(J_1 \pm m_1 + 1)(J_1 \pm m_1 + 2)}{2[J_1](J_1 + 1)}} \quad (\text{C.12})$$

$$= \sqrt{\frac{(J \pm m - 1)(J \pm m)}{2J(2J - 1)}} \quad (\text{C.13})$$

$$\begin{aligned} \langle (J_1, 1), m_1, \pm 1 | J_1, m_1 \pm 1 \rangle &= \langle (J, 1), m \mp 1, \pm 1 | J, m \rangle \\ &= \mp \sqrt{\frac{(J_1 \pm m)(J_1 \mp m + 1)}{2J_1(J_1 + 1)}} \end{aligned} \quad (\text{C.14})$$

$$= \mp \sqrt{\frac{(J_1 \pm m_1 + 1)(J_1 \mp m_1)}{2J_1(J_1 + 1)}} \quad (\text{C.15})$$

$$= \mp \sqrt{\frac{(J \pm m)(J \mp m + 1)}{2J(J + 1)}} \quad (\text{C.16})$$

$$\begin{aligned} \langle (J_1, 1), m_1, \pm 1 | J_1 - 1, m_1 \pm 1 \rangle &= \langle (J + 1, 1), m \mp 1, \pm 1 | J, m \rangle \\ &= \sqrt{\frac{(J_1 \mp m)(J_1 \mp m + 1)}{2J_1[J_1]}} \end{aligned} \quad (\text{C.17})$$

$$= \sqrt{\frac{(J_1 \mp m_1 - 1)(J_1 \mp m_1)}{2J_1[J_1]}} \quad (\text{C.18})$$

$$= \sqrt{\frac{(J \mp m + 1)(J \mp m + 2)}{2(J + 1)(2J + 3)}} \quad (\text{C.19})$$

C.3.2 With $m = m_1$:

$$\begin{aligned} \langle (J_1, 1), m_1, 0 | J_1 \pm 1, m_1 \rangle &= \langle (J \mp 1, 1), m, 0 | J, m \rangle \\ &= \pm \sqrt{\frac{(J_1 - m + \frac{1}{2} \pm \frac{1}{2})(J_1 + m + \frac{1}{2} \pm \frac{1}{2})}{[J_1](J_1 + \frac{1}{2} \pm \frac{1}{2})}} \end{aligned} \quad (\text{C.20})$$

$$= \pm \sqrt{\frac{(J_1 - m_1 + \frac{1}{2} \pm \frac{1}{2})(J_1 + m_1 + \frac{1}{2} \pm \frac{1}{2})}{[J_1](J_1 + \frac{1}{2} \pm \frac{1}{2})}} \quad (\text{C.21})$$

$$= \pm \sqrt{\frac{(J - m + \frac{1}{2} \mp \frac{1}{2})(J + m + \frac{1}{2} \mp \frac{1}{2})}{(2J + 1 \mp 2)(J + \frac{1}{2} \mp \frac{1}{2})}} \quad (\text{C.22})$$

$$\begin{aligned} \langle (J_1, 1), m_1, 0 | J_1, m_1 \rangle &= \langle (J, 1), m, 0 | J, m \rangle \\ &= \frac{m_1}{\sqrt{J_1(J_1 + 1)}} = \frac{m}{\sqrt{J(J + 1)}} \end{aligned} \quad (\text{C.23})$$

C.4 For the case $\vec{J}_1 + \frac{3}{2}$

C.4.1 With $m = m_1 \pm \frac{3}{2}$:

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{3}{2} \middle| J_1 + \frac{3}{2}, m_1 \pm \frac{3}{2} \right\rangle &= \left\langle \left(J - \frac{3}{2}, \frac{3}{2} \right), m \mp \frac{3}{2}, \pm \frac{3}{2} \middle| J, m \right\rangle \\ &= \sqrt{\frac{(J_1 \pm m - \frac{1}{2})(J_1 \pm m + \frac{1}{2})(J_1 \pm m + \frac{3}{2})}{2[J_1](J_1 + 1)(2J_1 + 3)}} \end{aligned} \quad (\text{C.24})$$

$$= \sqrt{\frac{(J_1 \pm m_1 + 1)(J_1 \pm m_1 + 2)(J_1 \pm m_1 + 3)}{2[J_1](J_1 + 1)(2J_1 + 3)}} \quad (\text{C.25})$$

$$= \sqrt{\frac{(J \pm m - 2)(J \pm m - 1)(J \pm m)}{4J(J - 1)(2J - 1)}} \quad (\text{C.26})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{3}{2} \middle| J_1 + \frac{1}{2}, m_1 \pm \frac{3}{2} \right\rangle &= \left\langle \left(J - \frac{1}{2}, \frac{3}{2} \right), m \mp \frac{3}{2}, \pm \frac{3}{2} \middle| J, m \right\rangle \\ &= \mp \sqrt{\frac{3(J_1 \pm m - \frac{1}{2})(J_1 \pm m + \frac{1}{2})(J_1 \mp m + \frac{3}{2})}{2J_1[J_1](2J_1 + 3)}} \end{aligned} \quad (\text{C.27})$$

$$= \mp \sqrt{\frac{3(J_1 \pm m_1 + 1)(J_1 \pm m_1 + 2)(J_1 \mp m_1)}{2J_1[J_1](2J_1 + 3)}} \quad (\text{C.28})$$

$$= \mp \sqrt{\frac{3(J \pm m - 1)(J \pm m)(J \mp m + 1)}{4J(2J - 1)(J + 1)}} \quad (\text{C.29})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{3}{2} \middle| J_1 - \frac{1}{2}, m_1 \pm \frac{3}{2} \right\rangle &= \left\langle \left(J + \frac{1}{2}, \frac{3}{2} \right), m \mp \frac{3}{2}, \pm \frac{3}{2} \middle| J, m \right\rangle \\ &= \sqrt{\frac{3(J_1 \pm m - \frac{1}{2})(J_1 \mp m + \frac{1}{2})(J_1 \mp m + \frac{3}{2})}{2[J_1](J_1 + 1)(2J_1 - 1)}} \end{aligned} \quad (\text{C.30})$$

$$= \sqrt{\frac{3(J_1 \pm m_1 + 1)(J_1 \mp m_1 - 1)(J_1 \mp m_1)}{2[J_1](J_1 + 1)(2J_1 - 1)}} \quad (\text{C.31})$$

$$= \sqrt{\frac{3(J \pm m)(J \mp m + 1)(J \mp m + 2)}{4J(J + 1)(2J + 3)}} \quad (\text{C.32})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{3}{2} \middle| J_1 - \frac{3}{2}, m_1 \pm \frac{3}{2} \right\rangle &= \left\langle \left(J + \frac{3}{2}, \frac{3}{2} \right), m \mp \frac{3}{2}, \pm \frac{3}{2} \middle| J, m \right\rangle \\ &= \mp \sqrt{\frac{(J_1 \mp m - \frac{1}{2})(J_1 \mp m + \frac{1}{2})(J_1 \mp m + \frac{3}{2})}{2J_1[J_1](2J_1 - 1)}} \end{aligned} \quad (\text{C.33})$$

$$= \mp \sqrt{\frac{(J_1 \mp m_1 - 2)(J_1 \mp m_1 - 1)(J_1 \mp m_1)}{2J_1[J_1](2J_1 - 1)}} \quad (\text{C.34})$$

$$= \mp \sqrt{\frac{(J \mp m + 1)(J \mp m + 2)(J \mp m + 3)}{4(2J + 3)(J + 2)(J + 1)}} \quad (\text{C.35})$$

C.4.2 With $m = m_1 \pm \frac{1}{2}$:

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 + \frac{3}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J - \frac{3}{2}, \frac{3}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= \sqrt{\frac{3 (J_1 \pm m + \frac{1}{2}) (J_1 + m + \frac{3}{2}) (J_1 - m + \frac{3}{2})}{2[J_1] (J_1 + 1) (2J_1 + 3)}} \end{aligned} \quad (\text{C.36})$$

$$= \sqrt{\frac{3 (J_1 \pm m_1 + 1) (J_1 + m_1 + \frac{3 \pm 1}{2}) (J_1 - m_1 + \frac{3 \mp 1}{2})}{2[J_1] (J_1 + 1) (2J_1 + 3)}} \quad (\text{C.37})$$

$$= \sqrt{\frac{3 (J \pm m - 1) (J + m) (J - m)}{4J (J - 1) (2J - 1)}} \quad (\text{C.38})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 + \frac{1}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J - \frac{1}{2}, \frac{3}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= \mp \left(J_1 \mp 3m + \frac{3}{2} \right) \sqrt{\frac{J_1 \pm m + \frac{1}{2}}{2J_1[J_1] (2J_1 + 3)}} \end{aligned} \quad (\text{C.39})$$

$$= \mp (J_1 \mp 3m_1) \sqrt{\frac{J_1 \pm m_1 + 1}{2J_1[J_1] (2J_1 + 3)}} \quad (\text{C.40})$$

$$= \mp (J \mp 3m + 1) \sqrt{\frac{J \pm m}{4J (2J - 1) (J + 1)}} \quad (\text{C.41})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 - \frac{1}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J + \frac{1}{2}, \frac{3}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= - \left(J_1 \pm 3m - \frac{1}{2} \right) \sqrt{\frac{J_1 \mp m + \frac{1}{2}}{2[J_1] (J_1 + 1) (2J_1 - 1)}} \end{aligned} \quad (\text{C.42})$$

$$= - (J_1 \pm 3m_1 + 1) \sqrt{\frac{J_1 \mp m_1}{2[J_1] (J_1 + 1) (2J_1 - 1)}} \quad (\text{C.43})$$

$$= - (J \pm 3m) \sqrt{\frac{J \mp m + 1}{4J (J + 1) (2J + 3)}} \quad (\text{C.44})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 - \frac{3}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J + \frac{3}{2}, \frac{3}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= \pm \sqrt{\frac{3 (J_1 + m - \frac{1}{2}) (J_1 - m - \frac{1}{2}) (J_1 \mp m + \frac{1}{2})}{2J_1[J_1] (2J_1 - 1)}} \end{aligned} \quad (\text{C.45})$$

$$= \pm \sqrt{\frac{3 (J_1 + m_1 - \frac{1 \mp 1}{2}) (J_1 - m_1 - \frac{1 \pm 1}{2}) (J_1 \mp m_1)}{2J_1[J_1] (2J_1 - 1)}} \quad (\text{C.46})$$

$$= \pm \sqrt{\frac{3 (J + m + 1) (J - m + 1) (J \mp m + 2)}{4 (2J + 3) (J + 2) (J + 1)}} \quad (\text{C.47})$$

C.5 Expansion of Zero Field Eigenbasis for $I = 0$

$$\left| S_{\frac{1}{2}}, \frac{1}{2}, +\frac{1}{2} \right\rangle = \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.48})$$

$$\left| S_{\frac{1}{2}}, \frac{1}{2}, -\frac{1}{2} \right\rangle = \left| -\frac{1}{2} \right\rangle_S \quad (\text{C.49})$$

$$\left| P_{\frac{1}{2}}, \frac{1}{2}, +\frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} | +1 \rangle_L \left| -\frac{1}{2} \right\rangle_S - \sqrt{\frac{1}{3}} | 0 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.50})$$

$$\left| P_{\frac{1}{2}}, \frac{1}{2}, -\frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} | 0 \rangle_L \left| -\frac{1}{2} \right\rangle_S - \sqrt{\frac{2}{3}} | -1 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.51})$$

$$\left| P_{\frac{3}{2}}, \frac{3}{2}, +\frac{3}{2} \right\rangle = | +1 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.52})$$

$$\left| P_{\frac{3}{2}}, \frac{3}{2}, +\frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} | +1 \rangle_L \left| -\frac{1}{2} \right\rangle_S + \sqrt{\frac{2}{3}} | 0 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.53})$$

$$\left| P_{\frac{3}{2}}, \frac{3}{2}, -\frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} | 0 \rangle_L \left| -\frac{1}{2} \right\rangle_S + \sqrt{\frac{1}{3}} | -1 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.54})$$

$$\left| P_{\frac{3}{2}}, \frac{3}{2}, -\frac{3}{2} \right\rangle = | -1 \rangle_L \left| -\frac{1}{2} \right\rangle_S \quad (\text{C.55})$$