

On Using Weak Laser Light-Alkali Atom Interactions
to Study Spin-Exchange Optical Pumping

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Abstract

Light can be easily linearly or circularly polarized. The degree of circular polarization can be measured and modulated. Light preferably interacts with atoms via a dipole interaction. Atoms in a magnetic field anisotropically couple to the different polarization components of the light. If the light is in the form of a weak probe beam, then it negligibly effects the atomic vapor. Consequently the atomic polarizability can be calculated using perturbation theory. The effect on the amplitude and phase of the weak probe beam as a function of wavelength is given by the imaginary and real parts of the complex index of refraction of the atomic vapor, which is derived directly from the atomic polarizability. These quantities will be evaluated for alkali metal atoms. Observables related to this interaction will be used to infer the alkali polarization, alkali density, hybrid alkali density ratio, noble gas polarization, noble gas density, and various rates relevant to spin-exchange optical pumping. Experimental considerations will be discussed. This note is meant to be detailed, explicit, and self-contained.

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Chapter 1

Quantum Mechanical Treatment of an Alkali Atom 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:

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

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

g is the unitless Landé factor. Note that the sign of the magnetic moment is carried implicitly in g or alternatively μ_J . For example, $g \approx -2$ for the electron, $g \approx 2(2.79)$ for the proton, and $g \approx 2(-1.91)$ for the neutron. 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:

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

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 [Ramsey, Norman F. *Molecular Beams*. London: OUP, section IX.5.1 (1963)]. 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 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 (Woodgate, G.K. *Elementary Atomic Structure, Second Edition*. Oxford: Oxford University Press, 2002):

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 independant 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 quadrapole 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 [Russell, H.N. and F.A. Saunders. *Astrophysical Journal* (61). p28 (1925)] term 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.2 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 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.1.1):

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

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

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 $n^2S_{\frac{1}{2}}$ 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.3). 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:

$$E_{\pm(L+\frac{1}{2})} = E_0^L - \frac{h\nu_{so}}{2[L]} \pm \mu_B \left(L + \frac{1}{2} \right) B + \frac{h\nu_{so}}{2} \sqrt{1 \pm \frac{4(L+\frac{1}{2})}{[L]}y + y^2} \quad (1.67)$$

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

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

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

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

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

Low Field Energies

At low field, see table (A.3), to second order in B , the energies for the $J = L \pm \frac{1}{2}$ terms with $L > 0$ are:

$$E = E_0^L - \frac{h\nu_{so}}{2[L]} + \mu_B m_J B \pm \frac{h\nu_{so}}{2} \left(1 + \frac{2m_J}{[L]} y + \frac{1}{2} \left(1 - \frac{4m_J^2}{[L]^2} \right) y^2 + \mathcal{O}(y^3) \right) \quad (1.73)$$

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

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

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

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

$$E_{\frac{1}{2}, -\frac{1}{2}}^S = E_0^S - \left[\frac{g_S}{-2} \right] \mu_B B \quad (1.77)$$

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

$$E_{\frac{1}{2}, -\frac{1}{2}}^P = E_0^P - \left(\frac{2}{3} \right) h\nu_{so} - \left[2 + \frac{g_S}{2} \right] \left(\frac{1}{3} \right) \mu_B B - \left(\frac{2}{9} y^2 \right) h\nu_{so} \quad (1.79)$$

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

$$E_{\frac{3}{2}, -\frac{3}{2}}^P = E_0^P + \left(\frac{1}{3} \right) h\nu_{so} - \left[\frac{1}{2} - \frac{g_S}{4} \right] 2\mu_B B \quad (1.81)$$

$$E_{\frac{3}{2}, -\frac{1}{2}}^P = E_0^P + \left(\frac{1}{3} \right) h\nu_{so} - \left[\frac{1}{2} - \frac{g_S}{4} \right] \left(\frac{2}{3} \right) \mu_B B + \left(\frac{2}{9} y^2 \right) h\nu_{so} \quad (1.82)$$

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

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

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:

$$|L_{\pm}, m_J\rangle = a_1^{\pm} \left| L + \frac{1}{2}, m_J \right\rangle + a_2^{\pm} \left| L - \frac{1}{2}, m_J \right\rangle \quad (1.85)$$

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:

$$\langle m_J^{\pm} | m_J^{\pm} \rangle = (a_1^{\pm})^2 + (a_2^{\pm})^2 = 1 \quad (1.86)$$

$$\langle m_J^{-} | m_J^{+} \rangle = a_1^{-} a_1^{+} + a_2^{-} a_2^{+} = 0 \quad (1.87)$$

Some algebra gives:

$$(a_2^{\pm})^2 = 1 - (a_1^{\pm})^2 \quad (1.88)$$

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

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

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

$$(a_1^{-})^2 = (a_2^{+})^2 \quad (1.90)$$

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

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

$$a_1^{\pm} = \pm a_2^{\mp} \quad (1.93)$$

To recap, orthonormality implies equation (1.93).

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):

$$\hat{M} |a\rangle = \pm \lambda |a\rangle \quad (1.94)$$

$$\begin{bmatrix} 1 + 2\alpha y & -2\beta y \\ -2\beta y & -(1 + 2\alpha y) \end{bmatrix} \begin{bmatrix} a_1^{\pm} \\ a_2^{\pm} \end{bmatrix} = \pm \lambda \begin{bmatrix} a_1^{\pm} \\ a_2^{\pm} \end{bmatrix} \quad (1.95)$$

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

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

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

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

$$(1 + 2\alpha y \mp \lambda)^2 (a_1^{\pm})^2 = 4\beta^2 y^2 (1 - (a_1^{\pm})^2) \quad (1.99)$$

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

$$a_2^{\pm} = \frac{1 + 2\alpha y \mp \lambda}{\sqrt{(1 + 2\alpha y \mp \lambda)^2 + 4\beta^2 y^2}} \quad (1.101)$$

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 (Spiegel, Murray R. Mathematical Handbook of Formulas and Tables, New York: McGraw-Hill, 1993. page 110, equations 20.10 and 20.11):

$$\sqrt{1+x} \simeq 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \frac{1}{16}x^3 - \frac{5}{128}x^4 + \mathcal{O}(x^5) \quad (1.102)$$

$$\frac{1}{\sqrt{1+x}} \simeq 1 - \frac{1}{2}x + \frac{3}{8}x^2 - \frac{5}{16}x^3 + \frac{35}{128}x^4 + \mathcal{O}(x^5) \quad (1.103)$$

$$\sqrt{1+ax+bx^2} \simeq 1 + \frac{a}{2}x + \left(\frac{b}{2} - \frac{a^2}{8}\right)x^2 + \left(\frac{a^3}{16} - \frac{ab}{4}\right)x^3 + \left(\frac{3a^2b}{16} - \frac{b^2}{8} - \frac{5a^4}{128}\right)x^4 + \mathcal{O}(x^5) \quad (1.104)$$

$$\begin{aligned} \frac{1}{\sqrt{1+ax+bx^2}} &\simeq 1 - \frac{a}{2}x + \left(\frac{3a^2}{8} - \frac{b}{2}\right)x^2 + \left(\frac{3ab}{4} - \frac{5a^3}{16}\right)x^3 \\ &+ \left(\frac{35a^4}{128} + \frac{3b^2}{8} - \frac{15a^2b}{16}\right)x^4 + \mathcal{O}(x^5) \end{aligned} \quad (1.105)$$

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

$$\lambda = \sqrt{1+4\alpha y + y^2} \quad (1.106)$$

$$\simeq 1 + 2\alpha y + \left(\frac{1}{2} - 2\alpha^2\right)y^2 + (4\alpha^3 - \alpha)y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right)y^4 + \mathcal{O}(y^5) \quad (1.107)$$

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

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

$$d = (1 + 2\alpha y \mp \lambda)^2 + 4\beta^2 y^2 \quad (1.109)$$

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

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

$$= 2 + 8\alpha y + 2y^2 \mp 2\lambda \mp 4\alpha y \lambda \quad (1.112)$$

$$= 2 + 8\alpha y + 2y^2 \mp 2(1 + 2\alpha y)\lambda \quad (1.113)$$

$$\simeq 2 + 8\alpha y + 2y^2 \mp 2(1 + 2\alpha y) \left(1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3 + \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4\right)y^4\right) \quad (1.114)$$

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

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

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

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

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

$$\simeq 4\beta^2 y^2 - 2 \left(3\alpha^2 - \frac{1}{8} - 10 \left(\frac{1}{16} - \beta^4 - 2\alpha^2 \beta^2 \right) - 8\beta^2 \alpha^2 \right) y^4 \quad (1.120)$$

$$\simeq 4\beta^2 y^2 - 2 \left(3\alpha^2 - \frac{3}{4} + 10\beta^4 + 12\alpha^2 \beta^2 \right) y^4 \quad (1.121)$$

$$\simeq 4\beta^2 y^2 - (-6\beta^2 + 20\beta^4 + 24\alpha^2 \beta^2) y^4 \quad (1.122)$$

$$\simeq 4\beta^2 y^2 \left(1 + \frac{6}{4} y^2 - 5\beta^2 y^2 - 6\alpha^2 y^2 \right) \quad (1.123)$$

$$\simeq 4\beta^2 y^2 (1 + 6\alpha^2 y^2 + 6\beta^2 y^2 - 5\beta^2 y^2 - 6\alpha^2 y^2) \quad (1.124)$$

$$\simeq 4\beta^2 y^2 (1 + \beta^2 y^2) \quad (1.125)$$

$$d_- \simeq 2 + 8\alpha y + 2y^2 + 2 + 8\alpha y + (2 - 4\beta^2) y^2 + 2 \left(3\alpha^2 - \frac{1}{8} - 10\alpha^4 - 8\beta^2 \alpha^2 \right) y^4 \quad (1.126)$$

$$\simeq 4 + 16\alpha y + 4(1 - \beta^2) y^2 \quad (1.127)$$

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

$$d_+^{-\frac{1}{2}} \simeq \left(\sqrt{4\beta^2 y^2 (1 + \beta^2 y^2)} \right)^{-1} \simeq \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2 \right) \quad (1.128)$$

$$d_-^{-\frac{1}{2}} \simeq (4 + 16\alpha y + 4(1 - \beta^2) y^2)^{-\frac{1}{2}} \quad (1.129)$$

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

$$\simeq \frac{1}{2} \left(1 - \left(\frac{4\alpha}{2} \right) y + \left(\frac{3 \cdot 16\alpha^2}{8} - \frac{1 - \beta^2}{2} \right) y^2 \right) \quad (1.131)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(6\alpha^2 - \frac{1}{2} + \frac{\beta^2}{2} \right) y^2 \right) \quad (1.132)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(\frac{6}{4} - 6\beta^2 - \frac{1}{2} + \frac{\beta^2}{2} \right) y^2 \right) \quad (1.133)$$

$$\simeq \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2} \beta^2 \right) y^2 \right) \quad (1.134)$$

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

$$n_1^\pm = 2\beta y \quad (1.135)$$

$$n_2^\pm = 1 + 2\alpha y \mp \lambda \quad (1.136)$$

$$\simeq 1 + 2\alpha y \mp (1 + 2\alpha y + 2\beta^2 y^2 - 4\beta^2 \alpha y^3) \quad (1.137)$$

$$n_2^+ \simeq 1 + 2\alpha y - 1 - 2\alpha y - 2\beta^2 y^2 + 4\beta^2 \alpha y^3 \quad (1.138)$$

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

$$n_2^- \simeq 1 + 2\alpha y + 1 + 2\alpha y + 2\beta^2 y^2 \quad (1.140)$$

$$\simeq 2 + 4\alpha y + 2\beta^2 y^2 \quad (1.141)$$

Finally let's calculate the the mixing coefficients:

$$a_1^+ = \frac{n_1^+}{\sqrt{d_+}} = \frac{2\beta y}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} \quad (1.142)$$

$$= (2\beta y) \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2 \right) \quad (1.143)$$

$$\simeq 1 - \frac{\beta^2}{2} y^2 \quad (1.144)$$

$$a_2^+ = \frac{n_2^+}{\sqrt{d_+}} = \frac{1 + 2\alpha y - \lambda}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} \quad (1.145)$$

$$= (-2\beta^2 y^2 + 4\beta^2 \alpha y^3) \frac{1}{2\beta y} \left(1 - \frac{\beta^2}{2} y^2\right) \quad (1.146)$$

$$\simeq -(\beta y - 2\alpha\beta y^2) \left(1 - \frac{\beta^2}{2} y^2\right) \quad (1.147)$$

$$\simeq -\beta y + 2\alpha\beta y^2 \quad (1.148)$$

$$a_1^- = \frac{n_1^-}{\sqrt{d_-}} = \frac{2\beta y}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \quad (1.149)$$

$$\simeq (2\beta y) \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2\right) y^2\right) \quad (1.150)$$

$$\simeq \beta y - 2\alpha\beta y^2 \quad (1.151)$$

$$a_2^- = \frac{n_2^-}{\sqrt{d_-}} = \frac{1 + 2\alpha y + \lambda}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \quad (1.152)$$

$$\simeq (2 + 4\alpha y + 2\beta^2 y^2) \frac{1}{2} \left(1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2\right) y^2\right) \quad (1.153)$$

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

$$\simeq 1 - 2\alpha y + \left(1 - \frac{11}{2}\beta^2\right) y^2 + 2\alpha y - 4\alpha^2 y^2 + \beta^2 y^2 \quad (1.155)$$

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

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

$$\simeq 1 - \frac{\beta^2}{2} y^2 \quad (1.158)$$

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):

$$a_1 = \frac{2\beta y}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} = \frac{1 + 2\alpha y + \lambda}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \simeq 1 - \frac{\beta^2}{2} y^2 \quad (1.159)$$

$$a_2 = \frac{1 + 2\alpha y - \lambda}{\sqrt{(1 + 2\alpha y - \lambda)^2 + 4\beta^2 y^2}} = \frac{-2\beta y}{\sqrt{(1 + 2\alpha y + \lambda)^2 + 4\beta^2 y^2}} \simeq -\beta y + 2\alpha\beta y^2 \quad (1.160)$$

$$\frac{\beta^2}{2} = \frac{1}{8} \left(1 - \frac{4m_J^2}{[L]^2}\right) \quad (1.161)$$

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

$$|L_+, m_J\rangle = a_1 \left|L \pm \frac{1}{2}, m_J\right\rangle + a_2 \left|L \mp \frac{1}{2}, m_J\right\rangle \quad (1.163)$$

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

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:

$$a_1 \simeq 1 - \frac{y^2}{9} \quad (1.165)$$

$$a_2^\pm \simeq -\frac{\sqrt{2}}{3}y \left(1 \mp \frac{y}{3}\right) \quad (1.166)$$

$$\left|P_{+, +\frac{1}{2}}\right\rangle = a_1 \left|P_{\frac{3}{2}, +\frac{1}{2}}\right\rangle + a_2^+ \left|P_{\frac{1}{2}, +\frac{1}{2}}\right\rangle \quad (1.167)$$

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

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

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

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 labelled 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:

$$\omega_{\frac{1}{2}}^0 = \frac{E_0^P - E_0^S}{\hbar} - \left(\frac{2}{3}\right) \omega_{so} = 2\pi\nu_{\frac{1}{2}}^0 \quad (1.171)$$

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

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

$$\omega_{\frac{1}{2}} = \omega_{\frac{1}{2}}^0 + \delta\omega_{\frac{1}{2}} \quad (1.174)$$

$$\omega_{\frac{3}{2}} = \omega_{\frac{3}{2}}^0 + \delta\omega_{\frac{3}{2}} \quad (1.175)$$

$$\delta\omega = \delta\omega_{\frac{3}{2}} - \delta\omega_{\frac{1}{2}} \quad (1.176)$$

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

$$\left|S_{\frac{1}{2}, -\frac{1}{2}}\right\rangle \leftrightarrow a_1 \left|P_{\frac{1}{2}, -\frac{1}{2}}\right\rangle - a_2^- \left|P_{\frac{3}{2}, -\frac{1}{2}}\right\rangle \implies \omega = \omega_{\frac{1}{2}} + \frac{2y}{3} \left(1 - \frac{y}{3}\right) \omega_{so} \quad (1.177)$$

$$\left|S_{\frac{1}{2}, -\frac{1}{2}}\right\rangle \leftrightarrow a_1 \left|P_{\frac{3}{2}, -\frac{1}{2}}\right\rangle + a_2^- \left|P_{\frac{1}{2}, -\frac{1}{2}}\right\rangle \implies \omega = \omega_{\frac{3}{2}} + \frac{y}{3} \left(1 + \frac{2y}{3}\right) \omega_{so} \quad (1.178)$$

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

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

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

$$\left| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \leftrightarrow a_1 \left| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle - a_2^+ \left| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle \implies \omega = \omega_{\frac{1}{2}} + \frac{4y}{3} \left(\left[\frac{\frac{1}{2} - \frac{g_S}{4}}{-1 - g_S} \right] - \frac{y}{6} \right) \omega_{so} \quad (1.181)$$

$$\left| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \leftrightarrow a_1 \left| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle + a_2^+ \left| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \implies \omega = \omega_{\frac{3}{2}} + \frac{5y}{3} \left(\left[\frac{\frac{1}{5} - \frac{2g_S}{5}}{-1 - g_S} \right] + \frac{2y}{15} \right) \omega_{so} \quad (1.182)$$

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

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

$$\left| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \leftrightarrow a_1 \left| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle - a_2^- \left| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle \implies \omega = \omega_{\frac{1}{2}} - \frac{4y}{3} \left(\left[\frac{\frac{1}{2} - \frac{g_S}{4}}{-1 - g_S} \right] + \frac{y}{6} \right) \omega_{so} \quad (1.184)$$

$$\left| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \leftrightarrow a_1 \left| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle + a_2^- \left| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \implies \omega = \omega_{\frac{3}{2}} - \frac{5y}{3} \left(\left[\frac{\frac{1}{5} - \frac{2g_S}{5}}{-1 - g_S} \right] - \frac{2y}{15} \right) \omega_{so} \quad (1.185)$$

$$\left| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \leftrightarrow \left| P_{\frac{3}{2}}, -\frac{3}{2} \right\rangle \implies \omega = \omega_{\frac{3}{2}} - \frac{y\omega_{so}}{[-1 - g_S]} \quad (1.186)$$

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:

$$\mathcal{H}_{hfs} = A_{hfs} \vec{I} \cdot \vec{J} \quad (1.187)$$

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:

$$\vec{F}^2 = (\vec{I} + \vec{J})^2 = \vec{I}^2 + 2\vec{I} \cdot \vec{J} + \vec{J}^2 \quad (1.188)$$

$$\mathcal{H}_{hfs} = \frac{A_{hfs}}{2} (\vec{F}^2 - \vec{I}^2 - \vec{J}^2) \quad (1.189)$$

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

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{hfs} - \vec{\mu}_I \cdot \vec{B} - \vec{\mu}_J \cdot \vec{B} \quad (1.190)$$

To recap:

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

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.

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

$$\mathcal{H} = \mathcal{H}_0 + \left(-\frac{A_{hfs}}{2} (\vec{I}^2 + \vec{J}^2) - g_I \mu_N B F_z \right) + \left(\frac{A_{hfs}}{2} \vec{F}^2 + (g_I \mu_N - g_J \mu_B) B J_z \right) \quad (1.191)$$

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 (Breit, G. and I.I. Rabi, Phys. Rev. 38, 2082-2083 (1931)), 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}' ,

$$\mathcal{H}' = \frac{A_{hfs}}{2} \vec{F}^2 + (g_I \mu_N - g_S \mu_B) B J_z \quad (1.192)$$

$$\hat{\mathcal{H}}' = \frac{A_{hfs}}{2} \begin{bmatrix} (I + \frac{1}{2})(I + \frac{3}{2}) & 0 \\ 0 & (I - \frac{1}{2})(I + \frac{1}{2}) \end{bmatrix} + (g_I \mu_N - g_S \mu_S) B \begin{bmatrix} \alpha_+ & \beta_- \\ \beta_+ & \alpha_- \end{bmatrix} \quad (1.193)$$

$$\alpha_{\pm} = \left\langle I \pm \frac{1}{2}, m_F \left| \hat{J}_z \right| I \pm \frac{1}{2}, m_F \right\rangle \quad (1.194)$$

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

The first term can be simplified to give:

$$\frac{A_{hfs}}{2} \hat{F}^2 = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \left(I + \frac{1}{2} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \quad (1.196)$$

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

$$|I, m_I\rangle |J, m_J\rangle = |m_I, m_J\rangle \quad (1.197)$$

$$|F, m_F\rangle = \sum |m_I, m_J\rangle \underbrace{\langle m_I, m_J | F, m_F \rangle}_{\text{Clebsch-Gordon}} \quad (1.198)$$

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

$$\left\langle m_F \mp \frac{1}{2}, \pm \frac{1}{2} \middle| I + \frac{1}{2}, m_F \right\rangle = \frac{1}{\sqrt{[I]}} \sqrt{I + \frac{1}{2} \pm m_F} \quad (1.199)$$

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

which gives:

$$\alpha_{\pm} = \pm(\alpha) = \pm \left(\frac{m_F}{[I]} \right) \quad (1.200)$$

$$\beta_{\pm} = -(\beta) = - \left(\frac{\sqrt{(I + \frac{1}{2})^2 - m_F^2}}{[I]} \right) \quad (1.201)$$

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

$$\mathcal{H}' = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right)^2 + \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \begin{bmatrix} 1 + 2\alpha x & -2\beta x \\ -2\beta x & -(1 + 2\alpha x) \end{bmatrix} \quad (1.202)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{2B}{A[I]} \quad (1.203)$$

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

$$\pm \left(\lambda = \sqrt{1 + 4\alpha x + x^2} \right) \quad (1.204)$$

The total energy is therefore:

$$E = E_0 - \frac{A_{hfs}}{2} \left(I(I+1) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right) - g_I \mu_N m_F B + E' \quad (1.205)$$

$$E' = \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right)^2 \pm \frac{A_{hfs}}{2} \left(I + \frac{1}{2} \right) \lambda \quad (1.206)$$

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:

$$\Delta E = \frac{A_{hfs}[I]}{2} = h\nu_{hfs} \quad (1.207)$$

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

$$E = -\frac{h\nu_{hfs}}{2[I]} - g_I \mu_N B m_F \pm \frac{h\nu_{hfs}}{2} \sqrt{1 + \frac{4m_F}{[I]} x + x^2} \quad (1.208)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{B}{h\nu_{hfs}} \quad (1.209)$$

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:

$$E_{\pm(I+\frac{1}{2})} = \frac{I}{[I]} h\nu_{hfs} \pm \left(\left[\frac{g_S}{-2} \right] \mu_B - g_I \mu_N I \right) B \quad (1.210)$$

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:

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + \frac{1}{2}x(2a + x) - \frac{1}{2 \cdot 4}x^2(2a + x)^2 + \frac{1 \cdot 3}{2 \cdot 4 \cdot 6}x^3(2a + x)^3 - \frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6 \cdot 8}x^4(2a + x)^4 \\ &\quad + \frac{1 \cdot 3 \cdot 5 \cdot 7}{2 \cdot 4 \cdot 6 \cdot 8 \cdot 10}x^5(2a + x)^5 - \frac{1 \cdot 3 \cdot 5 \cdot 7 \cdot 9}{2 \cdot 4 \cdot 6 \cdot 8 \cdot 10 \cdot 12}x^6(2a + x)^6 + \dots \end{aligned} \quad (1.211)$$

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

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + \frac{1}{2}x(2a + x) - \frac{1}{8}x^2(4a^2 + x^2 + 4ax) + \frac{1}{16}x^3(8a^3 + 12a^2x + 6ax^2 + x^3) \\ &\quad - \frac{5}{128}x^4(16a^4 + 32a^3x + 24a^2x^2 + 8ax^3 + x^4) \\ &\quad + \frac{7}{256}x^5(32a^5 + 80a^4x + 80a^3x^2 + 40a^2x^3 + 10ax^4 + x^5) \\ &\quad - \frac{21}{1024}x^5(64a^6 + 192a^5x + 240a^4x^2 + 160a^3x^3 + 60a^2x^4 + 12ax^5 + x^6) \dots \end{aligned} \quad (1.212)$$

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

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + \frac{1}{2}x(2a + x) - \frac{1}{8}x^2(4a^2 + x^2 + 4ax) + \frac{1}{16}x^3(8a^3 + 12a^2x + 6ax^2 + x^3) \\ &\quad - \frac{5}{16}x^4(2a^4 + 4a^3x + 3a^2x^2) + \frac{7}{16}x^5(2a^5 + 5a^4x) - \frac{21}{16}x^6a^6 + \mathcal{O}(x^7) \end{aligned} \quad (1.213)$$

Collecting all the terms order by order:

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + (a)x + \left(\frac{1}{2} - \frac{a^2}{2} \right) x^2 + \left(-\frac{a}{2} + \frac{a^3}{2} \right) x^3 + \left(-\frac{1}{8} + \frac{3a^2}{4} - \frac{5a^4}{8} \right) x^4 \\ &\quad + \left(\frac{3a}{8} - \frac{5a^3}{4} + \frac{7a^5}{8} \right) x^5 + \left(\frac{1}{16} - \frac{15a^2}{16} - \frac{21a^6}{16} + \frac{35a^4}{16} \right) x^6 + \mathcal{O}(x^7) \end{aligned} \quad (1.214)$$

Pulling out common factors:

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + ax + \frac{1}{2}(1 - a^2)x^2 - \frac{a}{2}(1 - a^2)x^3 - \frac{1}{8}(1 - 6a^2 + 5a^4)x^4 \\ &\quad + \frac{3a}{8} \left(1 - \frac{10a^2}{3} + \frac{7a^4}{3} \right) x^5 + \frac{1}{16}(1 - 15a^2 - 21a^6 + 35a^4)x^6 + \mathcal{O}(x^7) \end{aligned} \quad (1.215)$$

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

$$\sqrt{1 + 2ax + x^2} = \sqrt{1 \pm 2x + x^2} = \sqrt{(1 \pm x)^2} = 1 \pm x \quad (1.216)$$

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

$$\begin{aligned} \sqrt{1 + 2ax + x^2} &= 1 + ax + \frac{1}{2}(1 - a^2)x^2 - \frac{a}{2}(1 - a^2)x^3 + \frac{1}{8}(5a^2 - 1)(1 - a^2)x^4 \\ &\quad + \frac{3a}{8} \left(1 - \frac{7a^2}{3} \right) (1 - a^2)x^5 - \frac{1}{16}(14a^2 - 21a^2 - 1)(1 - a^2)x^6 + \mathcal{O}(x^7) \end{aligned} \quad (1.217)$$

Making the substitution $a = 2m_F/[I]$, dividing both sides of the Breit-Rabi equation (1.208) by $h\nu_{hfs}$, and using the sixth order expansion that was just calculated gives:

$$\pm \frac{E_{\pm}}{h\nu_{hfs}} = a_0 + a_1 x + \left[1 - \left(\frac{2m_F}{[I]} \right)^2 \right] \left[\sum_{n=2}^6 a_n x^n \right] \quad (1.218)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{B}{h\nu_{hfs}} \quad (1.219)$$

$$[I] = 2I + 1 \quad (1.220)$$

$$a_0 = \left(\frac{I + \frac{1}{2} \mp \frac{1}{2}}{[I]} \right) \quad (1.221)$$

$$a_1 = \frac{m_F}{[I]} \left(\frac{1 \pm \frac{g_I \mu_N}{g_S \mu_B} ([I] \mp 1)}{1 - \frac{g_I \mu_N}{g_S \mu_B}} \right) \approx \frac{m_F}{[I]} + \mathcal{O}(10^{-3}) \quad (1.222)$$

$$a_2 = \frac{1}{4} \quad (1.223)$$

$$a_3 = -\frac{m_F}{2[I]} \quad (1.224)$$

$$a_4 = \frac{1}{16} \left[5 \left(\frac{2m_F}{[I]} \right)^2 - 1 \right] \quad (1.225)$$

$$a_5 = \frac{3m_F}{8[I]} \left[1 - \frac{7}{3} \left(\frac{2m_F}{[I]} \right)^2 \right] \quad (1.226)$$

$$a_6 = -\frac{1}{32} \left[14 \left(\frac{2m_F}{[I]} \right)^2 - 21 \left(\frac{2m_F}{[I]} \right)^4 - 1 \right] \quad (1.227)$$

where \pm refers to the $F = I \pm \frac{1}{2}$ manifold. Note that eqn. (1.210) 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. (1.218) must disappear order by order. Consequently eqn. (1.218) is written such that the disappearance of higher order terms is evident.

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):

$$|m_F^{\pm}\rangle = a_1^{\pm} \left| I + \frac{1}{2}, m_F \right\rangle + a_2^{\pm} \left| I - \frac{1}{2}, m_F \right\rangle \quad (1.228)$$

$$|F, m_F\rangle = \sum_{m_J = -\frac{1}{2}}^{+\frac{1}{2}} |m_F - m_J, m_J\rangle \langle m_F - m_J, m_J | F, m_F\rangle \quad (1.229)$$

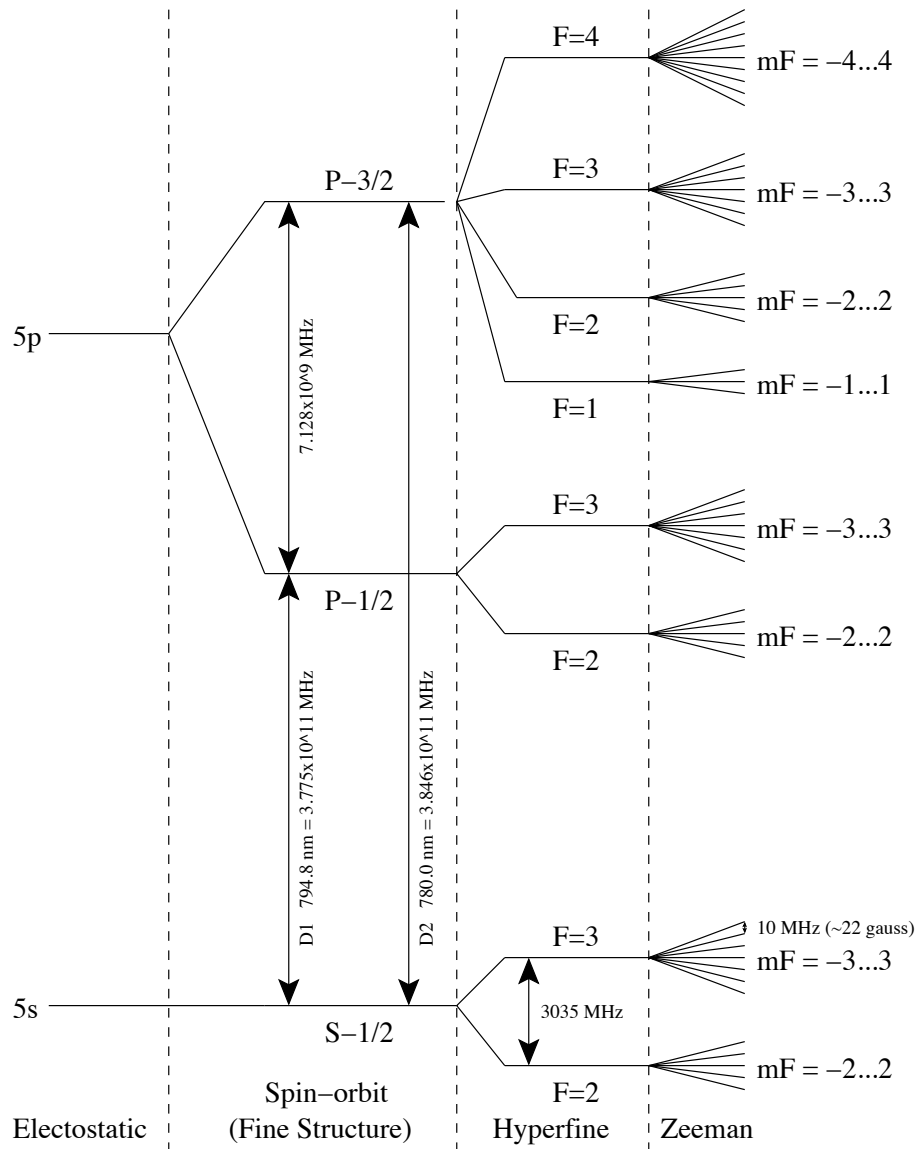


Figure 1.1: Qualitative Energy Level Diagram for Rubidium-85 ($I = 5/2$) in a Weak Field

$$b_1^\pm(m_F) = \left\langle m_F - \frac{1}{2}, +\frac{1}{2} \middle| I \pm \frac{1}{2}, m_F \right\rangle \quad (1.230)$$

$$b_2^\pm(m_F) = \left\langle m_F + \frac{1}{2}, -\frac{1}{2} \middle| I \pm \frac{1}{2}, m_F \right\rangle \quad (1.231)$$

$$\left| I \pm \frac{1}{2}, m_F \right\rangle = b_1^\pm \left| m_F - \frac{1}{2}, +\frac{1}{2} \right\rangle + b_2^\pm \left| m_F + \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (1.232)$$

The values for $a_{1,2}^\pm$ come from the diagonalization of eqn. (1.202) where λ_\pm are the eigenvalues given by eqn. (1.204), α and β are defined by eqns. (1.200) and (1.201), and $b_{1,2}^\pm$ are from eqns. (C.9) and (C.10):

$$a_1^\pm = \frac{2\beta x}{\sqrt{(1 + 2\alpha x \mp \lambda)^2 + 4\beta^2 x^2}} \quad (1.233)$$

$$a_2^\pm = \frac{1 + 2\alpha x \mp \lambda}{\sqrt{(1 + 2\alpha x \mp \lambda)^2 + 4\beta^2 x^2}} \quad (1.234)$$

$$a_1^\pm = \pm a_2^\mp \quad (1.235)$$

$$b_1^\pm = \pm \sqrt{\frac{I \pm m_F + \frac{1}{2}}{[I]}} \quad (1.236)$$

$$b_2^\pm = + \sqrt{\frac{I \mp m_F + \frac{1}{2}}{[I]}} \quad (1.237)$$

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

$$a_1 \equiv a_1^+ = a_2^- \quad (1.238)$$

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

$$b_1 \equiv b_1^+ = b_2^- \quad (1.240)$$

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

$$\left| I \pm \frac{1}{2}, m_F \right\rangle = b_1 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm b_2 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \quad (1.242)$$

$$|m_F^\pm\rangle = a_1 \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 \left| I \mp \frac{1}{2}, m_F \right\rangle \quad (1.243)$$

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

$$\begin{aligned} |m_F^\pm\rangle &= a_1 \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 \left| I \mp \frac{1}{2}, m_F \right\rangle \\ &= a_1 \left(b_1 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm b_2 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right) \\ &\quad \pm a_2 \left(b_1 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \mp b_2 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \right) \\ &= (a_1 b_1 - a_2 b_2) \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm (a_1 b_2 + a_2 b_1) \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \end{aligned} \quad (1.244)$$

1.3.5 Transition Frequencies: EPR Spectrum

Introduction

EPR stands for *E*lectron *P*aramagnetic *R*esonance. 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

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

Table 1.2: Transitions are labelled by the higher m_F 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:

$$g_S = -2 [1 + \mathcal{O}(10^{-3})] \quad (1.245)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{B}{h \nu_{hfs}} \quad (1.246)$$

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

$$\nu_{\pm} = \frac{\nu_{hfs}}{2} \left(\sqrt{1 + \frac{4m_F}{[I]}x + x^2} - \sqrt{1 + \frac{4(m_F - 1)}{[I]}x + x^2} \right) \mp \frac{g_I \mu_N B}{h} \quad (1.247)$$

where the overall sign was chosen to give a positive frequency.

End Transition Frequencies

Transitions involving the edge states are called “end” transitions. The frequency of an end transition has a simpler form:

$$m_F = \pm \left(I + \frac{1}{2} \right) \rightarrow 4m_F = \pm 2[I] \rightarrow \sqrt{1 + \frac{4m_F}{[I]}x + x^2} = 1 \pm x \quad (1.248)$$

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

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

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

where \pm 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. (1.251) in terms of x and isolating

the square root term:

$$\nu_{\pm} = \frac{(-g_S\mu_B - g_I\mu_N)}{(-g_S\mu_B + g_I\mu_N)} \left(\frac{\nu_{hfs}}{2}\right) x \pm \frac{\nu_{hfs}}{2} \left[1 - \sqrt{1 \pm 2 \left(\frac{2I-1}{[I]}\right) x + x^2}\right] \quad (1.252)$$

$$= \frac{\nu_{hfs}}{2} \left(\left[\frac{-g_S\mu_B - g_I\mu_N}{-g_S\mu_B + g_I\mu_N} \right] x \pm 1 \mp \sqrt{1 \pm 2 \left(\frac{2I-1}{[I]}\right) x + x^2} \right) \quad (1.253)$$

$$= \frac{\nu_{hfs}}{2} \left(\underbrace{\left[\frac{-g_S\mu_B - g_I\mu_N}{-g_S\mu_B + g_I\mu_N} \right]}_a x \pm 1 \mp \sqrt{1 \pm 2 \underbrace{\left[\frac{2I-1}{[I]} \right]}_b x + x^2} \right) \quad (1.254)$$

$$\nu = \frac{\nu_{hfs}}{2} \left(ax + s - s\sqrt{1 + 2sbx + x^2} \right) \quad (1.255)$$

$$s = \pm 1 \rightarrow s^2 = 1 \quad (1.256)$$

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

$$n - ax - s = s\sqrt{1 + 2sbx + x^2} \quad (1.258)$$

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

$$(n - ax - s)^2 = \left(-s\sqrt{1 + 2sbx + x^2}\right)^2 \quad (1.259)$$

$$n^2 + a^2x^2 + 1 - 2nax - 2sn + 2sax = 1 + 2sbx + x^2 \quad (1.260)$$

$$0 = 1 + 2sbx + x^2 - n^2 - a^2x^2 - 1 + 2nax + 2sn - 2sax \quad (1.261)$$

$$0 = (1 - a^2)x^2 + 2(sb - sa + na)x + 2sn - n^2 \quad (1.262)$$

$$0 = x^2 + 2\left(\frac{sb - sa + na}{1 - a^2}\right)x + \frac{2sn - n^2}{1 - a^2} \quad (1.263)$$

This is solved by using the quadratic formula (Press, William H. Brian P. Flannery, Saul A. Teukolsky, and William T. Vetterling. Numerical Recipes in C: The Art of Scientific Computing, 1st Edition. Cambridge: Cambridge University Press, 1988. pg 156-7, section 5.5):

$$\mathcal{A}x^2 + \mathcal{B}x + \mathcal{C} = 0 \quad (1.264)$$

$$q \equiv -\frac{1}{2} \left[\mathcal{B} + \text{sgn}(\mathcal{B})\sqrt{\mathcal{B}^2 - 4\mathcal{A}\mathcal{C}} \right] \quad (1.265)$$

$$x_1 = \frac{q}{\mathcal{A}} \quad \& \quad x_2 = \frac{\mathcal{C}}{q} \quad (1.266)$$

In principle, the “traditional” quadratic formula is formally equivalent to the solutions (1.266). 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. The sign of \mathcal{B} depends on s and the frequency of the transition, ν . The correct solution $x_{1,2}$ depends on the field. Since the two solutions differ by orders of magnitude, the correct solution is manifest. We’ll consider only the low field solutions ($x \ll 1$ and $\nu \ll \nu_{hfs}$), which corresponds to the second solution, x_2 . Making the following substitutions and noting the following relations:

$$a = \frac{a_1}{a_2} = \frac{a_x - a_y}{a_x + a_y} = \frac{-g_S\mu_B - g_I\mu_N}{-g_S\mu_B + g_I\mu_N} \quad (1.267)$$

$$1 - a^2 = 1 - \frac{a_1^2}{a_2^2} = \frac{a_2^2 - a_1^2}{a_2^2} = \frac{(a_x + a_y)^2 - (a_x - a_y)^2}{a_2^2} = \frac{4a_x a_y}{a_2^2} \quad (1.268)$$

$$b - 1 = \frac{2I-1}{[I]} - 1 = \frac{2I-1-2I-1}{[I]} = -\frac{2}{[I]} \quad (1.269)$$

$$b + 1 = \frac{2I-1}{[I]} + 1 = \frac{2I-1+2I+1}{[I]} = +\frac{4I}{[I]} \quad (1.270)$$

gives for the $\mathcal{A}, \mathcal{B}, \mathcal{C}$ coefficients:

$$\mathcal{A} = 1 \quad (1.271)$$

$$\mathcal{B} = 2 \left(\frac{sb - sa + na}{1 - a^2} \right) = 2a_2 \left(\frac{sba_2 - sa_1 + na_1}{4a_x a_y} \right) \quad (1.272)$$

$$= 2(a_x + a_y) \left(\frac{sba_x + sba_y - sa_x + sa_y + na_x - na_y}{4a_x a_y} \right) \quad (1.273)$$

$$= \left(\frac{a_x + a_y}{2sa_x a_y} \right) [a_x(b - 1 + sn) + a_y(b + 1 - sn)] \quad (1.274)$$

$$\mathcal{C} = \frac{2sn - n^2}{1 - a^2} = n \frac{(a_x + a_y)^2}{4a_x a_y} (2s - n) = n(2 - sn) \frac{(a_x + a_y)^2}{4sa_x a_y} \quad (1.275)$$

The discriminant is:

$$\mathcal{B}^2 - 4\mathcal{A}\mathcal{C} = \left(\frac{a_x + a_y}{2sa_x a_y} \right)^2 [a_x(b - 1 + sn) + a_y(b + 1 - sn)]^2 - 4n(2 - sn) \frac{(a_x + a_y)^2}{4sa_x a_y} \quad (1.276)$$

$$= (a_x + a_y)^2 \left(\frac{[a_x(b - 1 + sn) + a_y(b + 1 - sn)]^2}{4a_x^2 a_y^2} - \frac{n(2 - sn)}{sa_x a_y} \right) \quad (1.277)$$

$$= (a_x + a_y)^2 \left(\frac{[a_x(b - 1 + sn) + a_y(b + 1 - sn)]^2 - 4sa_x a_y n(2 - sn)}{4a_x^2 a_y^2} \right)$$

$$= \left(\frac{a_x + a_y}{2a_x a_y} \right)^2 [a_x^2(b - 1 + sn)^2 + a_y^2(b + 1 - sn)^2 \quad (1.278)$$

$$+ 2a_x a_y(b - 1 + sn)(b + 1 - sn) - 4sa_x a_y n(2 - sn)]$$

$$= \left(\frac{a_x + a_y}{2a_x a_y} \right)^2 \times [a_x^2(b - 1 + sn)^2 + a_y^2(b + 1 - sn)^2 + 2a_x a_y(b^2 - 1 - 2sn + n^2)] \quad (1.279)$$

To determine the sign of \mathcal{B} , we need to consider the sign of $s[a_x(b - 1 + sn) + a_y(b + 1 - sn)]$ because $a_x \gg a_y > 0$. For $s = -1$:

$$\begin{aligned} -a_x(b - 1 - n) - a_y(b + 1 + n) &> 0 \\ n &> \frac{a_x(b - 1) + a_y(b + 1)}{a_x - a_y} \end{aligned}$$

$$\nu > \frac{\nu_{hfs}}{[I]} \left(\frac{-1 + g'}{1 - \frac{g'}{2I}} \right) \leftrightarrow \text{sgn}(\mathcal{B}) = +1 \quad (1.280)$$

$$g' = \frac{a_y}{a_x} = \left[\frac{-2}{gS} \right] \frac{gI\mu_N I}{\mu_B} \approx 10^{-3} \quad (1.281)$$

Since g' is very small, ν always satisfies (1.280) and consequently for $s = -1$, $\mathcal{B} > 0$. For $s = +1$:

$$\begin{aligned} a_x(b - 1 + n) + a_y(b + 1 - n) &> 0 \\ n &> \frac{a_x(1 - b) - a_y(b + 1)}{a_x - a_y} \end{aligned}$$

$$\nu > \frac{\nu_{hfs}}{[I]} \left(\frac{1 + g'}{1 + \frac{g'}{2I}} \right) \leftrightarrow \text{sgn}(\mathcal{B}) = +1 \quad (1.282)$$

$$\nu < \frac{\nu_{hfs}}{[I]} \left(\frac{1 + g'}{1 + \frac{g'}{2I}} \right) \leftrightarrow \text{sgn}(\mathcal{B}) = -1 \quad (1.283)$$

$$g' = \frac{a_y}{a_x} = \left[\frac{-2}{gS} \right] \frac{gI\mu_N I}{\mu_B} \approx 10^{-3}$$

For low field, ν satisfies (1.283) and consequently for $s = +1$, $\mathcal{B} < 0$. Knowledge of the sign of \mathcal{B} ($= -s$) allows us to calculate q and therefore the solution x_2 :

$$q = \left(\frac{a_x + a_y}{-4sa_x a_y} \right) [a_x (b - 1 + sn) + a_y (b + 1 - sn)] - \left(\frac{a_x + a_y}{-4sa_x a_y} \right) \times \sqrt{\left[a_x^2 (b - 1 + sn)^2 + a_y^2 (b + 1 - sn)^2 + 2a_x a_y (b^2 - 1 - 2sn + n^2) \right]} \quad (1.284)$$

$$x_2 = \frac{C}{q} = \frac{n(2 - sn)(a_x + a_y)^2}{4sa_x a_y q} = \frac{n(2 - sn)(a_x + a_y)}{a_x(1 - b - sn) + a_y(sn - 1 - b) + \sqrt{\dots}} \quad (1.285)$$

$$x = (a_x + a_y) \frac{B}{h\nu_{hfs}} = x_2 \quad (1.286)$$

$$B(\nu) = \frac{h\nu_{hfs} n(2 - sn)}{a_x(1 - b - sn) + a_y(sn - 1 - b) + \sqrt{\dots}} \quad (1.287)$$

Relabelling and rearranging things:

$$B(\nu) = \left[\frac{-2}{gs} \right] \left(\frac{h\nu_{hfs}}{\mu_B} \right) \frac{\nu_0 (1 - s\nu_0/[I])}{(1 - s\nu_0) - g' \left(1 - \frac{s}{2I} \nu_0 \right) + \sqrt{\dots}} \quad (1.288)$$

$$\dots = (1 - s\nu_0)^2 - 2g' \left(1 + \frac{s[I]}{2I} \nu_0 - \frac{\nu_0^2}{2I} \right) + g'^2 \left(1 - \frac{s}{2I} \nu_0 \right)^2 \quad (1.289)$$

$$\nu_0 = [I] \frac{\nu}{\nu_{hfs}} \left(= \frac{n}{1 - b} \right) \quad (1.290)$$

$$g' = \left[\frac{-2}{gs} \right] \frac{gI\mu_N I}{\mu_B} \left(= 2I \frac{a_y}{a_x} \right) \quad (1.291)$$

Equation (1.288) gives the field B given the end transition frequency ν involving one of the edge states $m_F = s \left(I + \frac{1}{2} \right)$ when the field is low $\nu_0 < 1$. Specifically, equation (1.288) is applicable to the alkali metal transitions listed in table (1.3). The equation is exact. The stipulation that the field be low is *not* because of a low field approximation, but because:

1. the choice of two solutions from the quadratic formula
2. the interpretation of the transition. At high field, the nuclear and electron spins decouple, so it is no longer appropriate to talk about transitions between the hyperfine levels $m_F \leftrightarrow m_F - 1$.

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:

$$\Delta\nu_{\text{twin}} = \nu_{\text{lower}} - \nu_{\text{upper}} = +2gI \frac{\mu_N}{h} B \quad (1.292)$$

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:

$$^{39}\text{K} : \nu(F = 1, m_F = \pm 1 \leftrightarrow 0) - \nu(F = 2, m_F = \pm 1 \leftrightarrow 0) = 3.98 \text{ kHz} \quad (1.293)$$

$$^{85}\text{Rb} : \nu(F = 2, m_F = \pm 2 \leftrightarrow \pm 1 \leftrightarrow 0) - \nu(F = 3, m_F = \pm 2 \leftrightarrow \pm 1 \leftrightarrow 0) = 8.25 \text{ kHz} \quad (1.294)$$

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 (1.288) is valid with $s = \pm$

Low Field Frequency Expansion

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

$$\begin{aligned}
\nu_{\pm} &= \frac{\nu_{hfs} \Delta \mp \frac{g_I \mu_N B}{h}}{2} \\
\Delta &= \sqrt{1 + 2ax + x^2} - \sqrt{1 + 2a'x + x^2} \\
&= (a - a')x + \left(-\frac{a^2 - a'^2}{2}\right)x^2 \\
&\quad + \left(-\frac{a - a'}{2} + \frac{a^3 - a'^3}{2}\right)x^3 \\
&\quad + \left(3\frac{a^2 - a'^2}{4} - 5\frac{a^4 - a'^4}{8}\right)x^4 \\
&\quad + \left(3\frac{a - a'}{8} - 5\frac{a^3 - a'^3}{4} + 7\frac{a^5 - a'^5}{8}\right)x^5 \\
&\quad + \left(-15\frac{a^2 - a'^2}{16} - 21\frac{a^6 - a'^6}{16} + 35\frac{a^4 - a'^4}{16}\right)x^6
\end{aligned} \tag{1.295}$$

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

$$a^n - a'^n = \left(\frac{2m_F}{[I]}\right)^n - \left(\frac{2(m_F - 1)}{[I]}\right)^n = \left[\frac{2}{b}\right]^n [m_F^n - (m_F - 1)^n] \tag{1.296}$$

Factoring out b^n from each term:

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

$$+ \left[-\frac{35b^2}{2} (1 - 4m_F + 6m_F^2 - 4m_F^3) + \frac{15b^4}{8} (1 - 2m_F) \right] \frac{x^6}{b^6} \quad (1.297)$$

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 :

$$\frac{\nu_{\pm}}{\nu_{hfs}} = \sum_{n=1}^6 c_n \frac{x^n}{[I]^n} \quad (1.298)$$

$$x = (g_I \mu_N - g_S \mu_B) \frac{B}{h \nu_{hfs}} \quad (1.299)$$

$$[I] = 2I + 1 \quad (1.300)$$

$$c_1 = \frac{1 \pm \frac{g_I \mu_N}{g_S \mu_B} ([I] \mp 1)}{1 - \frac{g_I \mu_N}{g_S \mu_B}} = 1 \pm \mathcal{O}(10^{-3}) \quad (1.301)$$

$$c_2 = 1 - 2m_F \quad (1.302)$$

$$c_3 = 2 \left(1 - 3m_F + 3m_F^2 - \frac{[I]^2}{4} \right) \quad (1.303)$$

$$c_4 = 5 (1 - 4m_F + 6m_F^2 - 4m_F^3) - \frac{3[I]^2}{2} (1 - 2m_F) \quad (1.304)$$

$$c_5 = 14 (1 - 5m_F + 10m_F^2 - 10m_F^3 + 5m_F^4) - 5[I]^2 (1 - 3m_F + 3m_F^2) + \frac{3[I]^4}{8} \quad (1.305)$$

$$c_6 = 42 (1 - 6m_F + 15m_F^2 - 20m_F^3 + 15m_F^4 - 6m_F^5) - \frac{35[I]^2}{2} (1 - 4m_F + 6m_F^2 - 4m_F^3) + \frac{15[I]^4}{8} (1 - 2m_F) \quad (1.306)$$

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 (1.298) for *any* transition at low field. Thus applying the quadratic formula (1.266) and noting that $\mu_N/\mu_B \ll 1$ and $g_S \approx -2$, we get the field corresponding to a particular transition frequency at low fields#check#how accurate is this approximation?:

$$B \approx \left(\frac{h\nu}{\mu_B} \right) \frac{[I]}{1 + \sqrt{1 + 4(1 - 2m_F)\nu/\nu_{hfs}}} \quad (1.307)$$

Low Field Adjacent Transition Frequency Difference

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

$$\left| \frac{\nu(m_F + 1 \leftrightarrow m_F) - \nu(m_F \leftrightarrow m_F - 1)}{\nu_{hfs}} \right| = 2 \frac{x^2}{[I]^2} = 2 \left[(g_I \mu_N - g_S \mu_B) \frac{B}{[I] h \nu_{hfs}} \right]^2 \quad (1.308)$$

Low Field Frequency Derivative with respect to Field

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

$$\frac{d\nu}{dB} = \mp \frac{g_I \mu_N}{h} + \frac{(g_I \mu_N - g_S \mu_B)}{2h[I]} \left(\frac{2m_F + [I]x}{\sqrt{1 + \frac{4m_F}{[I]}x + x^2}} - \frac{2m_F - 2 + [I]x}{\sqrt{1 + \frac{4(m_F-1)}{[I]}x + x^2}} \right) \quad (1.309)$$

The derivative can be “expanded” in x at low field by taking the derivative of equation (1.298) term by term. To fifth order in field, the derivative of the frequency with respect to the field is:

$$\frac{d\nu_{\pm}}{dB} = \frac{(g_I\mu_N - g_S\mu_B)}{h[I]} \sum_{n=0}^5 b_n \frac{x^n}{[I]^n} \quad (1.310)$$

$$x = (g_I\mu_N - g_S\mu_B) \frac{B}{h\nu_{hf_s}} \quad (1.311)$$

$$[I] = 2I + 1 \quad (1.312)$$

$$b_0 = \frac{1 \pm \frac{g_I\mu_N}{g_S\mu_B} ([I] \mp 1)}{1 - \frac{g_I\mu_N}{g_S\mu_B}} = 1 \pm \mathcal{O}(10^{-3}) \quad (1.313)$$

$$b_1 = 2(1 - 2m_F) \quad (1.314)$$

$$b_2 = 6 \left(1 - 3m_F + 3m_F^2 - \frac{[I]^2}{4} \right) \quad (1.315)$$

$$b_3 = 20(1 - 4m_F + 6m_F^2 - 4m_F^3) - 6[I]^2(1 - 2m_F) \quad (1.316)$$

$$b_4 = 70(1 - 5m_F + 10m_F^2 - 10m_F^3 + 5m_F^4) - 25[I]^2(1 - 3m_F + 3m_F^2) + \frac{15[I]^4}{8} \quad (1.317)$$

$$b_5 = 252(1 - 6m_F + 15m_F^2 - 20m_F^3 + 15m_F^4 - 6m_F^5) - 105[I]^2(1 - 4m_F + 6m_F^2 - 4m_F^3) + \frac{45[I]^4}{4}(1 - 2m_F) \quad (1.318)$$

For the end transitions, the coefficients for the expansion of the derivative of the EPR frequency are:

$$b_0 = \frac{1 + \frac{g_I\mu_N}{g_S\mu_B}(2I)}{1 - \frac{g_I\mu_N}{g_S\mu_B}} = 1 \pm \mathcal{O}(10^{-3}) \quad (1.319)$$

$$b_1 = \mp 4I \quad (1.320)$$

$$b_2 = 6I(2I - 1) \quad (1.321)$$

$$b_3 = \mp 8I(4I^2 - 6I + 1) \quad (1.322)$$

$$b_4 = 10I(2I - 1)(4I^2 - 10I + 1) \quad (1.323)$$

$$b_5 = \mp 12I(16I^4 - 80I^3 + 80I^2 - 20I + 1) \quad (1.324)$$

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

Chapter 2

Atomic Population Distribution

2.1 Density Matrix

To discuss the relative population of each state, it is useful to introduce the density matrix (U. Fano, Rev. Mod. Phys. 29, pg 74-93, 1957). It is often used to represent a large ensemble of systems in a statistical mixture of possibly coherent pure quantum states. To be explicit, given a statistical probability p_k of being in the pure quantum state $|\psi_k\rangle$, the density operator in the basis $\{|u_n\rangle\}$ is:

$$\begin{aligned}\hat{\rho} &= \sum_k p_k |\psi_k\rangle \langle\psi_k| \\ &= \sum_k p_k \sum_{n,m} \langle\psi_k|u_m\rangle \langle u_n|\psi_k\rangle |u_n\rangle \langle u_m|\end{aligned}\quad (2.1)$$

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

$$\rho_{nn} = \sum_k p_k |\langle u_n|\psi_k\rangle|^2 \quad (2.2)$$

which implies that $\text{Tr}(\hat{\rho}) = 1$ as one would expect. Off diagonal elements are called coherences. The ensemble averaged expectation value of some operator \hat{M} is given by:

$$\langle \hat{M} \rangle = \text{Tr}(\hat{\rho}\hat{M}) \quad (2.3)$$

For example, consider a vapor of alkali metal in a field at thermal equilibrium. We'll assume that all the atoms are in the ground RS term with eigenbasis:

$$|u_+\rangle = \left| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \quad (2.4)$$

$$|u_-\rangle = \left| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \quad (2.5)$$

The state of a single atom labelled by l is:

$$|\psi_l\rangle = c_{l+} e^{i\phi_{l+}} |u_+\rangle + c_{l-} e^{i\phi_{l-}} |u_-\rangle \quad (2.6)$$

The density matrix for this particular atom is:

$$\hat{\rho}_l = |\psi_l\rangle \langle\psi_l| \quad (2.7)$$

$$= (c_{l+} e^{i\phi_{l+}} |u_+\rangle + c_{l-} e^{i\phi_{l-}} |u_-\rangle) (c_{l+} e^{-i\phi_{l+}} \langle u_+| + c_{l-} e^{-i\phi_{l-}} \langle u_-|) \quad (2.8)$$

$$= \begin{bmatrix} c_{l+}^2 & c_{l+} c_{l-} e^{i(\phi_{l+} - \phi_{l-})} \\ c_{l+} c_{l-} e^{-i(\phi_{l+} - \phi_{l-})} & c_{l-}^2 \end{bmatrix} \quad (2.9)$$

Averaging over all atoms in the vapor gives the ensemble averaged density operator:

$$\hat{\rho} = \frac{1}{N} \sum_{l=1}^N \hat{\rho}_l \quad (2.10)$$

$$= \frac{\sum_{l=1}^N}{N} \begin{bmatrix} c_{l+}^2 & c_{l+}c_{l-}e^{i(\phi_{l+}-\phi_{l-})} \\ c_{l+}c_{l-}e^{-i(\phi_{l+}-\phi_{l-})} & c_{l-}^2 \end{bmatrix} \quad (2.11)$$

If the sample of atoms is incoherent, then the off-diagonal elements average to zero. If there is some coherence among the atoms, then these off-diagonal elements are non-zero. Coherence refers to the a systematic non-random phase relationship among quantum states of the atoms in the ensemble. We'll assume that our sample does not and therefore is completely incoherent. If there are n_k atoms that share the same $c_{k\pm}$, then we can rewrite the density matrix as:

$$\frac{\sum_{l=1}^N}{N} c_{l+}c_{l-}e^{-i(\phi_{l+}-\phi_{l-})} \approx 0 \quad (2.12)$$

$$\hat{\rho} = \sum_k n_k \begin{bmatrix} c_{k+}^2 & 0 \\ 0 & c_{k-}^2 \end{bmatrix} \quad (2.13)$$

Taking advantage of the normalization condition $c_{k+}^2 + c_{k-}^2 = 1$ to relabel things and noting that $\frac{n_k}{N}$ is simply the statistical probability of an atom being in a state with c_k :

$$\hat{\rho} = \sum_k p_k \begin{bmatrix} c_k^2 & 0 \\ 0 & 1 - c_k^2 \end{bmatrix} = \begin{bmatrix} \sum_k p_k c_k^2 & 0 \\ 0 & \sum_k p_k (1 - c_k^2) \end{bmatrix} \quad (2.14)$$

The values of the sums of diagonal elements are constrained by statistical mechanics when the system is at thermal equilibrium. For a canonical ensemble (fixed number of particles in equilibrium with a heat reservoir at a common temperature T), the relative population of each state is given by:

$$P_n = \frac{\exp\left(-\frac{E_n}{kT}\right)}{Z} \quad (2.15)$$

$$Z = \sum_n \exp\left(-\frac{E_n}{kT}\right) \quad (2.16)$$

where Z is the partition function. The energies for the ground RS terms (which will be labeled by \pm) are:

$$E\left(\left|S_{\frac{1}{2}}, +\frac{1}{2}\right\rangle\right) = E_0^S + \left[\frac{gS}{-2}\right] \mu_B B \quad (2.17)$$

$$E\left(\left|S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle\right) = E_0^S - \left[\frac{gS}{-2}\right] \mu_B B \quad (2.18)$$

This gives for the relative population of each state at thermodynamic equilibrium:

$$Z = \exp\left(-\frac{E_+}{kT}\right) + \exp\left(-\frac{E_-}{kT}\right) \quad (2.19)$$

$$= \exp\left(-\frac{E_0^S + \left[\frac{gS}{-2}\right] \mu_B B}{kT}\right) + \exp\left(-\frac{E_0^S - \left[\frac{gS}{-2}\right] \mu_B B}{kT}\right) \quad (2.20)$$

$$= \exp\left(-\frac{E_0^S}{kT}\right) \left[\exp\left(-\left[\frac{gS}{-2}\right] \frac{\mu_B B}{kT}\right) + \exp\left(+\left[\frac{gS}{-2}\right] \frac{\mu_B B}{kT}\right) \right] \quad (2.21)$$

$$P_{\pm} = \frac{\exp\left(-\frac{E_0^S}{kT}\right) \exp\left(\mp \left[\frac{gS}{-2}\right] \frac{\mu_B B}{kT}\right)}{\exp\left(-\frac{E_0^S}{kT}\right) \left[\exp\left(+\left[\frac{gS}{-2}\right] \frac{\mu_B B}{kT}\right) + \exp\left(-\left[\frac{gS}{-2}\right] \frac{\mu_B B}{kT}\right) \right]} \quad (2.22)$$

$$= \frac{\exp\left(\mp \left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right)}{\exp\left(+ \left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right) + \exp\left(- \left[\frac{g_S}{-2}\right] \frac{\mu_B B}{kT}\right)} \quad (2.23)$$

$$P_{m_J} = \frac{\exp(m_J \beta)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \quad (2.24)$$

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 peccadillos and will be more apparent when we discuss the role of nuclear spin in spin-exchange collisions in section (2.2). For the $S_{\frac{1}{2}}$ ground states at thermal equilibrium, the spin temperature is:

$$\beta = \frac{g_S \mu_B B}{kT} = \left[\frac{g_S}{-2}\right] \left(\frac{-2\mu_B B}{kT}\right) \quad (2.25)$$

Connecting this to the density matrix for the system yields the following relationship between the diagonal elements and the relative populations given by Boltzmann statistics:

$$P_+ = \frac{\exp\left(+\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} = \sum_k p_k c_k^2 \quad (2.26)$$

$$P_- = \frac{\exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} = \sum_k p_k (1 - c_k^2) \quad (2.27)$$

$$\hat{\rho} = \begin{bmatrix} P_+ & 0 \\ 0 & P_- \end{bmatrix} \quad (2.28)$$

Knowing the form of the density matrix allows us to calculate the longitudinal (along the axis of the field) polarization at thermal equilibrium:

$$P \equiv \frac{\langle \hat{J}_z \rangle}{J} = \frac{\text{Tr}(\hat{\rho} \hat{J}_z)}{\frac{1}{2}} \quad (2.29)$$

$$= 2 \text{Tr} \left\{ \begin{bmatrix} P_+ & 0 \\ 0 & P_- \end{bmatrix} \begin{bmatrix} +\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} \right\} \quad (2.30)$$

$$= 2 \text{Tr} \left\{ \begin{bmatrix} +\frac{P_+}{2} & 0 \\ 0 & -\frac{P_-}{2} \end{bmatrix} \right\} \quad (2.31)$$

$$= 2 \left(+\frac{P_+}{2} - \frac{P_-}{2} \right) \quad (2.32)$$

$$= P_+ - P_- \quad (2.33)$$

As should come as no surprise, the polarization for a two state system is simply the difference between the relative populations of the two states. We can now express the polarization as a function of the spin temperature:

$$P = \frac{\exp\left(+\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} - \frac{\exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \quad (2.34)$$

$$= \frac{\exp\left(+\frac{\beta}{2}\right) - \exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \quad (2.35)$$

$$P = \tanh\left(\frac{\beta}{2}\right) \quad (2.36)$$

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:

$$P = \frac{\exp\left(+\frac{\beta}{2}\right) - \exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} = \frac{x - \frac{1}{x}}{x + \frac{1}{x}} = \frac{x^2 - 1}{x^2 + 1} \quad (2.37)$$

$$Px^2 + P = x^2 - 1 \quad (2.38)$$

$$(P - 1)x^2 = -P - 1 \quad (2.39)$$

$$x^2 = \left[\exp\left(+\frac{\beta}{2}\right) \right]^2 = \frac{1 + P}{1 - P} \quad (2.40)$$

$$\beta = \log\left(\frac{1 + P}{1 - P}\right) \quad (2.41)$$

2.2 Spin Temperature

It has been shown (Young, A.R., Appelt, S., Baranga, A. Ben-Amar, Erickson, C., and Happer, W., App Phys Lett (70), 3081-3 (1997)) that under the optical pumping, spin exchange, high pressure conditions that exist within a cell, the diagonal elements of the density operator for both manifolds are:

$$\rho_{m_F} = \frac{e^{\beta m_F}}{Z_F} = \frac{e^{\beta m_J} e^{\beta m_I}}{Z_J Z_I} \quad (2.42)$$

$$Z_F = \sum_{m_F=-F}^{+F} e^{\beta m_F} \quad (2.43)$$

$$Z_J = \sum_{m_J=-J}^{+J} e^{\beta m_J} \quad (2.44)$$

$$Z_I = \sum_{m_I=-I}^{+I} e^{\beta m_I} \quad (2.45)$$

$$m_F = m_J + m_I \quad (2.46)$$

The meaning of β , spin temperature, is best described by the original reference by Anderson et al. (L.W. Anderson, F.M. Pipkin, J.C. Baird, Jr., Phys Rev 116, p 87-98 (1959)):

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. This gives the relative population of the $|m_F - \frac{1}{2} \mp \frac{1}{2}\rangle$ state:

$$\rho_{\mp} = \frac{e^{\beta(m_F - \frac{1}{2} \mp \frac{1}{2})}}{Z_F} \quad (2.47)$$

from which the relative population difference is easily obtained:

$$\begin{aligned} \rho_+ - \rho_- &= \frac{e^{\beta m_F}}{Z_F} - \frac{e^{\beta(m_F-1)}}{Z_F} = \frac{e^{\beta m_F}}{Z_F} (1 - e^{-\beta}) \\ &= \frac{e^{\beta m_F}}{Z_F} \left[1 - \exp\left(-\log\left[\frac{1+P}{1-P}\right]\right) \right] \\ &= \frac{e^{\beta m_F}}{Z_F} \left[1 - \left(\frac{1-P}{1+P}\right) \right] \\ &= \frac{e^{\beta m_F}}{Z_F} \left(\frac{2P}{1+P} \right) \end{aligned} \quad (2.48)$$

where P is the electron spin polarization.

2.3 Polarization

Chapter 3

A Brief Mathematical Description of Polarized Light

3.1 Representing Electromagnetic Plane Waves

3.1.1 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:

$$\vec{E}(\vec{r}, t) = E_x(z, t)\hat{x} + E_y(z, t)\hat{y} = E_{0x}\hat{x} \cos(kz - \omega t) + E_{0y}\hat{y} \cos(kz - \omega t + \phi) \quad (3.1)$$

$$\vec{B}(\vec{r}, t) = \sqrt{\mu\epsilon} [\hat{z} \times \vec{E}(\vec{r}, t)] = \mu\vec{H}(\vec{r}, t) \quad (3.2)$$

$$= \sqrt{\mu\epsilon} [E_{0x}\hat{y} \cos(kz - \omega t) - E_{0y}\hat{x} \cos(kz - \omega t + \phi)] \quad (3.3)$$

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:

$$\vec{S}(\vec{r}, t) = \vec{E}(\vec{r}, t) \times \vec{H}(\vec{r}, t) = \frac{1}{\mu} \vec{E}(\vec{r}, t) \times \vec{B}(\vec{r}, t) = \sqrt{\frac{\epsilon}{\mu}} \vec{E}(\vec{r}, t) \times [\hat{z} \times \vec{E}(\vec{r}, t)] \quad (3.4)$$

$$= \sqrt{\frac{\epsilon}{\mu}} (\hat{z} [\vec{E}(\vec{r}, t) \cdot \vec{E}(\vec{r}, t)] - \vec{E}(\vec{r}, t) [\hat{z} \cdot \vec{E}(\vec{r}, t)]) \quad (3.5)$$

$$= \hat{z} \sqrt{\frac{\epsilon}{\mu}} [\vec{E}(\vec{r}, t) \cdot \vec{E}(\vec{r}, t)] \quad (3.6)$$

$$= \hat{z} \sqrt{\frac{\epsilon}{\mu}} E_{0x}^2 \left[\cos^2(kz) \cos^2(\omega t) + \sin^2(kz) \sin^2(\omega t) + \frac{1}{2} \sin(2kz) \sin(2\omega t) \right] \\ + \hat{z} \sqrt{\frac{\epsilon}{\mu}} E_{0y}^2 \left[\cos^2(kz + \phi) \cos^2(\omega t) + \sin^2(kz + \phi) \sin^2(\omega t) + \frac{1}{2} \sin(2kz + 2\phi) \sin(2\omega t) \right] \quad (3.7)$$

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

$$I \equiv \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} \hat{z} \cdot \vec{S}(\vec{r}, t) dt \quad (3.8)$$

$$\frac{1}{2} = \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} \cos^2(\omega t) dt = \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} \sin^2(\omega t) dt \quad (3.9)$$

$$I = \sqrt{\frac{\epsilon}{\mu}} \left(\frac{E_{0x}^2}{2} [\cos^2(kz) + \sin^2(kz)] + \frac{E_{0y}^2}{2} [\cos^2(kz + \phi) + \sin^2(kz + \phi)] \right) \quad (3.10)$$

$$= \frac{1}{2} \sqrt{\frac{\epsilon}{\mu}} [E_{0x}^2 + E_{0y}^2] = \sqrt{\frac{\epsilon}{\mu}} \langle |\vec{E}|^2 \rangle_{\text{time}} \quad (3.11)$$

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

$$\sqrt{\langle |\vec{E}|^2 \rangle_{\text{time}}} = \sqrt{\frac{E_{0x}^2 + E_{0y}^2}{2}} \quad (3.12)$$

3.1.2 Complex Representation: The Jones Calculus

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

$$\vec{E}(z, t) = E_x(z, t)\hat{x} + E_y(z, t)\hat{y} = |E\rangle e^{ikz - i\omega t} \quad (3.13)$$

$$E_x(z, t) = E_{0x} \exp(ikz - i\omega t + i\alpha_x) \quad (3.14)$$

$$E_y(z, t) = E_{0y} \exp(ikz - i\omega t + i\alpha_y) \quad (3.15)$$

$$|E\rangle \equiv \begin{bmatrix} E_{0x} e^{i\alpha_x} \\ E_{0y} e^{i\alpha_y} \end{bmatrix} \quad (3.16)$$

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):

$$\left(\frac{E_x}{E_{0x}}\right)^2 + \left(\frac{E_y}{E_{0y}}\right)^2 - 2\left(\frac{E_x}{E_{0x}}\right)\left(\frac{E_y}{E_{0y}}\right)\cos(\alpha) = \sin^2(\alpha) \quad (3.17)$$

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

$$\vec{E}^* \cdot \vec{E} = \langle E|E\rangle = E_{0x}^2 + E_{0y}^2 \quad (3.18)$$

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

$$|\vec{E}|_{\text{time}}^2 \equiv \frac{\vec{E}^* \cdot \vec{E}}{2} = \frac{E_{0x}^2 + E_{0y}^2}{2} \quad (3.19)$$

and finally the intensity is:

$$I = \sqrt{\frac{\epsilon}{\mu}} \langle \vec{E}^* \cdot \vec{E} \rangle_{\text{time}} = \sqrt{\frac{\epsilon}{\mu}} \frac{\langle E|E\rangle}{2} = \frac{\langle B|B\rangle}{2\mu\sqrt{\epsilon\mu}} \quad (3.20)$$

3.2 Linear Polarization

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

$$\alpha = \pm n\pi \quad (3.21)$$

or in other words the two components are in phase. Eqn. (3.17) becomes degenerate,

$$\left(\frac{E_x}{E_{0x}}\right)^2 + \left(\frac{E_y}{E_{0y}}\right)^2 \mp 2\left(\frac{E_x}{E_{0x}}\right)\left(\frac{E_y}{E_{0y}}\right) = 0 \quad (3.22)$$

with solutions

$$\frac{E_y}{E_{0y}} = \mp \frac{E_x}{E_{0x}} \quad (3.23)$$

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

$$|\mathcal{P}\rangle = |x\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (3.24)$$

Vertical linearly polarized light is denoted by

$$|\mathcal{S}\rangle = |y\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (3.25)$$

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

$$|\theta\rangle = \begin{bmatrix} \cos(\theta) \\ \sin(\theta) \end{bmatrix} \quad (3.26)$$

3.3 Circular Polarization

When the relative phase shift is a quarter wave,

$$\alpha = \pm(2n + 1)\frac{\pi}{2} \quad (3.27)$$

and the magnitudes of the two components are identical,

$$E_{0x} = E_{0y} \quad (3.28)$$

then eqn. (3.17) reduces to an equation for a circle:

$$E_x^2 + E_y^2 = 1 \quad (3.29)$$

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,

$$|\mathcal{R}\rangle = |+\rangle = \frac{\sqrt{2}}{2} \begin{bmatrix} 1 \\ +i \end{bmatrix} \quad (3.30)$$

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

$$|\mathcal{L}\rangle = |-\rangle = \frac{\sqrt{2}}{2} \begin{bmatrix} 1 \\ -i \end{bmatrix} \quad (3.31)$$

is antiparallel. Note that the standard optics convention is opposite to the helicity convention. In the helicity convention, for right circularly polarized light, \vec{E} rotates counterclockwise in the 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. (3.1). Unless otherwise noted, *the helicity convention* will be used. See Crawford, Jr. F.S. Waves: Berkeley Physics Course, Volume 3. McGraw Hill 1968 page 400 for further discussion regarding handedness convention.

3.4 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:

$$|E\rangle = E_0 e^{i\phi_p} \left[\sqrt{\frac{1+P}{2}} e^{-i\theta} |\mathcal{R}\rangle + \sqrt{\frac{1-P}{2}} e^{+i\theta} |\mathcal{L}\rangle \right] \quad (3.32)$$

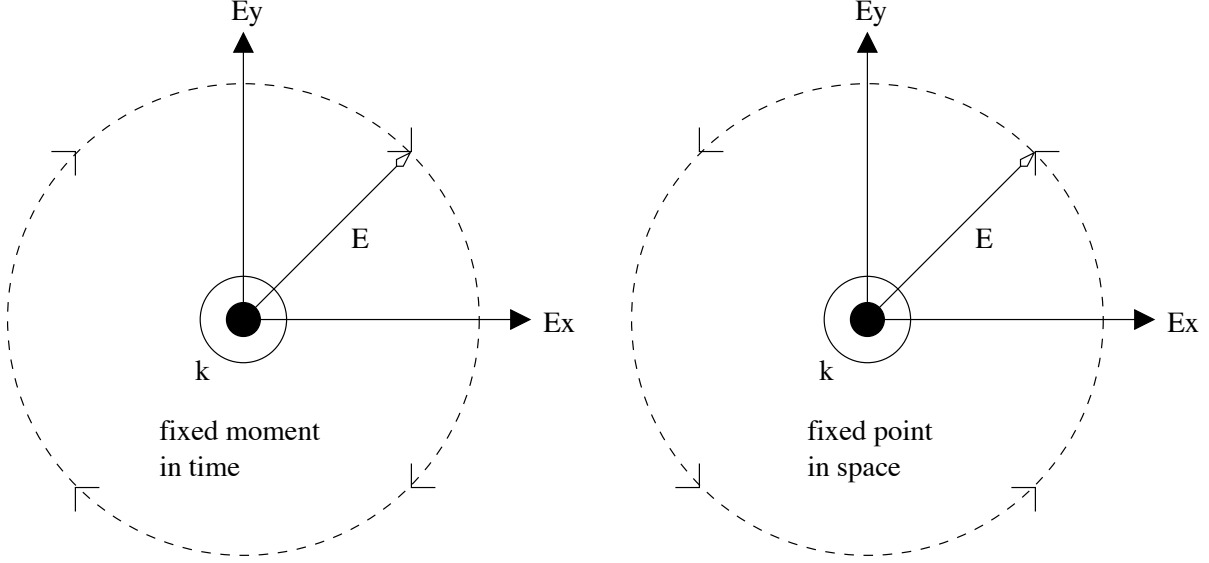


Figure 3.1: Right (helicity) circularly polarized light. Left: fixed time, forward in space. Right: fixed space, forward in time.

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:

$$|E\rangle = E_0 e^{i\phi_p} \left[\left(\sqrt{1-P} \frac{e^{+i\theta}}{2} + \sqrt{1+P} \frac{e^{-i\theta}}{2} \right) |\mathcal{P}\rangle + \left(\sqrt{1-P} \frac{e^{+i\theta}}{2i} - \sqrt{1+P} \frac{e^{-i\theta}}{2i} \right) |\mathcal{S}\rangle \right] \quad (3.33)$$

The magnitude of \vec{E} is:

$$\sqrt{\langle E|E\rangle} = \sqrt{\langle E_{\mathcal{R}}|E_{\mathcal{R}}\rangle + \langle E_{\mathcal{L}}|E_{\mathcal{L}}\rangle} = \sqrt{\left(\frac{1+P}{2}\right) E_0^2 + \left(\frac{1-P}{2}\right) E_0^2} = E_0 \quad (3.34)$$

The degree of circular polarization of the light is:

$$\frac{\langle E_{\mathcal{R}}|E_{\mathcal{R}}\rangle - \langle E_{\mathcal{L}}|E_{\mathcal{L}}\rangle}{\langle E|E\rangle} = \frac{\left(\frac{1+P}{2}\right) E_0^2 - \left(\frac{1-P}{2}\right) E_0^2}{E_0^2} = P \quad (3.35)$$

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

$$|E\rangle = E_0 e^{i\phi_p} \left[\left(\frac{e^{+i\theta}}{2} + \frac{e^{-i\theta}}{2} \right) |\mathcal{P}\rangle + \left(\frac{e^{+i\theta}}{2i} - \frac{e^{-i\theta}}{2i} \right) |\mathcal{S}\rangle \right] = E_0 e^{i\phi_p} [\cos(\theta) |\mathcal{P}\rangle + \sin(\theta) |\mathcal{S}\rangle] \quad (3.36)$$

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.

3.5 Projecting onto an Atomic Coordinate System

The rectangular light coordinate system is defined by:

$$1_{\text{axis}} = |\mathcal{P}\rangle \quad 2_{\text{axis}} = |\mathcal{S}\rangle \quad 3_{\text{axis}} = |\mathcal{P}\rangle \times |\mathcal{S}\rangle = |\mathcal{Z}\rangle \quad (3.37)$$

where $|\mathcal{Z}\rangle$ is the light propagation direction. The rectangular atomic coordinate system is defined by:

$$1_{\text{axis}} = \hat{x} \quad 2_{\text{axis}} = \hat{y} \quad 3_{\text{axis}} = \hat{z} \quad (3.38)$$

where the z -axis is traditionally taken to be the quantization axis (direction of the main magnetic “holding” field). One useful way to decompose the light coordinates in the atomic coordinate representation is:

$$|\mathcal{P}\rangle = \cos(\Phi) \cos(\Theta) \hat{x} + \sin(\Phi) \cos(\Theta) \hat{y} - \sin(\Theta) \hat{z} \quad (3.39)$$

$$|\mathcal{S}\rangle = -\sin(\Phi) \hat{x} + \cos(\Phi) \hat{y} \quad (3.40)$$

$$|\mathcal{Z}\rangle = \cos(\Phi) \sin(\Theta) \hat{x} + \sin(\Phi) \sin(\Theta) \hat{y} + \cos(\Theta) \hat{z} \quad (3.41)$$

$$|\mathcal{R}\rangle = [\cos(\Phi) \cos(\Theta) - i \sin(\Phi)] \frac{\hat{x}}{\sqrt{2}} + [\sin(\Phi) \cos(\Theta) + i \cos(\Phi)] \frac{\hat{y}}{\sqrt{2}} - \sin(\Theta) \frac{\hat{z}}{\sqrt{2}} \quad (3.42)$$

$$|\mathcal{L}\rangle = [\cos(\Phi) \cos(\Theta) + i \sin(\Phi)] \frac{\hat{x}}{\sqrt{2}} + [\sin(\Phi) \cos(\Theta) - i \cos(\Phi)] \frac{\hat{y}}{\sqrt{2}} - \sin(\Theta) \frac{\hat{z}}{\sqrt{2}} \quad (3.43)$$

where Φ and Θ are azimuthal and polar angles of the $|\mathcal{Z}\rangle$ vector with respect to the spherical atomic coordinate system. #check#make a diagram depicting this. The light polarization vector couples to the atom most naturally in the irreducible spherical vector basis (see appendix B):

$$\hat{x} = \frac{\hat{\varepsilon}_- - \hat{\varepsilon}_+}{\sqrt{2}} \quad \hat{y} = i \left(\frac{\hat{\varepsilon}_- + \hat{\varepsilon}_+}{\sqrt{2}} \right) \quad \hat{z} = \hat{\varepsilon}_0 \quad (3.44)$$

Combining the projection and irreducible basis decomposition gives the following for the light coordinates:

$$|\mathcal{P}\rangle = -\sin(\Theta) \hat{\varepsilon}_0 - \exp(-i\Phi) \cos(\Theta) \frac{\hat{\varepsilon}_+}{\sqrt{2}} + \exp(+i\Phi) \cos(\Theta) \frac{\hat{\varepsilon}_-}{\sqrt{2}} \quad (3.45)$$

$$|\mathcal{S}\rangle = i \exp(-i\Phi) \frac{\hat{\varepsilon}_+}{\sqrt{2}} + i \exp(+i\Phi) \frac{\hat{\varepsilon}_-}{\sqrt{2}} \quad (3.46)$$

$$|\mathcal{Z}\rangle = +\cos(\Theta) \hat{\varepsilon}_0 - \exp(-i\Phi) \sin(\Theta) \frac{\hat{\varepsilon}_+}{\sqrt{2}} + \exp(+i\Phi) \sin(\Theta) \frac{\hat{\varepsilon}_-}{\sqrt{2}} \quad (3.47)$$

$$|\mathcal{R}\rangle = -\sin(\Theta) \frac{\hat{\varepsilon}_0}{\sqrt{2}} - \exp(-i\Phi) \left[\frac{1 + \cos(\Theta)}{2} \right] \hat{\varepsilon}_+ - \exp(+i\Phi) \left[\frac{1 - \cos(\Theta)}{2} \right] \hat{\varepsilon}_- \quad (3.48)$$

$$|\mathcal{L}\rangle = -\sin(\Theta) \frac{\hat{\varepsilon}_0}{\sqrt{2}} + \exp(-i\Phi) \left[\frac{1 - \cos(\Theta)}{2} \right] \hat{\varepsilon}_+ + \exp(+i\Phi) \left[\frac{1 + \cos(\Theta)}{2} \right] \hat{\varepsilon}_- \quad (3.49)$$

Only a real vector can be decomposed in the spherical basis in a *consistent* way. For example, $|\mathcal{P}\rangle$, $|\mathcal{S}\rangle$, & $|\mathcal{Z}\rangle$ are all real vectors and $|\mathcal{R}\rangle$ & $|\mathcal{L}\rangle$ are complex vectors; therefore their decompositions using the complex conjugates of the irreducible basis are:

$$|\mathcal{P}\rangle = -\sin(\Theta) \hat{\varepsilon}_0^* - \frac{\cos(\Theta)}{\sqrt{2}} \exp(+i\Phi) \hat{\varepsilon}_+^* + \frac{\cos(\Theta)}{\sqrt{2}} \exp(-i\Phi) \hat{\varepsilon}_-^* \quad (3.50)$$

$$|\mathcal{S}\rangle = -\frac{i}{\sqrt{2}} \exp(+i\Phi) \hat{\varepsilon}_+^* - \frac{i}{\sqrt{2}} \exp(-i\Phi) \hat{\varepsilon}_-^* \quad (3.51)$$

$$|\mathcal{Z}\rangle = +\cos(\Theta) \hat{\varepsilon}_0^* - \frac{\sin(\Theta)}{\sqrt{2}} \exp(+i\Phi) \hat{\varepsilon}_+^* + \frac{\sin(\Theta)}{\sqrt{2}} \exp(-i\Phi) \hat{\varepsilon}_-^* \quad (3.52)$$

$$|\mathcal{R}\rangle = -\frac{\sqrt{2}}{2} \sin(\Theta) \hat{\varepsilon}_0^* + \left[\frac{1 - \cos(\Theta)}{2} \right] \exp(+i\Phi) \hat{\varepsilon}_+^* + \left[\frac{1 + \cos(\Theta)}{2} \right] \exp(-i\Phi) \hat{\varepsilon}_-^* \quad (3.53)$$

$$|\mathcal{L}\rangle = -\frac{\sqrt{2}}{2} \sin(\Theta) \hat{\varepsilon}_0^* - \left[\frac{1 + \cos(\Theta)}{2} \right] \exp(+i\Phi) \hat{\varepsilon}_+^* - \left[\frac{1 - \cos(\Theta)}{2} \right] \exp(-i\Phi) \hat{\varepsilon}_-^* \quad (3.54)$$

Note the subtle difference in the two decompositions of $|\mathcal{R}\rangle$ & $|\mathcal{L}\rangle$.

3.6 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

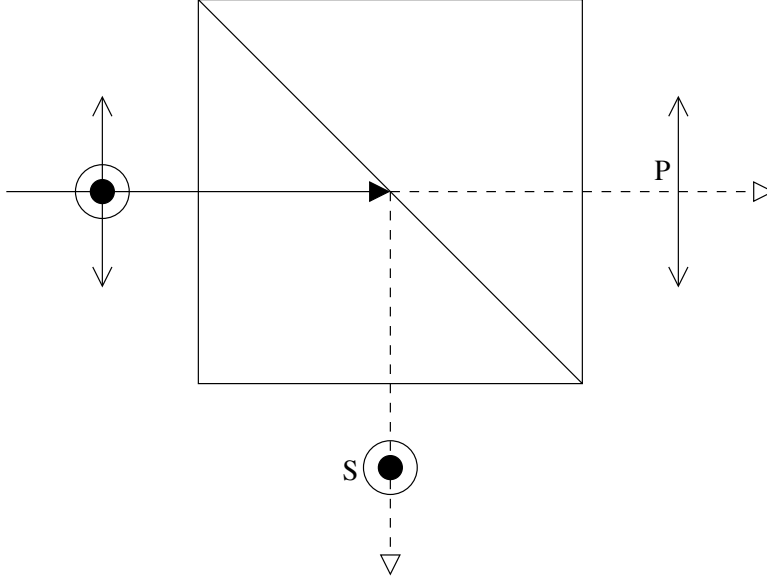


Figure 3.2: Top view of BSPC

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 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:

$$r_P = \sqrt{R_P} \approx 0.9975 \quad (3.55)$$

$$r_S = \sqrt{R_S} \approx 0.9995 \quad (3.56)$$

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:

$$\hat{M} = \begin{bmatrix} r_P & 0 \\ 0 & r_S e^{i\delta_m} \end{bmatrix} \quad (3.57)$$

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

3.7 Beam Splitting Polarizing Cubes

3.7.1 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. (3.2). The transmitted beam is selected by

$$\hat{C}_t = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \quad (3.58)$$

and the reflected beam is selected by

$$\hat{C}_r = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \quad (3.59)$$

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:

$$\hat{C}_t = \begin{bmatrix} t_1 & 0 \\ 0 & t_2 \end{bmatrix} \quad (3.60)$$

$$T_t = \frac{I_{\text{transmitted}}}{I_{\text{input}\mathcal{P}}} = t_1^2 + t_2^2 \quad (3.61)$$

$$e_t = \frac{I_{\text{transmitted}\mathcal{P}}}{I_{\text{transmitted}\mathcal{S}}} = \frac{t_1^2}{t_2^2} \quad (3.62)$$

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:

$$\hat{C}_t = \begin{bmatrix} \sqrt{\frac{T_t}{1+e_t^{-1}}} & 0 \\ 0 & \sqrt{\frac{T_t}{1+e_t}} \end{bmatrix} \quad (3.63)$$

$$\hat{C}_r = \begin{bmatrix} \sqrt{\frac{T_r}{1+e_r}} & 0 \\ 0 & \sqrt{\frac{T_r}{1+e_r^{-1}}} \end{bmatrix} \quad (3.64)$$

Given the specifications for our cube, the matrices are:

$$\hat{C}_t \approx \begin{bmatrix} 0.974 & 0 \\ 0 & 0.031 \end{bmatrix} \quad (3.65)$$

$$\hat{C}_r \approx \begin{bmatrix} 0.213 & 0 \\ 0 & 0.951 \end{bmatrix} \quad (3.66)$$

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

3.7.2 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 wrt 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:

$$\begin{aligned} I_t &= \left| \hat{C}_t |E\rangle \right|^2 = t_1^2 \langle E_{\mathcal{P}} | E_{\mathcal{P}} \rangle + t_2^2 \langle E_{\mathcal{S}} | E_{\mathcal{S}} \rangle \\ &= \frac{E_0^2 T_t e_t}{1 + e_t} \left(\frac{1 - P + 1 + P + 2\sqrt{1 - P^2} \cos(2\theta)}{4} \right) + \frac{E_0^2 T_t}{1 + e_t} \left(\frac{1 - P + 1 + P - 2\sqrt{1 - P^2} \cos(2\theta)}{4} \right) \\ &= \frac{E_0^2 T_t}{2} \left[1 + \left(\frac{e_t - 1}{e_t + 1} \right) \sqrt{1 - P^2} \cos(2\theta) \right] \end{aligned} \quad (3.67)$$

The maximum and minimum transmitted intensities are:

$$I_{\max} = \frac{E_0^2 T_t}{2} \left[1 + \left(\frac{e_t - 1}{e_t + 1} \right) \sqrt{1 - P^2} \right] \quad (3.68)$$

$$I_{\min} = \frac{E_0^2 T_t}{2} \left[1 - \left(\frac{e_t - 1}{e_t + 1} \right) \sqrt{1 - P^2} \right] \quad (3.69)$$

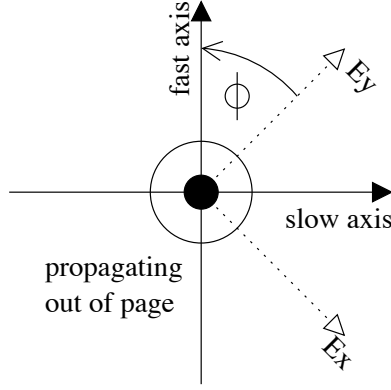


Figure 3.3: Coordinate System of a Waveplate #check#time or space convention fast axis?

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

$$f_c \equiv \frac{e_t - 1}{e_t + 1} \quad (3.70)$$

$$A_c \equiv \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} = f_c \sqrt{1 - P^2} \quad (3.71)$$

$$1 = P^2 + \left(\frac{A_c}{f_c}\right)^2 \quad (3.72)$$

where P is the degree of circular polarization.

3.8 Waveplates

3.8.1 Matrix Representation

A waveplate is an optical element that has different indices of refraction along two orthogonal axes, see fig. (3.3). 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,

$$\hat{R}(\phi) = \begin{bmatrix} \cos(\phi) & \sin(\phi) \\ -\sin(\phi) & \cos(\phi) \end{bmatrix} \quad (3.73)$$

followed by a relative phase retardation of β radians,

$$\hat{W}(\beta) = \begin{bmatrix} \exp\left(+i\frac{\beta}{2}\right) & 0 \\ 0 & \exp\left(-i\frac{\beta}{2}\right) \end{bmatrix} \quad (3.74)$$

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

$$\hat{W}(\phi, \beta) = \hat{R}(-\phi)\hat{W}(\beta)\hat{R}(\phi) \quad (3.75)$$

$$= \exp\left(-i\frac{\beta}{2}\right) \begin{bmatrix} 1 + 2i \exp\left(i\frac{\beta}{2}\right) \sin\left(\frac{\beta}{2}\right) \cos^2(\phi) & i \exp\left(i\frac{\beta}{2}\right) \sin\left(\frac{\beta}{2}\right) \sin(2\phi) \\ i \exp\left(i\frac{\beta}{2}\right) \sin\left(\frac{\beta}{2}\right) \sin(2\phi) & 1 + 2i \exp\left(i\frac{\beta}{2}\right) \sin\left(\frac{\beta}{2}\right) \sin^2(\phi) \end{bmatrix} \quad (3.76)$$

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

3.8.2 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:

$$\hat{W}_{\frac{1}{2}}(\phi) = i \begin{bmatrix} \cos(2\phi) & \sin(2\phi) \\ \sin(2\phi) & -\cos(2\phi) \end{bmatrix} \quad (3.77)$$

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 $\mathcal{L} \leftrightarrow \mathcal{R}$.

3.8.3 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:

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right) = \frac{\sqrt{2}}{2} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \quad (3.78)$$

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

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right) |\mathcal{P}\rangle = |\mathcal{R}\rangle \quad (3.79)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right) |\mathcal{R}\rangle = i |\mathcal{S}\rangle \quad (3.80)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right) |\mathcal{S}\rangle = i |\mathcal{L}\rangle \quad (3.81)$$

$$\hat{W}_{\frac{1}{4}}\left(\frac{\pi}{4}\right) |\mathcal{L}\rangle = |\mathcal{P}\rangle \quad (3.82)$$

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.

3.8.4 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 $\nu_{\text{mod}} (= \Omega_{\text{mod}}/2\pi)$:

$$\beta(t) = \beta_0 \sin(\Omega_{\text{mod}}t + \phi_{\text{mod}}) \quad (3.83)$$

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 the Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables (Edited by M. Abramowitz and I.A. Stegun, page 361, Dover, 1965):

$$\begin{aligned} \sin(\beta_0 \sin(\Omega_{\text{mod}}t)) &= 2 \sum_{n=0}^{\infty} J_{2n+1}(\beta_0) \sin((2n+1)\Omega_{\text{mod}}t) \\ &= 2J_1(\beta_0) \sin(\Omega_{\text{mod}}t) + \dots \end{aligned} \quad (3.84)$$

$$\begin{aligned} \sin(\beta_0 \cos(\Omega_{\text{mod}}t)) &= 2 \sum_{n=0}^{\infty} (-)^n J_{2n+1}(\beta_0) \cos((2n+1)\Omega_{\text{mod}}t) \\ &= 2J_1(\beta_0) \cos(\Omega_{\text{mod}}t) - \dots \end{aligned} \quad (3.85)$$

$$\begin{aligned}
\cos(\beta_0 \sin(\Omega_{\text{mod}} t)) &= J_0(\beta_0) + 2 \sum_{n=1}^{\infty} J_{2n}(\beta_0) \cos(2n\Omega_{\text{mod}} t) \\
&= J_0(\beta_0) + 2J_2(\beta_0) \cos(2\Omega_{\text{mod}} t) + \dots
\end{aligned} \tag{3.86}$$

$$\begin{aligned}
\cos(\beta_0 \cos(\Omega_{\text{mod}} t)) &= J_0(\beta_0) + 2 \sum_{n=1}^{\infty} (-1)^n J_{2n}(\beta_0) \cos(2n\Omega_{\text{mod}} t) \\
&= J_0(\beta_0) - 2J_2(\beta_0) \cos(2\Omega_{\text{mod}} t) + \dots
\end{aligned} \tag{3.87}$$

Chapter 4

Semiclassical Interaction with Light

4.1 General Formula for Atomic Polarizability

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 :

$$|\vec{k}| = \frac{\omega}{c}n = \frac{2\pi n}{\lambda_{\text{vac}}} \quad (4.1)$$

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. We will show later that 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:

$$|\vec{k}_q| = \frac{\omega}{c}n_q \quad (4.2)$$

where $q = 0, \pm 1$ labels the components relative to the atomic coordinate system. 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 $q = \pm 1$ 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:

$$n_q = \sqrt{\frac{\epsilon_q \mu_q}{\epsilon_0 \mu_0}} \quad (4.3)$$

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:

$$\vec{D} = \vec{\epsilon} \vec{E} = \epsilon_0 \vec{E} + \vec{P} = \epsilon_0 \vec{E} + [\mathcal{A}] \langle \vec{d} \rangle \quad (4.4)$$

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 following derivation is analogous to the one found in Wu, Z., M. Kitano, W. Happer, M. Hou, and J. Daniels. *App Opt* (25), 4483-92 (1986)). The Hamiltonian of the system is:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{W} \quad (4.5)$$

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

of \mathcal{H}_0 :

$$|\Psi\rangle = \sum_n c_n(t) e^{-i\omega_n t} |n\rangle \quad (4.6)$$

$$\hat{\mathcal{H}}_0 |n\rangle = E_n |n\rangle = \hbar\omega_n |n\rangle \quad (4.7)$$

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

$$\hat{\mathcal{H}} |\Psi\rangle = i\hbar \frac{\partial |\Psi\rangle}{\partial t} \quad (4.8)$$

Projecting $|k\rangle$ onto both sides of the previous equation and rearranging gives the exact equation:

$$\langle k | \hat{\mathcal{H}} |\Psi\rangle = \sum_n c_n(t) e^{-i\omega_n t} \langle k | \hat{\mathcal{H}}_0 + \hat{\mathcal{W}} |n\rangle \quad (4.9)$$

$$= c_k(t) e^{-i\omega_k t} \hbar\omega_k + \sum_n c_n(t) e^{-i\omega_n t} \langle k | \hat{\mathcal{W}} |n\rangle \quad (4.10)$$

$$= i\hbar \sum_n \frac{\partial c_n(t) e^{-i\omega_n t}}{\partial t} \langle k | n\rangle \quad (4.11)$$

$$= i\hbar [\dot{c}_k(t) - i\omega_k c_k(t)] e^{-i\omega_k t} \quad (4.12)$$

$$= [i\hbar \dot{c}_k(t) + \hbar\omega_k c_k(t)] e^{-i\omega_k t} \quad (4.13)$$

$$i\hbar \dot{c}_k(t) = \sum_n c_n(t) e^{i\omega_{kn} t} \langle k | \hat{\mathcal{W}} |n\rangle \quad (4.14)$$

$$\omega_{kn} \equiv \omega_k - \omega_n \quad (4.15)$$

To treat this system of coupled linear differential equations, the following approximations, assumptions, and simplifications will be made. First we will treat \mathcal{W} as a small perturbation (will be justified later). This means that the eigenstates of \mathcal{H}_0 are the eigenstates of \mathcal{H} to zeroth order. Second, we will only worry about the interaction between the atom and the electric field component of the electromagnetic wave. This can be justified by comparing the relative size of the interaction of the atom with the electric and magnetic fields of the wave:

$$\left| \frac{\mathcal{W}_{\mathcal{B}}}{\mathcal{W}_{\mathcal{E}}} \right| = \left| \frac{-\vec{\mu} \cdot \vec{B}}{-\vec{d} \cdot \vec{E}} \right| = \frac{-g\mu_B \mathcal{B}}{-(-er)\mathcal{E}} \approx \frac{2\mu_B \mathcal{B}}{5ea_0 c \mathcal{B}} \approx \frac{2\frac{e\hbar}{2m}}{5e\frac{4\pi\epsilon_0 \hbar^2}{me^2} c} \approx \frac{e^3 \hbar}{5e4\pi\epsilon_0 \hbar^2 c} \approx \frac{e^2}{20\pi\epsilon_0 \hbar c} \approx \frac{\alpha}{5} \approx 10^{-3} \quad (4.16)$$

where the characteristic size of a K or Rb atom is given in units of the Bohr radius, a_0 , and for electromagnetic waves $|\vec{E}| = c|\vec{B}|$. After dropping the magnetic dipole interaction term, \mathcal{W} will be expanded using the dipole approximation:

$$|\vec{k} \cdot \vec{r}| = kr = \frac{2\pi r}{\lambda} \approx \frac{2\pi 5a_0}{\lambda} \approx \frac{2\pi 5(0.053 \text{ nm})}{780 \text{ nm}} \approx 0.002 \ll 1 \quad (4.17)$$

$$\mathcal{W} = -\vec{d} \cdot \mathcal{R} \left\{ \vec{E}(\vec{r}, t) \right\} \quad (4.18)$$

$$= -(-e)\vec{r} \cdot \left[\frac{\vec{\mathcal{E}} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + \vec{\mathcal{E}}^* e^{-i(\vec{k} \cdot \vec{r} - \omega t)}}{2} \right] \quad (4.19)$$

$$= \frac{e\vec{r}}{2} \cdot \left[\vec{\mathcal{E}} \left(1 + i\vec{k} \cdot \vec{r} + \dots \right) e^{-i\omega t} + \vec{\mathcal{E}}^* \left(1 - i\vec{k} \cdot \vec{r} + \dots \right) e^{i\omega t} \right] \quad (4.20)$$

$$\approx \frac{e\vec{r}}{2} \cdot \left[\vec{\mathcal{E}} e^{-i\omega t} + \vec{\mathcal{E}}^* e^{i\omega t} \right] \quad (4.21)$$

Third, we'll assume that the frequency ω is tuned to near the D1 and D2 transition frequencies. This allows us to separate the $\{c_n\}$ states into two groups. We'll label the $S_{\frac{1}{2}}$ states by a_n and the $P_{\frac{1}{2}, \frac{3}{2}}$ states by b_k .

This condition splits equation (4.14) into the following two coupled differential equations:

$$i\hbar\dot{b}_k(t) = \sum_n a_n(t)e^{i\omega_{kn}t} \langle k|\hat{\mathcal{W}}|n\rangle + \sum_j b_j(t)e^{i\omega_{kj}t} \langle k|\hat{\mathcal{W}}|j\rangle \quad (4.22)$$

$$i\hbar\dot{a}_n(t) = \sum_m a_m(t)e^{i\omega_{nm}t} \langle n|\hat{\mathcal{W}}|m\rangle + \sum_k b_k(t)e^{i\omega_{nk}t} \langle n|\hat{\mathcal{W}}|k\rangle \quad (4.23)$$

where m, n only label $\{a\}$ states and j, k only label $\{b\}$ states. Note that all we've really done at this step is to *relabel* the states. Now, since we are only considering transitions *between* $\{a\}$ and $\{b\}$ states and not *among* $\{a\}$ states and $\{b\}$ states, $\langle m|\hat{\mathcal{W}}|n\rangle$ and $\langle j|\hat{\mathcal{W}}|k\rangle$ are both zero:

$$i\hbar\dot{b}_k(t) = \sum_n a_n(t)e^{i\omega_{kn}t} \langle k|\hat{\mathcal{W}}|n\rangle \quad (4.24)$$

$$i\hbar\dot{a}_n(t) = \sum_k b_k(t)e^{i\omega_{nk}t} \langle n|\hat{\mathcal{W}}|k\rangle \quad (4.25)$$

To reiterate, we are *choosing* ω to excite the D1 and D2 transitions between the appropriate states in $\{a_n\}$ and $\{b_k\}$. Fourth, as is standard practice (Demtröder, Wolfgang. Laser Spectroscopy: Basic Concepts and Instrumentation, Second Enlarged Edition. New York: Springer-Verlag, 1998. page 33, section 2.6.5), we will add by hand a phenomenological damping term γ_k which takes into account the finite lifetime of the excited states. Under our conditions, γ_k is dominated by pressure broadening, which we use to extract the ^3He density. Putting this all together gives:

$$i\hbar\dot{b}_k(t) = \frac{e}{2} \sum_n a_n(t)e^{i\omega_{kn}t} \left[\langle k|\vec{r} \cdot \vec{\mathcal{E}}|n\rangle e^{-i\omega t} + \langle k|\vec{r} \cdot \vec{\mathcal{E}}^*|n\rangle e^{+i\omega t} \right] - i\hbar b_k \frac{\gamma_k}{2} \quad (4.26)$$

$$i\hbar\dot{a}_n(t) = \frac{e}{2} \sum_k b_k(t)e^{i\omega_{nk}t} \left[\langle n|\vec{r} \cdot \vec{\mathcal{E}}|k\rangle e^{-i\omega t} + \langle n|\vec{r} \cdot \vec{\mathcal{E}}^*|k\rangle e^{+i\omega t} \right] \quad (4.27)$$

Fifth, we'll assume that the system is in equilibrium and that most alkali atoms are in a $\{a_n\}$ ground state. Under typical conditions in an optical pumping spin exchange cell, the optical pumping rate is about $R \approx (1 - 10^3)$ kHz, whereas the N_2 nonradiative quenching rate is about $\gamma_q \approx 500$ MHz. At equilibrium, the fractional population of the $\{b_k\}$ states is given by $\approx R/\gamma_q \leq 0.002$, therefore:

$$\frac{da_n}{dt} \approx 0 \Rightarrow a_n = \text{constant} \quad (4.28)$$

$$P_n = a_n^* a_n \quad (4.29)$$

where P_n the relative population of a ground state a_n . Since the time dependence of a_n has been removed, equation (4.26) is solved in the following way:

$$b_k(t) = u(t)v(t) \quad (4.30)$$

$$\dot{b}_k = \dot{u}v + u\dot{v} = f(t) - \frac{\gamma_k}{2}uv \quad (4.31)$$

$$\frac{\dot{b}_k}{uv} = \frac{\dot{u}}{u} + \frac{\dot{v}}{v} = \frac{f(t)}{uv} - \frac{\gamma_k}{2} \quad (4.32)$$

$$\frac{\dot{v}}{v} = -\frac{\gamma_k}{2} \rightarrow v(t) = v(0)e^{-\frac{\gamma_k}{2}t} \quad (4.33)$$

$$\frac{\dot{u}}{u} = \frac{f(t)}{uv} \rightarrow \dot{u} = \frac{f(t)e^{+\frac{\gamma_k}{2}t}}{v(0)} \quad (4.34)$$

$$u(t) = \int \frac{e}{2i\hbar v(0)} \sum_n a_n(t)e^{i\omega_{kn}t + \frac{\gamma_k}{2}t} \left[\langle k|\vec{r} \cdot \vec{\mathcal{E}}|n\rangle e^{-i\omega t} + \langle k|\vec{r} \cdot \vec{\mathcal{E}}^*|n\rangle e^{+i\omega t} \right] dt \quad (4.35)$$

$$= \frac{e}{2i\hbar v(0)} \sum_n a_n(t)e^{i\omega_{kn}t + \frac{\gamma_k}{2}t} \left[\frac{\langle k|\vec{r} \cdot \vec{\mathcal{E}}|n\rangle}{i\omega_{kn} - i\omega + \frac{\gamma_k}{2}} e^{-i\omega t} + \frac{\langle k|\vec{r} \cdot \vec{\mathcal{E}}^*|n\rangle}{i\omega_{kn} + i\omega + \frac{\gamma_k}{2}} e^{+i\omega t} \right] \quad (4.36)$$

which gives:

$$b_k(t) = \frac{e}{2\hbar} \sum_n a_n(t) e^{i\omega_{kn}t} \left[\frac{\langle k | \vec{r} \cdot \vec{\mathcal{E}} | n \rangle}{-\omega_{kn} + \omega + i\frac{\gamma_k}{2}} e^{-i\omega t} + \frac{\langle k | \vec{r} \cdot \vec{\mathcal{E}}^* | n \rangle}{-\omega_{kn} - \omega + i\frac{\gamma_k}{2}} e^{+i\omega t} \right] \quad (4.37)$$

The sixth approximation is that the second term is negligible relative to the first because $\omega \approx \omega_{kn}$. This is called the rotating wave approximation and dropping the second term gives:

$$b_k(t) = \frac{e}{2\hbar} \sum_n a_n(t) e^{i(\omega_{kn} - \omega)t} \left[\frac{\langle k | \vec{r} \cdot \vec{\mathcal{E}} | n \rangle}{\omega - \omega_{kn} + i\frac{\gamma_k}{2}} \right] \quad (4.38)$$

The expectation value of the dipole moment for a single atom $\langle \vec{d} \rangle$ can be calculated using eqn. (4.6):

$$\langle \vec{d} \rangle = -e \langle \Psi | \vec{r} | \Psi \rangle \quad (4.39)$$

$$= -e \left[\sum_m a_m^* e^{i\omega_m t} \langle m | + \sum_j b_j^*(t) e^{i\omega_j t} \langle j | \right] \vec{r} \left[\sum_n a_n e^{-i\omega_n t} | n \rangle + \sum_k b_k(t) e^{-i\omega_k t} | k \rangle \right] \quad (4.40)$$

$$= -e \sum_{m,n} a_m^* a_n e^{i\omega_{mn}t} \langle m | \vec{r} | n \rangle - e \sum_{b,j} b_j^* b_k e^{i\omega_{jk}t} \langle j | \vec{r} | k \rangle - e \left[\sum_{m,k} a_m^* b_k e^{i\omega_{mk}t} \langle m | \vec{r} | k \rangle + \mathcal{C.C.} \right] \quad (4.41)$$

The matrix elements connecting states within the same group are zero. Specifically, recall the Wigner-Eckart Theorem:

$$\langle J_f, m_f | \hat{T}_q^k | J_i, m_i \rangle = \frac{1}{\sqrt{2J_f + 1}} [\langle J_i, m_i | \langle k, q | | J_f, m_f \rangle] \langle J_f || T^k || J_i \rangle \quad (4.42)$$

For electric dipole transitions, the reduced matrix element is non-zero only between states of opposite parity. The parity of the states that we're considering are given by $(-1)^L$. Therefore states in the $\{a_n\} (L = S \rightarrow L = 0)$ and the $\{b_k\} (L = P \rightarrow L = 1)$ groups have even and odd parity respectively. Therefore the matrix elements between states within the same group ($\langle n | \vec{r} | n \rangle$ & $\langle j | \vec{r} | k \rangle$) vanish due to parity. This is another justification our separation of the states into two groups. Note also that the Clebsch-Gordon coefficient is nonzero only when $m_f = m_i + q$ and $J_f = |J_i - k| \dots J_i + k$. This means, in our case, that for a given matrix element of the form $\langle m | \vec{r} | k \rangle$, there will be at most only one component of \vec{r} that results in a non-zero matrix element. Dropping the vanishing $a_m^* a_n$ & $b_j^* b_k$ terms and plugging in eqn. (4.38) for b_k :

$$\langle \vec{d} \rangle = -e \sum_{m,k} a_m^* b_k e^{i\omega_{mk}t} \langle m | \vec{r} | k \rangle + \mathcal{C.C.} \quad (4.43)$$

$$= \frac{e^2}{2\hbar} \sum_{n,m,k} a_m^* a_n(t) e^{i(\omega_{mn} - \omega)t} \left[\frac{\langle m | \vec{r} | k \rangle \langle k | \vec{r} \cdot \vec{\mathcal{E}} | n \rangle}{\omega_{kn} - \omega - i\frac{\gamma_k}{2}} \right] + \mathcal{C.C.} \quad (4.44)$$

Averaging this single atom expectation value over all atoms in the cell:

$$\langle a_m^* a_m \rangle_{\text{cell}} = \delta_m^n P_n \quad (4.45)$$

$$\langle \vec{d} \rangle_{\text{cell}} = \frac{e^2}{2\hbar} \sum_{n,m,k} \delta_m^n P_n a_m^* a_n(t) e^{i(\omega_{mn} - \omega)t} \left[\frac{\langle m | \vec{r} | k \rangle \langle k | \vec{r} \cdot \vec{\mathcal{E}} | n \rangle}{\omega_{kn} - \omega - i\frac{\gamma_k}{2}} \right] + \mathcal{C.C.} \quad (4.46)$$

$$= \frac{e^2}{2\hbar} \sum_{n,k} P_n \left[\frac{\langle n | \vec{r} | k \rangle \langle k | \vec{r} \cdot \vec{\mathcal{E}} e^{-i\omega t} | n \rangle}{\omega_{kn} - \omega - i\frac{\gamma_k}{2}} \right] + \mathcal{C.C.} \quad (4.47)$$

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

$$\vec{d} = \vec{\alpha} \cdot \mathcal{R} \vec{E} = \vec{\alpha} \cdot \left[\frac{\vec{E} + \mathcal{C.C.}}{2} \right] \quad (4.48)$$

which immediately yields the atomic polarizability tensor:

$$\vec{\alpha} = \frac{e^2}{\hbar} \sum_{n,k} P_n \left[\frac{\langle n | \vec{r} | k \rangle \langle k | \vec{r} | n \rangle}{\omega_{kn} - \omega - i \frac{\gamma_k}{2}} \right] \quad (4.49)$$

4.2 Transition Matrix Elements: Oscillator Strength

4.2.1 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:

$$\left| \langle b | \vec{\varepsilon} \cdot \hat{\vec{d}} | a \rangle \right|^2 = \left| \langle b | \vec{\varepsilon} \cdot (-e\hat{\vec{r}}) | a \rangle \right|^2 = e^2 \left| \langle b | \vec{\varepsilon} \cdot \hat{\vec{r}} | a \rangle \right|^2 \quad (4.50)$$

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:

$$\langle J_f, m_f | \hat{T}_q^k | J_i, m_i \rangle = \text{CG} \left(\vec{J}_i + \vec{k} = \vec{J}_f ; m_i, q, m_f \right) \times \text{R.M.E.} (n_f, J_f; n_i, J_i) \quad (4.51)$$

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, see (Albert Messiah, Quantum Mechanics, Vol II, New York: John Wiley and Sons, 1962?, page 573, XIII.125) for example is:

$$\text{R.M.E.} = \frac{1}{\sqrt{[J_f]}} \times \langle n_f, J_f || T^k || n_i, J_i \rangle \quad (4.52)$$

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:

$$\text{R.M.E.} = \frac{(\pm)_{fi}}{\sqrt{[J_f]}} \times i \times \langle J_f || T^k || J_i \rangle \quad (4.53)$$

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 can be expressed as:

$$\langle J_f, m_f | \hat{T}_q^k | J_i, m_i \rangle = i \frac{(\pm)_{fi}}{\sqrt{[J_f]}} \langle (J_i, k) m_i, q | J_f, m_f \rangle \langle J_f || T^k || J_i \rangle \quad (4.54)$$

4.2.2 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 $\hat{\vec{r}}$ in the spherical tensor basis ($k = 1$):

$$\left| \langle J_f, m_f | r_q | J_i, m_i \rangle \right|^2 = \langle J_f, m_f | r_q | J_i, m_i \rangle^* \langle J_f, m_f | r_q | J_i, m_i \rangle \quad (4.55)$$

$$= \langle J_i, m_i | r_q^* | J_f, m_f \rangle \langle J_f, m_f | r_q | J_i, m_i \rangle \quad (4.56)$$

$$= (-1)^q \langle J_i, m_i | r_{-q} | J_f, m_f \rangle \langle J_f, m_f | r_q | J_i, m_i \rangle \quad (4.57)$$

Before expanding these matrix elements using the WET, we'll introduce the Wigner $3j$ symbol (E.P. Wigner, Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra, page 290, eqns 24.9a, 24.10, 24.10a, 24.10b) which is related to the Clebsch-Gordon coefficients by:

$$\begin{pmatrix} J_i & k & J_f \\ m_i & q & -m_f \end{pmatrix} = \frac{(-1)^{J_i-k+m_f}}{\sqrt{[J_f]}} \langle (J_i, k) m_i, q | J_f, m_f \rangle \delta_{m_i+q=m_f} \quad (4.58)$$

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:

$$\begin{pmatrix} J_i & k & J_f \\ m_i & q & -m_f \end{pmatrix} = \begin{pmatrix} J_f & J_i & k \\ -m_f & m_i & q \end{pmatrix} = \begin{pmatrix} k & J_f & J_i \\ q & -m_f & m_i \end{pmatrix} \quad (4.59)$$

$$= (-1)^{J_i+k+J_f} \begin{pmatrix} k & J_i & J_f \\ q & m_i & -m_f \end{pmatrix} \quad (4.60)$$

$$= (-1)^{J_i+k+J_f} \begin{pmatrix} J_i & k & J_f \\ -m_i & -q & m_f \end{pmatrix} \quad (4.61)$$

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

$$|\langle r_q \rangle|^2 = (-1)^q \langle J_i, m_i | r_{-q} | J_f, m_i + q \rangle \langle J_f, m_i + q | r_q | J_i, m_i \rangle \quad (4.62)$$

$$\begin{aligned} &= (-1)^q i(\pm)_{if} (-1)^{J_f-1+m_i} \begin{pmatrix} J_f & 1 & J_i \\ m_i + q & -q & -m_i \end{pmatrix} \langle J_i || r || J_f \rangle \\ &\quad \times (i)(\pm)_{fi} (-1)^{J_i-1+m_i+q} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} \langle J_f || r || J_i \rangle \end{aligned} \quad (4.63)$$

$$= (\pm)_{fi} (\pm)_{if} (-1)^{J_f+J_i+2m_i+1} \begin{pmatrix} J_f & 1 & J_i \\ m_i + q & -q & -m_i \end{pmatrix} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} |\langle J_f || r || J_i \rangle|^2 \quad (4.64)$$

$$= (\pm)_{fi} (\pm)_{if} (-1)^{2J_f+2J_i+2m_i+2} \begin{pmatrix} J_i & 1 & J_f \\ -m_i & -q & m_i + q \end{pmatrix} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} |\langle J_f || r || J_i \rangle|^2 \quad (4.65)$$

$$= (\pm)_{fi} (\pm)_{if} (-1)^{3J_f+3J_i+2m_i+1} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix} |\langle J_f || r || J_i \rangle|^2 \quad (4.66)$$

$$= (\pm)_{fi} (\pm)_{if} (-1)^{3J_f+3J_i+2m_i+1} \begin{pmatrix} J_i & 1 & J_f \\ m_i & q & -(m_i + q) \end{pmatrix}^2 |\langle J_f || r || J_i \rangle|^2 \quad (4.67)$$

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 ($J_i, |m_i|, J_f = \frac{1}{2}$):

$$+1 = [(\pm)_{fi} (\pm)_{if}]_{\frac{1}{2}} (-1)^{\frac{3}{2} + \frac{3}{2} \pm 1 + 1} \quad (4.68)$$

$$= [(\pm)_{fi} (\pm)_{if}]_{\frac{1}{2}} (-1)^{4 \pm 1} \quad (4.69)$$

$$= -[(\pm)_{fi} (\pm)_{if}]_{\frac{1}{2}} \quad (4.70)$$

$$s_1 = [(\pm)_{fi}]_{\frac{1}{2}} = -[(\pm)_{if}]_{\frac{1}{2}} \quad (4.71)$$

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

$$+1 = [(\pm)_{fi} (\pm)_{if}]_{\frac{3}{2}} (-1)^{\frac{9}{2} + \frac{3}{2} \pm 1 + 1} \quad (4.72)$$

$$= [(\pm)_{fi}(\pm)_{if}]_{\frac{3}{2}}(-1)^{7\pm 1} \quad (4.73)$$

$$= [(\pm)_{fi}(\pm)_{if}]_{\frac{3}{2}} \quad (4.74)$$

$$s_2 = [(\pm)_{fi}]_{\frac{3}{2}} = [(\pm)_{if}]_{\frac{3}{2}} \quad (4.75)$$

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.

4.2.3 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 A. Corney, Atomic and Laser Spectroscopy, Clarendon Press, Oxford, 1977, page 103, equation 4.23:

$$\tau_b^{-1} = A_b = \frac{e^2 \omega_{ab}^3}{3\pi \epsilon_0 \hbar c^3} \frac{\sum_{m_b}}{[J_b]} \sum_{m_a} \left| \langle J_a, m_a | \hat{r} | J_b, m_b \rangle \right|^2 \quad (4.76)$$

$$= \frac{4\alpha \omega_{ab}^3}{3c^2} \underbrace{\frac{\sum_{m_b}}{[J_b]}}_{\text{mean}} \underbrace{\sum_{m_a}}_{\text{sum}} \left| \langle J_a, m_a | \hat{r} | J_b, m_b \rangle \right|^2 \quad (4.77)$$

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 modelled 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:

$$f_{a \rightarrow b} = \pm \frac{2m\omega_{ab}}{3\hbar} \frac{\sum_{m_a}}{2J_a + 1} \sum_{m_b} \left| \langle J_a, m_b | \hat{r} | J_a, m_b \rangle \right|^2 \quad (4.78)$$

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 in E.U. Condon and G.H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, 1967, page 98) and for transitions between the lower state a and the higher state b , it is given by:

$$S_{ab} = S_{ba} = \sum_{m_a} \sum_{m_b} \left| \langle J_a, m_a | e\hat{r} | J_b, m_b \rangle \right|^2 \quad (4.79)$$

$$= \sum_{m_a} \sum_{m_b} \left| \langle J_b, m_b | e\hat{r} | J_a, m_a \rangle \right|^2 \quad (4.80)$$

$$= \frac{3\hbar e^2}{2m\omega_{ab}} \cdot [J_a] f_b \quad (4.81)$$

$$= \frac{3c^2 [J_b] e^2}{4\alpha\omega_{ab}^3} \cdot \frac{1}{\tau_b} \quad (4.82)$$

$$= \frac{3\pi\epsilon_0 \hbar c^3 [J_b]}{\omega_{ab}^3} \cdot A_b \quad (4.83)$$

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:

$$S_{ab} = \sum_{m_a} \sum_{m_b} \left| \langle J_b, m_b | e^{\hat{r}} | J_a, m_a \rangle \right|^2 \quad (4.84)$$

$$= \sum_{m_a} \sum_{m_b} \left| \langle J_b, m_b | e \sum_q (-1)^q \hat{r}_q \hat{\epsilon}_{-q} | J_a, m_a \rangle \right|^2 \quad (4.85)$$

$$= \sum_{m_a} \sum_{m_b} \langle J_a, m_a | e \sum_{q'} (-1)^{q'} \hat{r}_{q'} \hat{\epsilon}_{-q'} | J_b, m_b \rangle \cdot \langle J_b, m_b | e \sum_q (-1)^q \hat{r}_q \hat{\epsilon}_{-q} | J_a, m_a \rangle \quad (4.86)$$

$$= \sum_{m_a} \sum_{m_b} \sum_q (-1)^q \langle J_a, m_a | e \hat{r}_{-q} | J_b, m_b \rangle \langle J_b, m_b | e \hat{r}_q | J_a, m_a \rangle \quad (4.87)$$

$$= \pm s_{a,b}^2 i^2 \sum_{m_a, m_b, q} (-1)^q \frac{\langle (J_b, 1) m_b, -q | J_a, m_a \rangle}{\sqrt{[J_a]}} \langle J_a || e r || J_b \rangle \frac{\langle (J_a, 1) m_a, q | J_b, m_b \rangle}{\sqrt{[J_b]}} \langle J_b || e r || J_a \rangle \quad (4.88)$$

$$= |\langle J_b || e r || J_a \rangle|^2 \cdot \varsigma_b \quad (4.89)$$

$$\varsigma_b = \mp \sum_{m_a, q} \frac{(-1)^q}{\sqrt{[J_a][J_b]}} \langle (J_b, 1) m_a + q, -q | J_a, m_a \rangle \langle (J_a, 1) m_a, q | J_b, m_a + q \rangle \quad (4.90)$$

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 :

$$|\langle J_b || r || J_a \rangle|^2 = \frac{S_{ab}}{\varsigma_{ab} e^2} \quad (4.91)$$

$$= \frac{3\hbar}{2m\omega_{ab}} \cdot \frac{[J_a] f_b}{\varsigma_b} \quad (4.92)$$

$$= \frac{3c^2}{4\alpha\omega_{ab}^3} \cdot \frac{[J_b]}{\varsigma_b \tau_b} \quad (4.93)$$

$$= \frac{3\pi\epsilon_0 \hbar c^3}{e^2 \omega_{ab}^3} \cdot \frac{[J_b] A_b}{\varsigma_b} \quad (4.94)$$

4.2.4 Evaluation of the Clebsch-Gordon Coefficients and Sums

The general forms of the D1 matrix elements are:

$$\left\langle P_{\frac{1}{2}}, q \pm \frac{1}{2} \left| r_q \right| S_{\frac{1}{2}}, \pm \frac{1}{2} \right\rangle = \left\langle \left(\frac{1}{2}, 1 \right) \pm \frac{1}{2}, q \left| \frac{1}{2}, q \pm \frac{1}{2} \right\rangle \left(i \frac{s_1}{\sqrt{2}} \right) \langle P_{\frac{1}{2}} || r || S_{\frac{1}{2}} \rangle \quad (4.95)$$

$$= -i \frac{s_1}{\sqrt{2}} \left\langle \left(1, \frac{1}{2} \right) q, \pm \frac{1}{2} \left| \frac{1}{2}, q \pm \frac{1}{2} \right\rangle \langle P_{\frac{1}{2}} || r || S_{\frac{1}{2}} \rangle \quad (4.96)$$

$$= \pm i s_1 \sqrt{\frac{1 \mp q}{6}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.97)$$

$$\left\langle S_{\frac{1}{2}}, q \pm \frac{1}{2} \middle| r_q \middle| P_{\frac{1}{2}}, \pm \frac{1}{2} \right\rangle = \left\langle \left(\frac{1}{2}, 1 \right) \pm \frac{1}{2}, q \middle| \frac{1}{2}, q \pm \frac{1}{2} \right\rangle \left(-i \frac{s_1}{\sqrt{2}} \right) \langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle \quad (4.98)$$

$$= i \frac{s_1}{\sqrt{2}} \left\langle \left(1, \frac{1}{2} \right) q, \pm \frac{1}{2} \middle| \frac{1}{2}, q \pm \frac{1}{2} \right\rangle \langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle \quad (4.99)$$

$$= \mp i s_1 \sqrt{\frac{1 \mp q}{6}} \langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle \quad (4.100)$$

$$(4.101)$$

The general forms of the D2 matrix elements are:

$$\left\langle P_{\frac{3}{2}}, q \pm \frac{1}{2} \middle| r_q \middle| S_{\frac{1}{2}}, \pm \frac{1}{2} \right\rangle = \left\langle \left(\frac{1}{2}, 1 \right) \pm \frac{1}{2}, q \middle| \frac{3}{2}, q \pm \frac{1}{2} \right\rangle \left(i \frac{s_2}{2} \right) \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.102)$$

$$= i \frac{s_2}{2} \left\langle \left(1, \frac{1}{2} \right) q, \pm \frac{1}{2} \middle| \frac{3}{2}, q \pm \frac{1}{2} \right\rangle \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.103)$$

$$= i s_2 \sqrt{\frac{2 \pm q}{12}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.104)$$

$$\left\langle S_{\frac{1}{2}}, m \pm 1 \middle| r_{\pm} \middle| P_{\frac{3}{2}}, m \right\rangle = \left\langle \left(\frac{3}{2}, 1 \right) m, \pm 1 \middle| \frac{1}{2}, m \pm 1 \right\rangle \left(i \frac{s_2}{\sqrt{2}} \right) \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (4.105)$$

$$= i s_2 \sqrt{\frac{(\frac{1}{2} \mp m)(\frac{3}{2} \mp m)}{24}} \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (4.106)$$

$$\left\langle S_{\frac{1}{2}}, \pm \frac{1}{2} \middle| r_0 \middle| P_{\frac{3}{2}}, \pm \frac{1}{2} \right\rangle = \left\langle \left(\frac{3}{2}, 1 \right) \pm \frac{1}{2}, 0 \middle| \frac{1}{2}, \pm \frac{1}{2} \right\rangle \left(i \frac{s_2}{\sqrt{2}} \right) \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (4.107)$$

$$= -i s_2 \sqrt{\frac{1}{6}} \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (4.108)$$

The D1 matrix elements are:

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \middle| r_+ \middle| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, -\frac{1}{2} \middle| r_- \middle| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +i s_1 \sqrt{\frac{1}{3}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.109)$$

$$-\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \middle| r_0 \middle| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \middle| r_0 \middle| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +i s_1 \sqrt{\frac{1}{6}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.110)$$

$$-\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \middle| r_0 \middle| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, -\frac{1}{2} \middle| r_0 \middle| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = -i s_1 \sqrt{\frac{1}{6}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.111)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \middle| r_- \middle| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \middle| r_+ \middle| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = -i s_1 \sqrt{\frac{1}{3}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.112)$$

$$\langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle = \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.113)$$

The D2 matrix elements are:

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \middle| r_+ \middle| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \middle| r_- \middle| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +i s_2 \sqrt{\frac{1}{12}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.114)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \middle| r_+ \middle| P_{\frac{3}{2}}, -\frac{3}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{3}{2} \middle| r_- \middle| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +i s_2 \frac{1}{2} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.115)$$

$$-\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \middle| r_0 \middle| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \middle| r_0 \middle| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +i s_2 \sqrt{\frac{1}{6}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.116)$$

$$-\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \middle| r_0 \middle| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \middle| r_0 \middle| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +i s_2 \sqrt{\frac{1}{6}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.117)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{1}{12}} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.118)$$

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_- \right| P_{\frac{3}{2}}, +\frac{3}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{3}{2} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_2 \frac{1}{2} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.119)$$

$$\left\langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \right\rangle = \left\langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \right\rangle \quad (4.120)$$

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

$$s_{\frac{1}{2}} = s_1^2 \left[-\frac{i}{\sqrt{3}} \frac{i}{\sqrt{3}} + \frac{-i}{\sqrt{6}} \frac{i}{\sqrt{6}} + \frac{i}{\sqrt{6}} \frac{-i}{\sqrt{6}} - \frac{-i}{\sqrt{3}} \frac{-i}{\sqrt{3}} \right] = +1 \quad (4.121)$$

$$s_{\frac{3}{2}} = s_2^2 \left[-\frac{i}{\sqrt{12}} \frac{i}{\sqrt{12}} - \frac{i}{2} \frac{i}{2} + \frac{-i}{\sqrt{6}} \frac{i}{\sqrt{6}} + \frac{-i}{\sqrt{6}} \frac{i}{\sqrt{6}} - \frac{i}{\sqrt{12}} \frac{i}{\sqrt{12}} - \frac{i}{2} \frac{i}{2} \right] = +1 \quad (4.122)$$

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

$$\left| \langle P_J \| r \| S_{\frac{1}{2}} \rangle \right|^2 = \frac{3\hbar}{m\omega_J} f_J \quad (4.123)$$

4.2.5 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:

$$|\langle r_q \rangle|^2 = (-1)^q \left\langle \pm \frac{1}{2} \left| \right|_S \langle 0 | r_{-q} | q \rangle_L \left| \pm \frac{1}{2} \right\rangle_S \left\langle \pm \frac{1}{2} \left| \right|_S \langle q | r_q | 0 \rangle_L \left| \pm \frac{1}{2} \right\rangle_S \right. \quad (4.124)$$

$$= (-1)^q \langle 0 | r_{-q} | q \rangle_L \langle q | r_q | 0 \rangle_L \quad (4.125)$$

$$= (\pm)_{PS} (\pm)_{SP} (-1)^{3+1} \begin{pmatrix} 0 & 1 & 1 \\ 0 & q & -q \end{pmatrix}^2 |\langle P \| r \| S \rangle|^2 \quad (4.126)$$

$$+1 = (\pm)_{PS} (\pm)_{SP} (-1)^4 \quad (4.127)$$

$$= (\pm)_{PS} (\pm)_{SP} \quad (4.128)$$

$$s = (\pm)_{PS} = (\pm)_{SP} \quad (4.129)$$

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:

$$\left\langle P_{\frac{3}{2}}, +\frac{3}{2} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \langle +1 | \left\langle +\frac{1}{2} \left| \right|_S r_+ | 0 \rangle_L \left| +\frac{1}{2} \right\rangle_S \right. \quad (4.130)$$

$$= \langle +1 | r_+ | 0 \rangle_L \left\langle +\frac{1}{2} \left| +\frac{1}{2} \right\rangle_S \right. \quad (4.131)$$

$$= \langle (0, 1) 0, +1 | 1, +1 \rangle \left(\frac{is}{\sqrt{3}} \right) \langle P \| r \| S \rangle \quad (4.132)$$

$$= \frac{is}{\sqrt{3}} \langle P \| r \| S \rangle \quad (4.133)$$

$$= +is_2 \frac{1}{2} \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.134)$$

$$\left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = \left(\sqrt{\frac{2}{3}} \langle +1 | \left\langle -\frac{1}{2} \left| \right|_S - \sqrt{\frac{1}{3}} \langle 0 | \left\langle +\frac{1}{2} \left| \right|_S r_+ | 0 \rangle_L \left| -\frac{1}{2} \right\rangle_S \right. \right. \quad (4.135)$$

$$= \sqrt{\frac{2}{3}} \langle +1 | r_+ | 0 \rangle_L \left\langle -\frac{1}{2} \left| -\frac{1}{2} \right\rangle_S - \sqrt{\frac{1}{3}} \langle 0 | r_+ | 0 \rangle_L \left\langle +\frac{1}{2} \left| -\frac{1}{2} \right\rangle_S \right. \quad (4.136)$$

$$= \sqrt{\frac{2}{3}} \langle +1 | r_+ | 0 \rangle_L \quad (4.137)$$

$$= \sqrt{\frac{2}{3}} \langle (0, 1) 0, +1 | 1, +1 \rangle \left(\frac{is}{\sqrt{3}} \right) \langle P \| r \| S \rangle \quad (4.138)$$

$$= \frac{is\sqrt{2}}{3} \langle P \| r \| S \rangle \quad (4.139)$$

$$= -is_1 \sqrt{\frac{1}{3}} \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle \quad (4.140)$$

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

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_- \right| P_{\frac{3}{2}}, +\frac{3}{2} \right\rangle = \langle 0 |_L \left\langle +\frac{1}{2} \left| r_- \right| +1 \right\rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (4.141)$$

$$= \frac{is}{\sqrt{3}} \langle S \| r \| P \rangle \quad (4.142)$$

$$= +is_2 \frac{1}{2} \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle \quad (4.143)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \langle 0 |_L \left\langle -\frac{1}{2} \left| r_+ \right. \left(\sqrt{\frac{2}{3}} | +1 \rangle_L \left| -\frac{1}{2} \right\rangle_S - \sqrt{\frac{1}{3}} | 0 \rangle_L \left| +\frac{1}{2} \right\rangle_S \right) \right\rangle \quad (4.144)$$

$$= \frac{is\sqrt{2}}{3} \langle S \| r \| P \rangle \quad (4.145)$$

$$= -is_1 \sqrt{\frac{1}{3}} \langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle \quad (4.146)$$

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:

$$s_2 \langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle = +s \frac{2}{\sqrt{3}} \langle P \| r \| S \rangle \quad (4.147)$$

$$s_2 \langle S_{\frac{1}{2}} \| r \| P_{\frac{3}{2}} \rangle = +s \frac{2}{\sqrt{3}} \langle S \| r \| P \rangle \quad (4.148)$$

$$s_1 \langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle = -s \sqrt{\frac{2}{3}} \langle P \| r \| S \rangle \quad (4.149)$$

$$s_1 \langle S_{\frac{1}{2}} \| r \| P_{\frac{1}{2}} \rangle = -s \sqrt{\frac{2}{3}} \langle S \| r \| P \rangle \quad (4.150)$$

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

$$s_1 s_2 = -1 \quad (4.151)$$

$$\frac{\langle P_{\frac{3}{2}} \| r \| S_{\frac{1}{2}} \rangle}{\langle P_{\frac{1}{2}} \| r \| S_{\frac{1}{2}} \rangle} = -\sqrt{2} \frac{s_1}{s_2} = +\sqrt{2} \quad (4.152)$$

$$\langle P_J \| r \| S_{\frac{1}{2}} \rangle = \langle S_{\frac{1}{2}} \| r \| P_J \rangle = +\sqrt{\frac{3\hbar}{m\omega_J}} f_J \quad (4.153)$$

$$\frac{S_{\frac{3}{2}}}{S_{\frac{1}{2}}} = 2 \quad (4.154)$$

$$\frac{f_{\frac{3}{2}}}{f_{\frac{1}{2}}} = 2 \left(\frac{\omega_{\frac{3}{2}}}{\omega_{\frac{1}{2}}} \right) \quad (4.155)$$

$$\frac{\tau_{\frac{3}{2}}}{\tau_{\frac{1}{2}}} = \left(\frac{\omega_{\frac{1}{2}}}{\omega_{\frac{3}{2}}} \right)^3 \quad (4.156)$$

$$\frac{A_{\frac{3}{2}}}{A_{\frac{1}{2}}} = \left(\frac{\omega_{\frac{3}{2}}}{\omega_{\frac{1}{2}}} \right)^3 \quad (4.157)$$

4.2.6 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:

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_1 \sqrt{\frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}}} \quad (4.158)$$

$$-\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_0 \right| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_1 \sqrt{\frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}}} \quad (4.159)$$

$$-\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_0 \right| P_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = -is_1 \sqrt{\frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}}} \quad (4.160)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| P_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = -is_1 \sqrt{\frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}}} \quad (4.161)$$

The D2 matrix elements are:

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}}} \quad (4.162)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_+ \right| P_{\frac{3}{2}}, -\frac{3}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{3}{2} \left| r_- \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}}} \quad (4.163)$$

$$-\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_0 \right| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}}} \quad (4.164)$$

$$-\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_0 \right| P_{\frac{3}{2}}, -\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}}} \quad (4.165)$$

$$\left\langle S_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| P_{\frac{3}{2}}, +\frac{1}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}}} \quad (4.166)$$

$$\left\langle S_{\frac{1}{2}}, +\frac{1}{2} \left| r_- \right| P_{\frac{3}{2}}, +\frac{3}{2} \right\rangle = \left\langle P_{\frac{3}{2}}, +\frac{3}{2} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle = +is_2 \sqrt{\frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}}} \quad (4.167)$$

The modulus squared matrix elements for transitions involving the absorption of photon with helicity +1 are calculated below:

$$\left| \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}} \quad (4.168)$$

$$\left| \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (4.169)$$

$$\left| \left\langle P_{\frac{3}{2}}, +\frac{3}{2} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (4.170)$$

The modulus squared matrix elements for transitions involving the absorption of photon with helicity 0 are calculated below:

$$\left| \left\langle P_{\frac{1}{2}}, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}} \quad (4.171)$$

$$\left| \left\langle P_{\frac{1}{2}}, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}} \quad (4.172)$$

$$\left| \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}} \quad (4.173)$$

$$\left| \left\langle P_{\frac{3}{2}}, +\frac{1}{2} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}} \quad (4.174)$$

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

$$\left| \left\langle P_{\frac{1}{2}}, -\frac{1}{2} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}} \quad (4.175)$$

$$\left| \left\langle P_{\frac{3}{2}}, -\frac{1}{2} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (4.176)$$

$$\left| \left\langle P_{\frac{3}{2}}, -\frac{3}{2} \left| r_- \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \quad (4.177)$$

Because some of the excited eigenstates are mixed, now we'll evaluate the modulus squared matrix element in a general form.

$$|\langle r_q \rangle|^2 = \left| \left(c_1^* \langle P_{\frac{3}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right) + c_2^* \langle P_{\frac{1}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right) \right|^2 \quad (4.178)$$

$$= \left| c_1^* \langle P_{\frac{3}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right\rangle + c_2^* \langle P_{\frac{1}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right\rangle \right|^2 \quad (4.179)$$

$$\begin{aligned} &= |c_1|^2 \left| \langle P_{\frac{3}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right\rangle \right|^2 + |c_2|^2 \left| \langle P_{\frac{1}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right\rangle \right|^2 \\ &\quad + c_1^* \langle P_{\frac{3}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right\rangle \cdot c_2 \langle S_{\frac{1}{2}}, m \left| r_q^* \right| P_{\frac{1}{2}}, m+q \rangle \\ &\quad + c_1 \langle S_{\frac{1}{2}}, m \left| r_q^* \right| P_{\frac{3}{2}}, m+q \rangle \cdot c_2^* \langle P_{\frac{1}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \rangle \end{aligned} \quad (4.180)$$

The c_1 and c_2 are the fine mixing coefficients which are real:

$$\begin{aligned} |\langle r_q \rangle|^2 &= c_1^2 \left| \langle P_{\frac{3}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right\rangle \right|^2 + c_2^2 \left| \langle P_{\frac{1}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right\rangle \right|^2 \\ &\quad + (-1)^q c_1 c_2 \langle P_{\frac{3}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \right\rangle \langle S_{\frac{1}{2}}, m \left| r_{-q} \right| P_{\frac{1}{2}}, m+q \rangle \\ &\quad + (-1)^q c_1 c_2 \langle S_{\frac{1}{2}}, m \left| r_{-q} \right| P_{\frac{3}{2}}, m+q \rangle \langle P_{\frac{1}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \rangle \end{aligned} \quad (4.181)$$

Noting the following relationship:

$$\langle P_J, m+q \left| r_q \right| S_{\frac{1}{2}}, m \rangle = (-1)(-1)^q \langle S_{\frac{1}{2}}, m \left| r_{-q} \right| P_J, m+q \rangle \quad (4.182)$$

the cross terms can be written:

$$\begin{aligned} \text{cross terms} &= (-1)^q c_1 c_2 \langle P_{\frac{3}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \rangle \langle S_{\frac{1}{2}}, m \left| r_{-q} \right| P_{\frac{1}{2}}, m+q \rangle \\ &\quad + (-1)^q c_1 c_2 \langle S_{\frac{1}{2}}, m \left| r_{-q} \right| P_{\frac{3}{2}}, m+q \rangle \langle P_{\frac{1}{2}}, m+q \left| r_q \right| S_{\frac{1}{2}}, m \rangle \end{aligned} \quad (4.183)$$

$$\begin{aligned}
&= (-1)^q c_1 c_2 \langle P_{\frac{3}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle (-1)(-1)^q \langle P_{\frac{1}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \\
&\quad + (-1)^q c_1 c_2 (-1)(-1)^q \langle P_{\frac{3}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \langle P_{\frac{1}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle
\end{aligned} \tag{4.184}$$

$$= (-1)^{1+q+q} 2c_1 c_2 \langle P_{\frac{3}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \langle P_{\frac{1}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \tag{4.185}$$

$$= -2c_1 c_2 \langle P_{\frac{3}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \langle P_{\frac{1}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \tag{4.186}$$

Therefore the general form of the modulus square matrix element accounting for fine structure mixing is:

$$\begin{aligned}
|\langle r_q \rangle|^2 &= c_1^2 \left| \langle P_{\frac{3}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \right|^2 + c_2^2 \left| \langle P_{\frac{1}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \right|^2 \\
&\quad - 2c_1 c_2 \langle P_{\frac{3}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle \langle P_{\frac{1}{2}}, m+q | r_q | S_{\frac{1}{2}}, m \rangle
\end{aligned} \tag{4.187}$$

For the following, we've used equations (1.88) and (4.155). For the transitions involving light with +1 helicity:

$$\left| \left\langle P_{-, +\frac{1}{2}} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \tag{4.188}$$

$$\left| \left\langle P_{+, +\frac{1}{2}} \left| r_+ \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \tag{4.189}$$

$$\left| \left\langle P_{+, +\frac{3}{2}} \left| r_+ \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \tag{4.190}$$

For the transitions involving light with 0 helicity:

$$\left| \left\langle P_{-, -\frac{1}{2}} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \tag{4.191}$$

$$\left| \left\langle P_{+, -\frac{1}{2}} \left| r_0 \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \tag{4.192}$$

$$\left| \left\langle P_{-, +\frac{1}{2}} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{1}{2}}}{2m \omega_{\frac{1}{2}}} \right) \left[1 + a_1 a_2^+ 2\sqrt{2} + (a_2^+)^2 \right] \tag{4.193}$$

$$\left| \left\langle P_{+, +\frac{1}{2}} \left| r_0 \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{3}{2}}}{2m \omega_{\frac{3}{2}}} \right) \left[1 - a_1 a_2^+ \sqrt{2} - \frac{(a_2^+)^2}{2} \right] \tag{4.194}$$

For the transitions involving light with -1 helicity:

$$\left| \left\langle P_{-, -\frac{1}{2}} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{1}{2}}}{m \omega_{\frac{1}{2}}} \right) \left[1 + a_1 a_2^+ \sqrt{2} - \frac{(a_2^+)^2}{2} \right] \tag{4.195}$$

$$\left| \left\langle P_{+, -\frac{1}{2}} \left| r_- \right| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \right|^2 = \left(\frac{\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \right) \left[1 - a_1 a_2^+ 2\sqrt{2} + (a_2^+)^2 \right] \tag{4.196}$$

$$\left| \left\langle P_{+, -\frac{3}{2}} \left| r_- \right| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \right|^2 = \frac{3\hbar f_{\frac{3}{2}}}{4m \omega_{\frac{3}{2}}} \tag{4.197}$$

4.3 Explicit Calculation of Atomic Polarizability

The consequences of the previous section imply that we can write the atomic polarizability as:

$$\vec{\alpha} = \sum_q \hat{\epsilon}_q^* \alpha_q \hat{\epsilon}_q \tag{4.198}$$

Writing out equation (4.4) using the atomic polarizability and expanding in the spherical vector basis:

$$\vec{D} = \epsilon_0 \left(1 + \frac{[\mathcal{A}] \vec{\alpha}}{\epsilon_0} \right) \vec{E} \quad (4.199)$$

$$\sum_q D_q \hat{\epsilon}_q^* = \sum_q \epsilon_0 \left(1 + \frac{[\mathcal{A}]}{\epsilon_0} \sum_p \hat{\epsilon}_p^* \alpha_p \hat{\epsilon}_p \right) E_q \hat{\epsilon}_q^* \quad (4.200)$$

$$\sum_q D_q \hat{\epsilon}_q^* = \sum_q \epsilon_0 \left(E_q \hat{\epsilon}_q + \frac{[\mathcal{A}]}{\epsilon_0} \sum_p \hat{\epsilon}_p^* \alpha_p E_q \hat{\epsilon}_p \cdot \hat{\epsilon}_q^* \right) \quad (4.201)$$

$$\sum_q D_q \hat{\epsilon}_q^* = \sum_q \epsilon_0 \left(1 + \frac{[\mathcal{A}]}{\epsilon_0} \alpha_q \right) E_q \hat{\epsilon}_q^* \quad (4.202)$$

$$D_q = \epsilon_q E_q = \epsilon_0 \left(1 + \frac{[\mathcal{A}]}{\epsilon_0} \alpha_q \right) E_q \quad (4.203)$$

$$\epsilon_q = \epsilon_0 \left(1 + \frac{[\mathcal{A}]}{\epsilon_0} \alpha_q \right) \leftrightarrow n_q = \sqrt{1 + \frac{[\mathcal{A}]}{\epsilon_0} \alpha_q} \quad (4.204)$$

Using the result that $n + q = k$ from the previous section, the components of the atomic polarizability are:

$$\langle \vec{\alpha} \rangle = \frac{e^2}{\hbar} \sum_{n,k} P_n \left[\frac{\langle n | \vec{r} | k \rangle \langle k | \vec{r} | n \rangle}{\omega_{kn} - \omega - i \frac{\gamma_k}{2}} \right] \quad (4.205)$$

$$\sum_q \hat{\epsilon}_q^* \alpha_q \hat{\epsilon}_q = \frac{e^2}{\hbar} \sum_{q,n,k} P_n \left[\frac{\langle n | r_q^* \hat{\epsilon}_q | k \rangle \langle k | r_q \hat{\epsilon}_q^* | n \rangle}{\omega_{kn} - \omega - i \frac{\gamma_k}{2}} \right] \quad (4.206)$$

$$\alpha_q = \frac{e^2}{\hbar} \sum_{n,k} P_n \left[\frac{\langle n | r_q^* | k \rangle \langle k | r_q | n \rangle}{\omega_{kn} - \omega - i \frac{\gamma_k}{2}} \right] \quad (4.207)$$

$$\alpha_q = \frac{e^2}{\hbar} \sum_n P_n \frac{|\langle n + q | r_q | n \rangle|^2}{\omega_{n+q} - \omega_n - \omega - i \frac{\gamma_{n+q}}{2}} \quad (4.208)$$

The atomic polarizability for $q = +1$:

$$\begin{aligned} \frac{\hbar}{e^2} \alpha_+ &= + \left(\frac{1-P}{2} \right) \left| \left\langle P_-, +\frac{1}{2} \middle| r_+ \middle| S, -\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_-, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i \frac{\gamma_-}{2} \right)^{-1} \\ &+ \left(\frac{1-P}{2} \right) \left| \left\langle P_+, +\frac{1}{2} \middle| r_+ \middle| S, -\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_+, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i \frac{\gamma_+}{2} \right)^{-1} \\ &+ \left(\frac{1+P}{2} \right) \left| \left\langle P_+, +\frac{3}{2} \middle| r_+ \middle| S, +\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_+, +\frac{3}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i \frac{\gamma_+}{2} \right)^{-1} \end{aligned} \quad (4.209)$$

The atomic polarizability for $q = -1$:

$$\begin{aligned} \frac{\hbar}{e^2} \alpha_- &= + \left(\frac{1+P}{2} \right) \left| \left\langle P_-, -\frac{1}{2} \middle| r_- \middle| S, +\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_-, -\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i \frac{\gamma_-}{2} \right)^{-1} \\ &+ \left(\frac{1+P}{2} \right) \left| \left\langle P_+, -\frac{1}{2} \middle| r_- \middle| S, +\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_+, -\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i \frac{\gamma_+}{2} \right)^{-1} \\ &+ \left(\frac{1-P}{2} \right) \left| \left\langle P_+, -\frac{3}{2} \middle| r_- \middle| S, +\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_+, -\frac{3}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i \frac{\gamma_+}{2} \right)^{-1} \end{aligned} \quad (4.210)$$

The atomic polarizability for $q = 0$:

$$\frac{\hbar}{e^2} \alpha_0 = + \left(\frac{1-P}{2} \right) \left| \left\langle P_-, -\frac{1}{2} \middle| r_0 \middle| S, -\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_-, -\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i \frac{\gamma_-}{2} \right)^{-1}$$

$$\begin{aligned}
& + \left(\frac{1-P}{2}\right) \left| \left\langle P_+, -\frac{1}{2} \left| r_0 \right| S, -\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_+, -\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i\frac{\gamma_+}{2} \right)^{-1} \\
& + \left(\frac{1+P}{2}\right) \left| \left\langle P_-, +\frac{1}{2} \left| r_0 \right| S, +\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_-, +\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i\frac{\gamma_-}{2} \right)^{-1} \\
& + \left(\frac{1+P}{2}\right) \left| \left\langle P_+, +\frac{1}{2} \left| r_0 \right| S, +\frac{1}{2} \right\rangle \right|^2 \left(\omega_{[P_+, +\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i\frac{\gamma_+}{2} \right)^{-1}
\end{aligned} \tag{4.211}$$

Plugging in the values for the matrix elements, the atomic polarizability for $q = +1$:

$$\begin{aligned}
\frac{4m}{e^2} \alpha_+ & = + (1-P) \left(\frac{2f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \left(\omega_{[P_-, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i\frac{\gamma_-}{2} \right)^{-1} \\
& + (1-P) \left(\frac{f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \left(\omega_{[P_+, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i\frac{\gamma_+}{2} \right)^{-1} \\
& + (1+P) \left(\frac{3f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left(\omega_{[P_+, +\frac{3}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i\frac{\gamma_+}{2} \right)^{-1}
\end{aligned} \tag{4.212}$$

The atomic polarizability for $q = 0$:

$$\begin{aligned}
\frac{4m}{e^2} \alpha_0 & = + (1-P) \left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \left(\omega_{[P_-, -\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i\frac{\gamma_-}{2} \right)^{-1} \\
& + (1-P) \left(\frac{f_{\frac{3}{2}}}{\omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \left(\omega_{[P_+, -\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i\frac{\gamma_+}{2} \right)^{-1} \\
& + (1+P) \left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 + a_1 a_2^+ 2\sqrt{2} + (a_2^+)^2 \right] \left(\omega_{[P_-, +\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i\frac{\gamma_-}{2} \right)^{-1} \\
& + (1+P) \left(\frac{f_{\frac{3}{2}}}{\omega_{\frac{3}{2}}} \right) \left[1 - a_1 a_2^+ \sqrt{2} - \frac{(a_2^+)^2}{2} \right] \left(\omega_{[P_+, +\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i\frac{\gamma_+}{2} \right)^{-1}
\end{aligned} \tag{4.213}$$

The atomic polarizability for $q = -1$:

$$\begin{aligned}
\frac{4m}{e^2} \alpha_- & = + (1+P) \left(\frac{2f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 + a_1 a_2^+ \sqrt{2} - \frac{(a_2^+)^2}{2} \right] \left(\omega_{[P_-, -\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i\frac{\gamma_-}{2} \right)^{-1} \\
& + (1+P) \left(\frac{f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left[1 - a_1 a_2^+ 2\sqrt{2} + (a_2^+)^2 \right] \left(\omega_{[P_+, -\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i\frac{\gamma_+}{2} \right)^{-1} \\
& + (1-P) \left(\frac{3f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left(\omega_{[P_+, -\frac{3}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i\frac{\gamma_+}{2} \right)^{-1}
\end{aligned} \tag{4.214}$$

We can decompose the atomic polarizability into its real and imaginary parts using:

$$\left(\omega_0 - \omega - i\frac{\gamma}{2} \right)^{-1} = \frac{1}{\omega_0 - \omega - i\frac{\gamma}{2}} \left(\frac{\omega_0 - \omega + i\frac{\gamma}{2}}{\omega_0 - \omega + i\frac{\gamma}{2}} \right) \tag{4.215}$$

$$= \left[\frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \gamma^2/4} \right] + i \left[\frac{\gamma/2}{(\omega_0 - \omega)^2 + \gamma^2/4} \right] \tag{4.216}$$

The real and imaginary parts of the atomic polarizability for $q = +1$:

$$\frac{4m}{e^2} \Re \alpha_+ = + (1-P) \left(\frac{2f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \left[\frac{\omega_{[P_-, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega}{\left(\omega_{[P_-, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega \right)^2 + \gamma_-^2/4} \right]$$

$$\begin{aligned}
& + (1 - P) \left(\frac{f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \left[\frac{\omega_{[P_+, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega}{(\omega_{[P_+, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega)^2 + \gamma_+^2/4} \right] \\
& + (1 + P) \left(\frac{3f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left[\frac{\omega_{[P_+, +\frac{3}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega}{(\omega_{[P_+, +\frac{3}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega)^2 + \gamma_-^2/4} \right] \tag{4.217}
\end{aligned}$$

$$\begin{aligned}
\frac{4m}{e^2} \Im \alpha_+ & = + (1 - P) \left(\frac{2f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \left[\frac{\gamma_-/2}{(\omega_{[P_-, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega)^2 + \gamma_-^2/4} \right] \\
& + (1 - P) \left(\frac{f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \left[\frac{\gamma_+/2}{(\omega_{[P_+, +\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega)^2 + \gamma_+^2/4} \right] \\
& + (1 + P) \left(\frac{3f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left[\frac{\gamma_+/2}{(\omega_{[P_+, +\frac{3}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega)^2 + \gamma_-^2/4} \right] \tag{4.218}
\end{aligned}$$

The real and imaginary parts of the atomic polarizability for $q = 0$:

$$\begin{aligned}
\frac{4m}{e^2} \alpha_0 & = + (1 - P) \left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 - a_1 a_2^- 2\sqrt{2} + (a_2^-)^2 \right] \left(\omega_{[P_-, -\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i \frac{\gamma_-}{2} \right)^{-1} \\
& + (1 - P) \left(\frac{f_{\frac{3}{2}}}{\omega_{\frac{3}{2}}} \right) \left[1 + a_1 a_2^- \sqrt{2} - \frac{(a_2^-)^2}{2} \right] \left(\omega_{[P_+, -\frac{1}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i \frac{\gamma_+}{2} \right)^{-1} \\
& + (1 + P) \left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 + a_1 a_2^+ 2\sqrt{2} + (a_2^+)^2 \right] \left(\omega_{[P_-, +\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i \frac{\gamma_-}{2} \right)^{-1} \\
& + (1 + P) \left(\frac{f_{\frac{3}{2}}}{\omega_{\frac{3}{2}}} \right) \left[1 - a_1 a_2^+ \sqrt{2} - \frac{(a_2^+)^2}{2} \right] \left(\omega_{[P_+, +\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i \frac{\gamma_+}{2} \right)^{-1} \tag{4.219}
\end{aligned}$$

The real and imaginary parts of the atomic polarizability for $q = -1$:

$$\begin{aligned}
\frac{4m}{e^2} \alpha_- & = + (1 + P) \left(\frac{2f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left[1 + a_1 a_2^+ \sqrt{2} - \frac{(a_2^+)^2}{2} \right] \left(\omega_{[P_-, -\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i \frac{\gamma_-}{2} \right)^{-1} \\
& + (1 + P) \left(\frac{f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left[1 - a_1 a_2^+ 2\sqrt{2} + (a_2^+)^2 \right] \left(\omega_{[P_+, -\frac{1}{2}]} - \omega_{[S, +\frac{1}{2}]} - \omega - i \frac{\gamma_+}{2} \right)^{-1} \\
& + (1 - P) \left(\frac{3f_{\frac{3}{2}}}{2\omega_{\frac{3}{2}}} \right) \left(\omega_{[P_+, -\frac{3}{2}]} - \omega_{[S, -\frac{1}{2}]} - \omega - i \frac{\gamma_+}{2} \right)^{-1} \tag{4.220}
\end{aligned}$$

Before explicitly writing the forms of α_q for a polarized alkali vapor in a magnetic field, let's note the following:

1. The energies of the $\pm \frac{1}{2}$ states in the P terms will use the low field energies approximations. If necessary, the exact forms could be used.
2. The mixing coefficients a_1 & a_2^\pm are only relevant for the $m_J = \pm \frac{1}{2}$ states in the P terms. Only terms second order or higher in field in these coefficients depend on the sign of m_J .
3. P_\pm is the fraction of atoms in the $m_J = \pm \frac{1}{2}$ ground state. Since we've argued that most atoms are in the ground state: $P_+ + P_- \approx 1$ and the polarization is $P_+ - P_- \approx P$.

4. The electron mass is m and the absolute value of the electron charge is e .
5. In principle, the oscillator strengths $f_{\frac{1}{2},\frac{3}{2}}$ are affected by the temperature and the density of the buffer gas. We will make the approximation that for both Rb and K that $f_{\frac{1}{2}} \approx \frac{1}{3}$ and that $f_{\frac{3}{2}} \approx \frac{2}{3}$. Most book values are quoted with an uncertainty of about 10%. Therefore, using these approximate values for the oscillator strengths under most conditions is good enough.
6. To be consistent with the literature, we'll make the following substitutions:

$$\Delta_{\frac{1}{2},\frac{3}{2}} = \omega - \omega_{\frac{1}{2},\frac{3}{2}} \quad (4.221)$$

$$\Omega = \frac{\mu_B B}{\hbar} \quad (4.222)$$

Atomic Polarizability for Circularly Polarized Light

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

$$\begin{aligned} \frac{\hbar}{e^2} \alpha_+ &= P_- \left[a_1^2 \left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) + a_2^2 \left(\frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right) \pm a_1 a_2 \sqrt{\left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) \left(\frac{\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{1}{2}} + \left(\frac{4}{3} \right) \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} + \left(\omega_{\frac{1}{2}} + \left(\frac{4}{3} \right) \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} \right] \\ &+ P_- \left[a_2^2 \left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) + a_1^2 \left(\frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right) \mp a_1 a_2 \sqrt{\left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) \left(\frac{\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{3}{2}} + \left(\frac{5}{3} \right) \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} + \left(\frac{5}{3} \right) \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \\ &+ P_+ \left[\frac{3\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right] \times \left[\left(\omega_{\frac{3}{2}} + \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} + \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \quad (4.223) \end{aligned}$$

The atomic polarizability for left circularly polarized light is:

$$\begin{aligned} \frac{\hbar}{e^2} \alpha_- &= P_+ \left[a_1^2 \left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) + a_2^2 \left(\frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right) \pm a_1 a_2 \sqrt{\left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) \left(\frac{\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{1}{2}} - \left(\frac{4}{3} \right) \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} + \left(\omega_{\frac{1}{2}} - \left(\frac{4}{3} \right) \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} \right] \\ &+ P_+ \left[a_2^2 \left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) + a_1^2 \left(\frac{\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right) \mp 2a_1 a_2 \sqrt{\left(\frac{\hbar}{m\omega_{\frac{1}{2}}} f_{\frac{1}{2}} \right) \left(\frac{\hbar}{m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right)} \right] \\ &\times \left[\left(\omega_{\frac{3}{2}} - \left(\frac{5}{3} \right) \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} - \left(\frac{5}{3} \right) \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \\ &+ P_- \left[\frac{3\hbar}{4m\omega_{\frac{3}{2}}} f_{\frac{3}{2}} \right] \times \left[\left(\omega_{\frac{3}{2}} - \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} - \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \quad (4.224) \end{aligned}$$

Rearranging a few things:

$$\frac{m}{e^2} \alpha_{\pm} = P_{\mp} \left[a_1^2 \left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) + a_2^2 \left(\frac{f_{\frac{3}{2}}}{4\omega_{\frac{3}{2}}} \right) \pm a_1 a_2 \sqrt{\left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left(\frac{f_{\frac{3}{2}}}{\omega_{\frac{3}{2}}} \right)} \right]$$

$$\begin{aligned}
& \times \left[\left(\omega_{\frac{1}{2}} \pm \left(\frac{4}{3} \right) \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} + \left(\omega_{\frac{1}{2}} \pm \left(\frac{4}{3} \right) \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} \right] \\
& + P_{\mp} \left[a_2^2 \left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) + a_1^2 \left(\frac{f_{\frac{3}{2}}}{4\omega_{\frac{3}{2}}} \right) \mp a_1 a_2 \sqrt{\left(\frac{f_{\frac{1}{2}}}{\omega_{\frac{1}{2}}} \right) \left(\frac{f_{\frac{3}{2}}}{\omega_{\frac{3}{2}}} \right)} \right] \\
& \times \left[\left(\omega_{\frac{3}{2}} \pm \left(\frac{5}{3} \right) \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} \pm \left(\frac{5}{3} \right) \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \\
& + P_{\pm} \left[\frac{3f_{\frac{3}{2}}}{4\omega_{\frac{3}{2}}} \right] \times \left[\left(\omega_{\frac{3}{2}} \pm \frac{\mu_B B}{\hbar} - \omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} + \left(\omega_{\frac{3}{2}} \pm \frac{\mu_B B}{\hbar} + \omega + \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \quad (4.225)
\end{aligned}$$

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

$$P_{\pm} = \frac{1 \pm P}{2} \quad (4.226)$$

$$\Delta_{\frac{1}{2}, \frac{3}{2}} = \omega - \omega_{\frac{1}{2}, \frac{3}{2}} \quad (4.227)$$

$$\Omega = \frac{\mu_B B}{\hbar} \quad (4.228)$$

$$\begin{aligned}
\frac{m}{e^2} \alpha_{\pm} &= P_{\mp} \left[1 \cdot \left(\frac{1}{\omega} \right) + 0 \cdot \left(\frac{2}{4\omega} \right) \pm \beta y \sqrt{\left(\frac{1}{\omega} \right) \left(\frac{2}{\omega} \right)} \right] \times \left[\left(-\Delta_{\frac{1}{2}} \pm \left(\frac{4}{3} \right) \Omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} \right] \\
& + P_{\mp} \left[0 \cdot \left(\frac{1}{\omega} \right) + 1 \cdot \left(\frac{2}{4\omega} \right) \mp \beta y \sqrt{\left(\frac{1}{\omega} \right) \left(\frac{2}{\omega} \right)} \right] \times \left[\left(-\Delta_{\frac{3}{2}} \pm \left(\frac{5}{3} \right) \Omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \\
& + P_{\pm} \left[\frac{3 \frac{2}{3}}{4\omega} \right] \times \left[\left(-\Delta_{\frac{3}{2}} \pm \Omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \right] \quad (4.229)
\end{aligned}$$

$$\beta y = \frac{\sqrt{\left(1 + \frac{1}{2}\right)^2 - \frac{1}{4}}}{3} (-1 - 2) \frac{\mu_B B}{\hbar \omega_{so}} = \frac{\sqrt{2}}{3} \frac{\Omega}{\omega_{so}} \quad (4.230)$$

$$(4.231)$$

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

$$\begin{aligned}
\left(\frac{m\omega}{e^2} \right) \alpha_{\pm} &= \frac{1 \mp P}{2} \left[\frac{1}{3} \pm \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left(-\Delta_{\frac{1}{2}} \pm \left(\frac{4}{3} \right) \Omega - \frac{i}{2} \gamma_{\frac{1}{2}} \right)^{-1} + \frac{1 \mp P}{2} \left[\frac{1}{6} \mp \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left(-\Delta_{\frac{3}{2}} \pm \left(\frac{5}{3} \right) \Omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \\
& + \frac{1 \pm P}{4} \left(-\Delta_{\frac{3}{2}} \pm \Omega - \frac{i}{2} \gamma_{\frac{3}{2}} \right)^{-1} \quad (4.232)
\end{aligned}$$

4.4 Effect of Buffer Gas Collisions

see romalis and walkup papers

4.5 Real Part of the Polarizability

Recall the following relations in SI units:

$$k_{\pm} = \mathcal{R}e \frac{\omega}{c} n_{\pm} \quad (4.233)$$

$$= \mathcal{R}e \frac{\omega}{c} \sqrt{\frac{\epsilon}{\epsilon_0}} \quad (4.234)$$

$$= \mathcal{R}e \frac{\omega}{c} \sqrt{\frac{\epsilon_0 + [\mathcal{A}] \alpha_{\pm}}{\epsilon_0}} \quad (4.235)$$

$$= \mathcal{R}e \frac{\omega}{c} \sqrt{1 + \frac{[\mathcal{A}] \alpha_{\pm}}{\epsilon_0}} \quad (4.236)$$

$$\simeq \mathcal{R}e \frac{\omega}{c} \left(1 + \frac{[\mathcal{A}] \alpha_{\pm}}{2\epsilon_0} \right) \quad (4.237)$$

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

$$\phi = \frac{l}{2} (k_{\mathcal{L}} - k_{\mathcal{R}}) \quad (4.238)$$

$$= \frac{l}{2} (k_- - k_+) \quad (4.239)$$

$$= \frac{l}{2} \left(\mathcal{R}e \frac{\omega}{c} \left(1 + \frac{[\mathcal{A}] \alpha_-}{2\epsilon_0} \right) - \mathcal{R}e \frac{\omega}{c} \left(1 + \frac{[\mathcal{A}] \alpha_+}{2\epsilon_0} \right) \right) \quad (4.240)$$

$$= \frac{l\omega[\mathcal{A}]}{4c\epsilon_0} \mathcal{R}e (\alpha_- - \alpha_+) \quad (4.241)$$

$$(4.242)$$

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

$$\mathcal{R}e \left(-\Delta \pm g\Omega + \frac{i}{2}\gamma \right)^{-1} = \frac{-\Delta \pm g\Omega}{(-\Delta \pm g\Omega)^2 + \frac{\gamma^2}{4}} \quad (4.243)$$

$$= (-\Delta \pm g\Omega) \left[\Delta^2 + g^2\Omega^2 \mp 2g\Delta\Omega + \frac{\gamma^2}{4} \right]^{-1} \quad (4.244)$$

$$= \left(\frac{-\Delta \pm g\Omega}{\Delta^2 + \frac{\gamma^2}{4}} \right) \left[1 + \frac{g^2\Omega^2 \mp 2g\Delta\Omega}{\Delta^2 + \frac{\gamma^2}{4}} \right]^{-1} \quad (4.245)$$

$$\simeq \left(\frac{-\Delta \pm g\Omega}{\Delta^2 + \frac{\gamma^2}{4}} \right) \left[1 - \frac{g^2\Omega^2 \mp 2g\Delta\Omega}{\Delta^2 + \frac{\gamma^2}{4}} \right] \quad (4.246)$$

$$\simeq \frac{-\Delta \pm g\Omega \mp \frac{2\Delta^2 g\Omega}{\Delta^2 + \frac{\gamma^2}{4}}}{\Delta^2 + \frac{\gamma^2}{4}} \quad (4.247)$$

$$\simeq \frac{-\Delta \pm g\Omega \left(1 - \frac{2\Delta^2}{\Delta^2 + \frac{\gamma^2}{4}} \right)}{\Delta^2 + \frac{\gamma^2}{4}} \quad (4.248)$$

$$\simeq \frac{-\Delta \mp g\Omega \left(\frac{\Delta^2 - \frac{\gamma^2}{4}}{\Delta^2 + \frac{\gamma^2}{4}} \right)}{\Delta^2 + \frac{\gamma^2}{4}} \quad (4.249)$$

$$\simeq \frac{-\frac{1}{\Delta} \mp g \frac{\Omega}{\Delta^2} \left(\frac{1 - \frac{\gamma^2}{4\Delta^2}}{1 + \frac{\gamma^2}{4\Delta^2}} \right)}{1 + \frac{\gamma^2}{4\Delta^2}} \quad (4.250)$$

Putting this in:

$$\begin{aligned}
\left(\frac{m\omega}{e^2}\right) \alpha_{\pm} &= \frac{1 \mp P}{2} \left[\frac{1}{3} \pm \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{1}{2}}} \mp \frac{4\Omega}{3\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right] + \frac{1 \mp P}{2} \left[\frac{1}{6} \mp \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} \mp \frac{5\Omega}{3\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \\
&+ \frac{1 \pm P}{4} \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} \mp \frac{\Omega}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \tag{4.251}
\end{aligned}$$

$$\begin{aligned}
\frac{m\omega}{e^2} (\alpha_- - \alpha_+) &= \frac{1+P}{2} \left[\frac{1}{3} - \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{1}{2}}} + \frac{4\Omega}{3\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right] - \frac{1-P}{2} \left[\frac{1}{3} + \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{1}{2}}} - \frac{4\Omega}{3\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right] \\
&+ \frac{1+P}{2} \left[\frac{1}{6} + \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} + \frac{5\Omega}{3\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] - \frac{1-P}{2} \left[\frac{1}{6} - \frac{\Omega}{\omega_{so}} \frac{2}{9} \right] \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} - \frac{5\Omega}{3\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \\
&+ \frac{1-P}{4} \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} + \frac{\Omega}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] - \frac{1+P}{4} \left[\frac{-\frac{1}{\Delta_{\frac{3}{2}}} - \frac{\Omega}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \tag{4.252} \\
&= \left[\frac{\frac{1}{3}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right] \left[-\frac{P}{\Delta_{\frac{1}{2}}} + \frac{4\Omega}{3\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) \right] + \frac{\Omega}{9} \frac{2}{\omega_{so}\Delta_{\frac{1}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) - \frac{8P\Omega^2}{27\omega_{so}^2\Delta_{\frac{1}{2}}^2} \left[\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{\left(1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}\right)^2} \right]
\end{aligned}$$

$$\begin{aligned}
& + \left[\frac{\frac{1}{6} \mp \frac{\Omega}{\omega_{so}} \frac{2}{9}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \left[-\frac{P}{\Delta_{\frac{3}{2}}} + \frac{5\Omega}{3\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) \right] - \frac{\Omega}{9} \frac{2}{\omega_{so}\Delta_{\frac{3}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) + \frac{10P\Omega^2}{27\omega_{so}^2\Delta_{\frac{3}{2}}^2} \left[\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{\left(1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}\right)^2} \right] \\
& + \left[\frac{\frac{P}{2\Delta_{\frac{3}{2}}} + \frac{\Omega}{2\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right)}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right] \tag{4.253}
\end{aligned}$$

$$\begin{aligned}
& = \frac{P}{3} \left[\frac{1}{\Delta_{\frac{3}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) - \frac{1}{\Delta_{\frac{1}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) \right] \\
& + \frac{\Omega}{9} \left[\frac{4}{\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) + \frac{7}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) + \frac{2}{\omega_{so}\Delta_{\frac{1}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) - \frac{2}{\omega_{so}\Delta_{\frac{3}{2}}} \left(\frac{1}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) \right] \tag{4.254}
\end{aligned}$$

$$\begin{aligned}
& = \frac{P}{3} \left[\frac{\Delta_{\frac{3}{2}}}{\Delta_{\frac{3}{2}}^2 + \frac{1}{4}\gamma_{\frac{3}{2}}^2} - \frac{\Delta_{\frac{1}{2}}}{\Delta_{\frac{1}{2}}^2 + \frac{1}{4}\gamma_{\frac{1}{2}}^2} \right] \\
& + \frac{\Omega}{9} \left[\frac{4}{\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) + \frac{7}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) - \frac{2}{\Delta_{\frac{3}{2}}\Delta_{\frac{1}{2}}} \left(\frac{1 + \frac{\Delta_{\frac{1}{2}}\gamma_{\frac{3}{2}}^2 - \Delta_{\frac{3}{2}}\gamma_{\frac{1}{2}}^2}{4\omega_{so}\Delta_{\frac{3}{2}}\Delta_{\frac{1}{2}}}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2\gamma_{\frac{1}{2}}^2}{16\Delta_{\frac{3}{2}}^2\Delta_{\frac{1}{2}}^2}} \right) \right] \tag{4.255}
\end{aligned}$$

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

$$\begin{aligned}
\phi & = \frac{l\omega[\mathcal{A}]}{4c\epsilon_0} \text{Re}(\alpha_- - \alpha_+) \tag{4.256} \\
& = \frac{l\omega[\mathcal{A}]P}{12c\epsilon_0} \frac{e^2}{m\omega} \left[\frac{\Delta_{\frac{3}{2}}}{\Delta_{\frac{3}{2}}^2 + \frac{1}{4}\gamma_{\frac{3}{2}}^2} - \frac{\Delta_{\frac{1}{2}}}{\Delta_{\frac{1}{2}}^2 + \frac{1}{4}\gamma_{\frac{1}{2}}^2} \right] \\
& + \frac{l\omega[\mathcal{A}]\Omega}{36c\epsilon_0} \frac{e^2}{m\omega} \left[\frac{4}{\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) + \frac{7}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) - \frac{2}{\Delta_{\frac{3}{2}}\Delta_{\frac{1}{2}}} \left(\frac{1 + \frac{\Delta_{\frac{1}{2}}\gamma_{\frac{3}{2}}^2 - \Delta_{\frac{3}{2}}\gamma_{\frac{1}{2}}^2}{4\omega_{so}\Delta_{\frac{3}{2}}\Delta_{\frac{1}{2}}}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2\gamma_{\frac{1}{2}}^2}{16\Delta_{\frac{3}{2}}^2\Delta_{\frac{1}{2}}^2}} \right) \right] \tag{4.257}
\end{aligned}$$

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

$$\phi = \phi_P + \phi_B \tag{4.258}$$

$$\phi_P = l[\mathcal{A}]P_A \left(\frac{e^2}{12m\epsilon_0} \right) \left[\frac{\Delta_{\frac{3}{2}}}{\Delta_{\frac{3}{2}}^2 + \frac{1}{4}\gamma_{\frac{3}{2}}^2} - \frac{\Delta_{\frac{1}{2}}}{\Delta_{\frac{1}{2}}^2 + \frac{1}{4}\gamma_{\frac{1}{2}}^2} \right] \tag{4.259}$$

$$\phi_B = l[\mathcal{A}]B \left(\frac{e^2 \mu_B}{36mc\epsilon_0 \hbar} \right) \left[\frac{4}{\Delta_{\frac{1}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2}} \right) + \frac{7}{\Delta_{\frac{3}{2}}^2} \left(\frac{1 - \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}}{1 + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2}} \right) - \frac{2}{\Delta_{\frac{3}{2}} \Delta_{\frac{1}{2}}} \left(\frac{1 + \frac{\Delta_{\frac{1}{2}} \gamma_{\frac{3}{2}}^2 - \Delta_{\frac{3}{2}} \gamma_{\frac{1}{2}}^2}{4\omega_{so} \Delta_{\frac{3}{2}} \Delta_{\frac{1}{2}}}}{1 + \frac{\gamma_{\frac{1}{2}}^2}{4\Delta_{\frac{1}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2}{4\Delta_{\frac{3}{2}}^2} + \frac{\gamma_{\frac{3}{2}}^2 \gamma_{\frac{1}{2}}^2}{16\Delta_{\frac{3}{2}}^2 \Delta_{\frac{1}{2}}^2}} \right) \right] \quad (4.260)$$

$$\Delta_{\frac{1}{2}, \frac{3}{2}} = \omega - \omega_{\frac{1}{2}, \frac{3}{2}} = 2\pi \left(\nu - \nu_{\frac{1}{2}, \frac{3}{2}} \right) \quad (4.261)$$

$$\gamma_{\frac{1}{2}, \frac{3}{2}} = 2\pi \times \text{FWHM}_{\text{PB}}^{\frac{1}{2}, \frac{3}{2}} \quad (4.262)$$

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

$$\phi_P = l[\mathcal{A}]P_A \left(\frac{e^2}{12mc\epsilon_0} \right) \left[\frac{1}{\Delta_{\frac{3}{2}}} - \frac{1}{\Delta_{\frac{1}{2}}} \right] \quad (4.263)$$

$$\phi_B = l[\mathcal{A}]B \left(\frac{e^2 \mu_B}{36mc\epsilon_0 \hbar} \right) \left[\frac{4}{\Delta_{\frac{1}{2}}^2} + \frac{7}{\Delta_{\frac{3}{2}}^2} - \frac{2}{\Delta_{\frac{3}{2}} \Delta_{\frac{1}{2}}} \right] \quad (4.264)$$

4.6 Imaginary Part of the Polarizability

4.7 stuff

4.8 Description

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

4.9 General Formula for Rotation Angle

A linearly polarized probe beam can be written as

$$|\psi(z, t)\rangle = |\mathcal{P}\rangle e^{i(kz - \omega t)} \quad (4.265)$$

This can be rewritten in the circular polarization basis:

$$|\psi(z, t)\rangle = (|\mathcal{R}\rangle e^{ik_{\mathcal{R}}z} + |\mathcal{L}\rangle e^{ik_{\mathcal{L}}z}) \frac{e^{-i\omega t}}{\sqrt{2}} \quad (4.266)$$

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

$$|\psi(z', t)\rangle = (|\mathcal{R}\rangle e^{ik_{\mathcal{R}}l} + |\mathcal{L}\rangle e^{ik_{\mathcal{L}}l}) \frac{e^{i(kz' - \omega t)}}{\sqrt{2}} \quad (4.267)$$

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

$$|\psi\rangle = e^{i((k_{\mathcal{R}}+k_{\mathcal{L}})\frac{l}{2}+kz' - \omega t)} \left[\frac{e^{i(k_{\mathcal{R}}-k_{\mathcal{L}})\frac{l}{2}} |\mathcal{R}\rangle + e^{i(-k_{\mathcal{R}}+k_{\mathcal{L}})\frac{l}{2}} |\mathcal{L}\rangle}{\sqrt{2}} \right] \quad (4.268)$$

Making the substitution

$$\phi = \frac{l}{2} (k_{\mathcal{L}} - k_{\mathcal{R}}) \quad (4.269)$$

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

$$|\psi\rangle = e^{i((k_{\mathcal{R}}+k_{\mathcal{L}})\frac{l}{2}+kz' - \omega t)} \left[\cos(\phi) \left(\frac{|\mathcal{R}\rangle + |\mathcal{L}\rangle}{\sqrt{2}} \right) + \sin(\phi) \left(\frac{|\mathcal{R}\rangle - |\mathcal{L}\rangle}{\sqrt{2}i} \right) \right] \quad (4.270)$$

In the linear polarization basis, this is simply:

$$|\psi\rangle = e^{i((k_{\mathcal{R}}+k_{\mathcal{L}})\frac{l}{2}+kz' - \omega t)} [\cos(\phi) |\mathcal{P}\rangle + \sin(\phi) |\mathcal{S}\rangle] \quad (4.271)$$

Therefore ϕ is the Faraday rotation angle and it is defined by eqn. (4.269). Note that there is a relative phase shift between the two components circular polarization. There is no relative phase shift between the two components of linear polarization. The rotation angle is commonly observed by measuring the difference in intensities of the two components of a “probe” beam:

$$I_{\mathcal{P}} \propto |\langle \mathcal{P} | \psi \rangle|^2 = \cos^2(\phi) \quad (4.272)$$

$$I_{\mathcal{S}} \propto |\langle \mathcal{S} | \psi \rangle|^2 = \sin^2(\phi) \quad (4.273)$$

$$I_{\mathcal{P}} - I_{\mathcal{S}} \propto \cos^2(\phi) - \sin^2(\phi) = \cos(2\phi) \quad (4.274)$$

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 cancelled by a half waveplate with an angle of $-\phi/2$ between the its axis and the reference axis

Chapter 5

Interaction with a Weak RF Field

5.1 Description

5.1.1 Transition Rate

Transitions between adjacent hyperfine levels satisfy $\Delta m_F = \pm 1$ & $\Delta F = 0$ and occur between states of the same parity. The most probable way to induce these particular transitions is via a magnetic dipole interaction with an oscillating magnetic field of the appropriate frequency. Therefore we use a set of coils to produce a weak (a few milligauss) transverse field \vec{B}_{rf} to probe the various EPR transitions. The lineshape of each transition is proportional to the difference of the absorption and stimulated emission rates between the two levels. The transition probability rate for either process is given by Fermi's Golden Rule (Fermi, E. Notes On Quantum Mechanics, Chicago: University of Chicago Press, 1995. section 23, page 2, equation 13):

$$\frac{d\Gamma_{\pm}}{dE} = \frac{2\pi}{\hbar} \left| \left\langle m_F - \frac{1}{2} \pm \frac{1}{2} \left| \hat{W} \right| m_F - \frac{1}{2} \mp \frac{1}{2} \right\rangle \right|^2 \frac{d\rho_{\pm}}{dE} \quad (5.1)$$

where \hat{W} is the operator of the perturbation inducing the transition and the upper (lower) sign refers to absorption (stimulated emission). $\frac{d\rho_{\pm}}{dE}$ is the density of available states near the transition energy as a function of energy or, alternatively, the fractional probability of transition near the transition frequency. The modulus squared matrix element is identical for both absorption and stimulated emission, which is a manifestation of the principle of detailed balancing:

$$\left| \langle m_F | \hat{W} | m_F - 1 \rangle \right|^2 = \left| \langle m_F - 1 | \hat{W} | m_F \rangle \right|^2 \quad (5.2)$$

The width of the lineshape is inversely proportional to the lifetimes of the initial and final states and consequently the lineshape is ideally a lorentzian. For a vapor of alkali metal ("pure" or "hybrid"), the process that dominates lifetime of the each hyperfine level is spin-exchange between (alike or unlike) alkali metal atoms. Magnetic field inhomogenities and RF power can broaden the lineshape. However, the area under the peak is a very robust quantity because it is conserved and therefore should not depend on the details of the lineshape. The integral of the lineshape over frequency (or equivalently transition energy) is:

$$\Gamma = \int \left(\frac{d\Gamma_+}{dE} - \frac{d\Gamma_-}{dE} \right) dE \quad (5.3)$$

$$= \frac{2\pi}{\hbar} \left| \langle m_F - 1 | \hat{W} | m_F \rangle \right|^2 \int \left(\frac{d\rho_+}{dE} - \frac{d\rho_-}{dE} \right) dE \quad (5.4)$$

Therefore the area is the net transition probability rate:

$$\Gamma = \frac{2\pi}{\hbar} \left| \langle m_F - 1 | \hat{W} | m_F \rangle \right|^2 [\rho_+ - \rho_-] \quad (5.5)$$

where ρ_{\pm} is relative population of the state that is absorbing (emitting). First we will derive the the matrix element in Γ and then we will discuss the relative populations ρ_{\pm} .

5.1.2 Transition Matrix Element

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 3.9Ω & an inductance of $0.5 \mu\text{H}$ 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 dependant perturbation to our original hamiltonian:

$$\mathcal{H}_{EPR} = \mathcal{H} + \mathcal{W} \quad (5.6)$$

$$\mathcal{W} = -\vec{\mu}_I \cdot \vec{B}_{rf} - \vec{\mu}_J \cdot \vec{B}_{rf} \quad (5.7)$$

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:

$$W_{fi} = \frac{\hbar}{2} \langle m_F - 1 | \omega_I \hat{I}_- + \omega_J \hat{J}_- | m_F \rangle \quad (5.8)$$

$$= \frac{\hbar}{2} \langle m_F - 1 | \omega_I \hat{F}_- + (\omega_J - \omega_I) \hat{J}_- | m_F \rangle \quad (5.9)$$

$$= \frac{\hbar}{2} \langle f | \omega_I \hat{F}_- + (\omega_J - \omega_I) \hat{J}_- | i \rangle \quad (5.10)$$

$$\omega_I = -\frac{g_I \mu_N B_{RF}}{\hbar} \quad (5.11)$$

$$\omega_J = -\frac{g_S \mu_B B_{RF}}{\hbar} \quad (5.12)$$

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

$$\langle \hat{F}_- \rangle = \langle m_F^\pm - 1 | \hat{F}_- | m_F^\pm \rangle \quad (5.13)$$

$$= \left[a_1(m_F - 1) \left\langle I \pm \frac{1}{2}, m_F - 1 \right| \pm a_2(m_F - 1) \left\langle I \mp \frac{1}{2}, m_F - 1 \right| \right] \hat{F}_- \left[a_1(m_F) \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2(m_F) \left| I \mp \frac{1}{2}, m_F \right\rangle \right] \quad (5.14)$$

$$= \left[a_1(m_F - 1) \left\langle I \pm \frac{1}{2}, m_F - 1 \right| \pm a_2(m_F - 1) \left\langle I \mp \frac{1}{2}, m_F - 1 \right| \right] \left[f_\pm a_1(m_F) \left| I \pm \frac{1}{2}, m_F - 1 \right\rangle \pm f_\mp a_2(m_F) \left| I \mp \frac{1}{2}, m_F - 1 \right\rangle \right] \quad (5.15)$$

$$= f_\pm a_1(m_F) a_1(m_F - 1) + f_\mp a_2(m_F) a_2(m_F - 1) \quad (5.16)$$

$$= f_\pm a_1 f a_{1i} + f_\mp a_2 f a_{2i} \quad (5.17)$$

$$f_\pm = \sqrt{\left(I + \frac{1}{2}\right) \left(I + \frac{1}{2} \pm 1\right) - m_F(m_F - 1)} \quad (5.18)$$

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

$$\langle \hat{J}_- \rangle^\pm = \langle m_F^\pm - 1 | \hat{J}_- | m_F^\pm \rangle \quad (5.19)$$

$$= (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - 1 \mp \frac{1}{2}, \pm \frac{1}{2} \right| \pm (a_{1f} b_{2f} + a_{2f} b_{1f}) \times \left\langle m_F - 1 \pm \frac{1}{2}, \mp \frac{1}{2} \right| \hat{J}_- \left[(a_{1i} b_{1i} - a_{2i} b_{2i}) \times \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm (a_{1i} b_{2i} + a_{2i} b_{1i}) \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \right] \quad (5.20)$$

$$\begin{aligned}\langle \hat{J}_- \rangle^+ &= (a_{1f}b_{1f} - a_{2f}b_{2f}) \left\langle m_F - \frac{3}{2}, +\frac{1}{2} \right\rangle + (a_{1f}b_{2f} + a_{2f}b_{1f}) \\ &\quad \times \left\langle m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \left[\sqrt{\frac{1}{2} \frac{3}{2} + \frac{1}{2} \frac{1}{2}} \left[(a_{1i}b_{1i} - a_{2i}b_{2i}) \left| m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \right] \right.\end{aligned}\quad (5.21)$$

$$= [a_{1f}b_{2f} + a_{2f}b_{1f}] \times [a_{1i}b_{1i} - a_{2i}b_{2i}] \quad (5.22)$$

$$\begin{aligned}\langle \hat{J}_- \rangle^- &= (a_{1f}b_{1f} - a_{2f}b_{2f}) \left\langle m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle - (a_{1f}b_{2f} + a_{2f}b_{1f}) \\ &\quad \times \left\langle m_F - \frac{3}{2}, +\frac{1}{2} \right\rangle \left[\sqrt{\frac{1}{2} \frac{3}{2} + \frac{1}{2} \frac{1}{2}} \left[-(a_{1i}b_{2i} + a_{2i}b_{1i}) \left| m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \right] \right.\end{aligned}\quad (5.23)$$

$$= [a_{2f}b_{2f} - a_{1f}b_{1f}] \times [a_{1i}b_{2i} + a_{2i}b_{1i}] \quad (5.24)$$

Note the following relations:

$$b_{2f}b_{1i} = \frac{\sqrt{(I + \frac{1}{2})(I + \frac{3}{2}) - m_F(m_F - 1)}}{2I + 1} = \frac{f_+}{2I + 1} \quad (5.25)$$

$$b_{1f}b_{2i} = \frac{\sqrt{(I + \frac{1}{2})(I - \frac{1}{2}) - m_F(m_F - 1)}}{2I + 1} = \frac{f_-}{2I + 1} \quad (5.26)$$

$$b_{1f}b_{1i} = \frac{\sqrt{(I + \frac{1}{2})(I - \frac{1}{2}) + m_F(m_F - 1) + 2m_F(I + \frac{1}{2})}}{2I + 1} = \frac{g_-}{2I + 1} \quad (5.27)$$

$$b_{2f}b_{2i} = \frac{\sqrt{(I + \frac{1}{2})(I + \frac{3}{2}) + m_F(m_F - 1) - 2m_F(I + \frac{1}{2})}}{2I + 1} = \frac{g_+}{2I + 1} \quad (5.28)$$

$$g_{\pm} = \sqrt{\left(I + \frac{1}{2}\right) \left(I + \frac{1}{2} \pm 1\right) + m_F(m_F - 1) \mp 2m_F \left(I + \frac{1}{2}\right)} \quad (5.29)$$

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

$$\langle \hat{J}_- \rangle^+ = [a_{1f}b_{2f} + a_{2f}b_{1f}] \times [a_{1i}b_{1i} - a_{2i}b_{2i}] \quad (5.30)$$

$$= a_{1f}a_{1i} \frac{f_+}{2I + 1} + a_{2f}a_{1i} \frac{g_-}{2I + 1} - a_{1f}a_{2i} \frac{g_+}{2I + 1} - a_{2f}a_{2i} \frac{f_-}{2I + 1} \quad (5.31)$$

$$\langle \hat{J}_- \rangle^- = [a_{2f}b_{2f} - a_{1f}b_{1f}] \times [a_{1i}b_{2i} + a_{2i}b_{1i}] \quad (5.32)$$

$$= a_{2f}a_{1i} \frac{g_+}{2I + 1} - a_{1f}a_{1i} \frac{f_-}{2I + 1} + a_{2f}a_{2i} \frac{f_+}{2I + 1} - a_{1f}a_{2i} \frac{g_-}{2I + 1} \quad (5.33)$$

$$\langle \hat{J}_- \rangle^{\pm} = \pm a_{1f}a_{1i} \frac{f_{\pm}}{2I + 1} + a_{2f}a_{1i} \frac{g_{\mp}}{2I + 1} - a_{1f}a_{2i} \frac{g_{\pm}}{2I + 1} \mp a_{2f}a_{2i} \frac{f_{\mp}}{2I + 1} \quad (5.34)$$

Putting this altogether,

$$\begin{aligned}W_{fi} &= \frac{\hbar}{2} \omega_I (f_{\pm} a_{1f} a_{1i} + f_{\mp} a_{2f} a_{2i}) + \frac{\hbar}{2} (\omega_J - \omega_I) \\ &\quad \times \left(\pm a_{1f} a_{1i} \frac{f_{\pm}}{2I + 1} + a_{2f} a_{1i} \frac{g_{\mp}}{2I + 1} - a_{1f} a_{2i} \frac{g_{\pm}}{2I + 1} \mp a_{2f} a_{2i} \frac{f_{\mp}}{2I + 1} \right)\end{aligned}\quad (5.35)$$

$$\begin{aligned}&= \frac{\hbar}{2} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I + 1} \right) f_{\pm} a_{1f} a_{1i} + \frac{\hbar}{2} \left(\frac{2I\omega_I + (1 \pm 1)\omega_I \mp \omega_J}{2I + 1} \right) \\ &\quad \times f_{\mp} a_{2f} a_{2i} + \frac{\hbar}{2} \left(\frac{\omega_J - \omega_I}{2I + 1} \right) (g_{\mp} a_{2f} a_{1i} - g_{\pm} a_{1f} a_{2i})\end{aligned}\quad (5.36)$$

Using the small field approximations from before:

$$a_1 = 1 - \frac{\beta^2}{2}x^2 \quad (5.37)$$

$$a_2 = -\beta x + 2\alpha\beta x^2 \quad (5.38)$$

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

$$\begin{aligned} |W_{fi}|^2 &\simeq \frac{\hbar^2}{4} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I+1} \right)^2 f_{\pm}^2 - \frac{\hbar^2}{4} \left(\frac{2I\omega_I + (1 \mp 1)\omega_I \pm \omega_J}{2I+1} \right) \\ &\times \left(\frac{\omega_J - \omega_I}{2I+1} \right) f_{\pm} (g_{\mp}\beta_f - g_{\pm}\beta_i) x + \mathcal{O}(x^2) \end{aligned} \quad (5.39)$$

5.1.3 Area Under Curve

This gives the relative population of the $|m_F - \frac{1}{2} \mp \frac{1}{2}\rangle$ state:

$$\rho_{\pm} = \frac{e^{\beta(m_F - \frac{1}{2} \mp \frac{1}{2})}}{Z_F} \quad (5.40)$$

from which the relative population difference is easily obtained:

$$\rho_+ - \rho_- = \frac{e^{\beta(m_F-1)}}{Z_F} - \frac{e^{\beta m_F}}{Z_F} = \frac{e^{\beta m_F}}{Z_F} (e^{-\beta} - 1) \quad (5.41)$$

Putting together all of these results, we get

$$|\Gamma| = \frac{2\pi}{\hbar} |W_{fi}|^2 e^{\beta m_F} \left(\frac{1 - e^{-\beta}}{Z_F} \right) \quad (5.42)$$

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

$$A_{m_F} \simeq A_0 \left(\frac{2\pi}{\hbar} \right) \left[\frac{\hbar^2}{4} \left(\frac{\omega_J}{2I+1} \right)^2 f_{\pm}^2 \right] e^{\beta m_F} \left(\frac{1 - e^{-\beta}}{Z_F} \right) + \mathcal{O}(x) \quad (5.43)$$

$$\simeq A_0 \frac{2\pi}{\hbar} \left(\frac{B_{RF}}{2I+1} \right)^2 [F(F+1) - m_F(m_F-1)] e^{\beta m_F} \quad (5.44)$$

where A is a common factor for all transitions. Note that this β is the spin temperature and not the β defined in eqn. (1.201).

Chapter 6

Experimental Applications

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

6.1 General Considerations to Measure Faraday Rotation

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. Therefore, it is most natural to represent the polarization vector of the light in the atomic coordinate system. For an alkali atom in a magnetic field, this happens to be the irreducible spherical vector basis. We'll start with a arbitrarily polarized plane wave:

$$\vec{E} = |E\rangle e^{i\vec{k}\cdot\vec{r}-i\omega t} \quad (6.1)$$

$$|E\rangle = E_0 e^{i\phi_p} \left[\left(\sqrt{1-P} \frac{e^{+i\theta}}{2} + \sqrt{1+P} \frac{e^{-i\theta}}{2} \right) |\mathcal{P}\rangle + \left(\sqrt{1-P} \frac{e^{+i\theta}}{2i} - \sqrt{1+P} \frac{e^{-i\theta}}{2i} \right) |\mathcal{S}\rangle \right] \quad (6.2)$$

Going through a photoelastic modulator:

$$|E\rangle = E_0 e^{i\phi_p} \left[\left(\sqrt{1-P} \frac{e^{+i\theta_+}}{2} + \sqrt{1+P} \frac{e^{-i\theta_-}}{2} \right) |\mathcal{P}\rangle + \left(\sqrt{1-P} \frac{e^{+i\theta_-}}{2i} - \sqrt{1+P} \frac{e^{-i\theta_+}}{2i} \right) |\mathcal{S}\rangle \right] \quad (6.3)$$

$$\theta_{\pm} = \theta \pm \frac{\beta(t)}{2} \quad (6.4)$$

Projecting onto the atomic coordinate system with equations (3.45) and (3.46) gives in the atomic basis:

$$|E\rangle_0 = -\frac{E_0}{2} e^{i\phi_p} \sin(\Theta) \left[\sqrt{1-P} e^{+i\theta_+} + \sqrt{1+P} e^{-i\theta_-} \right] \quad (6.5)$$

$$|E\rangle_{\pm} = +\frac{E_0}{2\sqrt{2}} e^{i(\phi_p \mp \Phi)} \left[\{ e^{+i\theta_-} \mp e^{+i\theta_+} \cos(\Theta) \} \sqrt{1-P} - \{ e^{-i\theta_+} \pm e^{-i\theta_-} \cos(\Theta) \} \sqrt{1+P} \right] \quad (6.6)$$

Going through the atomic vapor, each polarization component q of the light propagates with wave vector \vec{k}_q :

$$\vec{E} = \sum_q |E\rangle_q \hat{\epsilon}_q e^{i(\vec{k}_q \cdot \vec{r} - \omega t)} \quad (6.7)$$

After traversing a distance of l in the atomic vapor and reentering a uniform and isotropic medium with wave vector \vec{k} , we get:

$$\vec{E} = e^{i(\vec{k} \cdot \vec{r} - \omega t)} \sum_q |E\rangle_q \hat{\epsilon}_q e^{i\vec{k}_q \cdot l} \quad (6.8)$$

The time averaged intensity of the light is:

$$I = \sqrt{\frac{\epsilon}{\mu}} \frac{\vec{E}^* \cdot \vec{E}}{2} = \sqrt{\frac{\epsilon}{\mu}} \sum_q \frac{\langle E | E \rangle_q}{2} e^{i(k_q - k_q^*)l} = \sqrt{\frac{\epsilon}{\mu}} \sum_q \frac{\langle E | E \rangle_q}{2} e^{-2l\Im k_q} \quad (6.9)$$

where the magnitudes of each component are:

$$\frac{\langle E | E \rangle_0}{E_0^2} = \frac{\sin^2(\Theta)}{2} \left[1 + \sqrt{1 - P^2} \cos(2\theta) \right] \quad (6.10)$$

$$\frac{\langle E | E \rangle_{\pm}}{E_0^2} = \frac{1 + \cos^2(\Theta)}{4} \pm \frac{P}{2} \cos(\Theta) \cos(\beta) - \frac{\sqrt{1 - P^2}}{4} \left[\sin^2(\Theta) \cos(2\theta) \pm 2 \cos(\Theta) \sin(2\theta) \sin(\beta) \right] \quad (6.11)$$

Using these above equations, the total intensity of light leaving the atomic vapor can be written as sum of three parts:

$$I = \sqrt{\frac{\epsilon}{\mu}} \frac{E_0^2}{2} (A_{\Sigma} + A_{\Delta} + A_{\beta}) \quad (6.12)$$

$$A_{\Sigma} = \frac{1}{4} \left[e^{-2l\Im k_+} + e^{-2l\Im k_-} + 2e^{-2l\Im k_0} \right] \quad (6.13)$$

$$A_{\Delta} = \left(\frac{\cos^2(\Theta) - \sqrt{1 - P^2} \sin^2(\Theta) \cos(2\theta)}{4} \right) \left[e^{-2l\Im k_+} + e^{-2l\Im k_-} - 2e^{-2l\Im k_0} \right] \quad (6.14)$$

$$A_{\beta} = \left[P \cos(\beta) - \sqrt{1 - P^2} \sin(\beta) \sin(2\theta) \right] \cos(\Theta) e^{-l\Im(k_- + k_+)} \sinh[l\Im(k_- - k_+)] \quad (6.15)$$

To get each component in the light coordinate system after leaving the atomic vapor, we project back using:

$$\hat{\epsilon}_0 = -\sin(\Theta) |\mathcal{P}\rangle + \cos(\Theta) |\mathcal{Z}\rangle \quad (6.16)$$

$$\hat{\epsilon}_{\pm} = \mp \frac{\exp(\pm i\Phi)}{\sqrt{2}} \left[\cos(\Theta) |\mathcal{P}\rangle \pm i |\mathcal{S}\rangle + \sin(\Theta) |\mathcal{Z}\rangle \right] \quad (6.17)$$

Note that there is no component of polarization along the direction of propagation of the light, so we'll just ignore the $|\mathcal{Z}\rangle$ terms. The effect of the atomic vapor can be written in matrix form in the linear polarization basis in the light coordinate system:

$$|E\rangle_{\text{aft}} = \hat{M} |E\rangle_{\text{bef}} \quad (6.18)$$

$$\hat{M} = e^{i(k_+ + k_-)l/2} \begin{bmatrix} \cos\left(\frac{k_+ - k_-}{2}l\right) \cos^2(\Theta) + e^{i(k_0 - \frac{k_+ + k_-}{2})l} \sin^2(\Theta) & \sin\left(\frac{k_+ - k_-}{2}l\right) \cos(\Theta) \\ -\sin\left(\frac{k_+ - k_-}{2}l\right) \cos(\Theta) & \cos\left(\frac{k_+ - k_-}{2}l\right) \end{bmatrix} \quad (6.19)$$

$$|E\rangle_{\text{bef}} = \frac{E_0 e^{i\phi_p}}{2} \begin{bmatrix} \sqrt{1 - P} e^{+i\theta_+} + \sqrt{1 + P} e^{-i\theta_-} \\ -i(\sqrt{1 - P} e^{+i\theta_-} - \sqrt{1 + P} e^{-i\theta_+}) \end{bmatrix} \quad (6.20)$$

We'll split this matrix into the following two parts:

$$\hat{M} = e^{i(k_+ + k_-)l/2} \left[\hat{M}_0 + 2 \sin^2\left(\frac{\Theta}{2}\right) \hat{M}_1 \right] \quad (6.21)$$

$$\hat{M}_0 = \begin{bmatrix} +\cos\left(\frac{k_+ - k_-}{2}l\right) & +\sin\left(\frac{k_+ - k_-}{2}l\right) \\ -\sin\left(\frac{k_+ - k_-}{2}l\right) & +\cos\left(\frac{k_+ - k_-}{2}l\right) \end{bmatrix} \quad (6.22)$$

$$\hat{M}_1 = \begin{bmatrix} 2 \left[e^{i(k_0 - \frac{k_+ + k_-}{2})l} - \cos\left(\frac{k_+ - k_-}{2}l\right) \right] \cos^2\left(\frac{\Theta}{2}\right) & -\sin\left(\frac{k_+ - k_-}{2}l\right) \\ +\sin\left(\frac{k_+ - k_-}{2}l\right) & 0 \end{bmatrix} \quad (6.23)$$

such that \hat{M}_1 drops away when $\Theta = 0$. Now we'll send the light through a half waveplate whose axis is at an angle ϕ_h :

$$\hat{W}_{\frac{1}{2}}\hat{M}_0 = i \begin{bmatrix} + \cos\left(\frac{k_+ - k_-}{2}l + 2\phi_h\right) & + \sin\left(\frac{k_+ - k_-}{2}l + 2\phi_h\right) \\ + \sin\left(\frac{k_+ - k_-}{2}l + 2\phi_h\right) & - \cos\left(\frac{k_+ - k_-}{2}l + 2\phi_h\right) \end{bmatrix} \quad (6.24)$$

$$\hat{W}_{\frac{1}{2}}\hat{M}_1 = i \begin{bmatrix} 2 \left[e^{i(k_0 - \frac{k_+ + k_-}{2})l} - \cos\left(\frac{k_+ - k_-}{2}l\right) \right] \cos^2\left(\frac{\Theta}{2}\right) \cos(2\phi_h) + \sin\left(\frac{k_+ - k_-}{2}l\right) \sin(2\phi_h) & - \sin\left(\frac{k_+ - k_-}{2}l\right) \cos(2\phi_h) \\ 2 \left[e^{i(k_0 - \frac{k_+ + k_-}{2})l} - \cos\left(\frac{k_+ - k_-}{2}l\right) \right] \cos^2\left(\frac{\Theta}{2}\right) \sin(2\phi_h) - \sin\left(\frac{k_+ - k_-}{2}l\right) \cos(2\phi_h) & - \sin\left(\frac{k_+ - k_-}{2}l\right) \sin(2\phi_h) \end{bmatrix} \quad (6.25)$$

The final polarization vector can be written as a sum of two parts:

$$|E\rangle_{\text{final}} = ie^{i(k_+ + k_-)l} \left[|E\rangle_{\text{ideal}} + 2 \sin^2\left(\frac{\Theta}{2}\right) \hat{M}_{\text{skew}} |E\rangle_{\text{bef}} \right] \quad (6.26)$$

$$|E\rangle_{\text{ideal}} = \frac{E_0 e^{i\phi_p}}{2} \begin{bmatrix} \sqrt{1 - P} e^{+i\theta} \left(\cos(\psi) e^{+i\frac{\beta}{2}} - i \sin(\psi) e^{-i\frac{\beta}{2}} \right) + \sqrt{1 + P} e^{-i\theta} \left(\cos(\psi) e^{+i\frac{\beta}{2}} + i \sin(\psi) e^{-i\frac{\beta}{2}} \right) \\ i \sqrt{1 - P} e^{+i\theta} \left(\cos(\psi) e^{-i\frac{\beta}{2}} - i \sin(\psi) e^{+i\frac{\beta}{2}} \right) - i \sqrt{1 + P} e^{-i\theta} \left(\cos(\psi) e^{-i\frac{\beta}{2}} + i \sin(\psi) e^{+i\frac{\beta}{2}} \right) \end{bmatrix} \quad (6.27)$$

$$\psi = (k_+ - k_-) \frac{l}{2} + 2\phi_h \quad (6.28)$$

$$\hat{M}_{\text{skew}} = \begin{bmatrix} 2 \left[e^{i(k_0 - \frac{k_+ + k_-}{2})l} - \cos\left(\frac{k_+ - k_-}{2}l\right) \right] \cos^2\left(\frac{\Theta}{2}\right) \cos(2\phi_h) + \sin\left(\frac{k_+ - k_-}{2}l\right) \sin(2\phi_h) & - \sin\left(\frac{k_+ - k_-}{2}l\right) \cos(2\phi_h) \\ 2 \left[e^{i(k_0 - \frac{k_+ + k_-}{2})l} - \cos\left(\frac{k_+ - k_-}{2}l\right) \right] \cos^2\left(\frac{\Theta}{2}\right) \sin(2\phi_h) - \sin\left(\frac{k_+ - k_-}{2}l\right) \cos(2\phi_h) & - \sin\left(\frac{k_+ - k_-}{2}l\right) \sin(2\phi_h) \end{bmatrix} \quad (6.29)$$

Note the following possible conditions:

1. If there is no atomic vapor, set $l = 0$.
2. If there is no PEM, set $\beta = 0$.
3. If there is no skewness or angle between the quantization axis of the atomic vapor and the direction of propagation of the light, set $\Theta = 0$.
4. A small skew angle effects the final polarization angle at second order $\sin^2(\Theta/2) \approx \Theta^2/4$.

Noting that ψ is complex, the intensities of the two components for the "ideal" case (skew angle is zero) are:

$$\zeta = \sqrt{\frac{\epsilon}{\mu}} \frac{E_0^2}{4} e^{-l\Im\{k_+ + k_-\}} \quad (6.30)$$

$$\frac{I_P}{\zeta} = |\cos(\psi)|^2 + |\sin(\psi)|^2 + iP \left(\cos(\psi^*) \sin(\psi) e^{-i\beta} - \cos(\psi) \sin(\psi^*) e^{+i\beta} \right) + \sqrt{1 - P^2} \times \Re \left\{ e^{+2i\theta} \left[|\cos(\psi)|^2 - |\sin(\psi)|^2 - i \cos(\psi^*) \sin(\psi) e^{-i\beta} - i \cos(\psi) \sin(\psi^*) e^{+i\beta} \right] \right\} \quad (6.31)$$

$$\frac{I_S}{\zeta} = |\cos(\psi)|^2 + |\sin(\psi)|^2 + iP \left(\cos(\psi^*) \sin(\psi) e^{+i\beta} - \cos(\psi) \sin(\psi^*) e^{-i\beta} \right) - \sqrt{1 - P^2} \times \Re \left\{ e^{+2i\theta} \left[|\cos(\psi)|^2 - |\sin(\psi)|^2 - i \cos(\psi^*) \sin(\psi) e^{+i\beta} - i \cos(\psi) \sin(\psi^*) e^{-i\beta} \right] \right\} \quad (6.32)$$

Using the following relations:

$$|\cos(\psi)|^2 = \cos(\psi) \cos(\psi^*) = \frac{1}{2} [\cosh(2\Im\psi) + \cos(2\Re\psi)] \quad (6.33)$$

$$|\sin(\psi)|^2 = \sin(\psi) \sin(\psi^*) = \frac{1}{2} [\cosh(2\Im\psi) - \cos(2\Re\psi)] \quad (6.34)$$

$$\sin(\psi) \cos(\psi^*) = \frac{1}{2} [+i \sinh(2\Im\psi) + \sin(2\Re\psi)] \quad (6.35)$$

$$\sin(\psi^*) \cos(\psi) = \frac{1}{2} [-i \sinh(2\Im\psi) + \sin(2\Re\psi)] \quad (6.36)$$

finally gives:

$$I_{\mathcal{P},\mathcal{S}} = \frac{I_\sigma \pm I_\delta}{2} \quad (6.37)$$

$$I_\sigma = 2\zeta \left[\cosh(2\Im\psi) + \sinh(2\Im\psi) \left(\sqrt{1-P^2} \sin(2\theta) \sin(\beta) - \cos(\beta) \right) \right] \quad (6.38)$$

$$I_\delta = 2\zeta \left[P \sin(\beta) \sin(2\Re\psi) + \sqrt{1-P^2} (\cos(2\theta) \cos(2\Re\psi) + \sin(2\theta) \sin(2\Re\psi) \cos(\beta)) \right] \quad (6.39)$$

Using the following expansions for the β terms:

$$\beta(t) = \beta_0 \cos(\Omega_{\text{mod}} t) \quad (6.40)$$

$$\sin(\beta_0 \cos(\Omega_{\text{mod}} t)) = 2J_1(\beta_0) \cos(\Omega_{\text{mod}} t) - \dots \quad (6.41)$$

$$\cos(\beta_0 \cos(\Omega_{\text{mod}} t)) = J_0(\beta_0) - 2J_2(\beta_0) \cos(2\Omega_{\text{mod}} t) + \dots \quad (6.42)$$

we can extract the DC, the RMS AC1, and the RMS AC2 components of the sum (σ) and difference (δ) signals:

$$I_\sigma(\text{DC}) = 2\zeta [\cosh(2\Im\psi) - J_0(\beta_0) \sinh(2\Im\psi)] \quad (6.43)$$

$$I_\sigma(\text{AC1}) = 2\zeta \sqrt{2} J_1(\beta_0) \sinh(2\Im\psi) \sqrt{1-P^2} \sin(2\theta) \quad (6.44)$$

$$I_\sigma(\text{AC2}) = 2\zeta \sqrt{2} J_2(\beta_0) \sinh(2\Im\psi) \quad (6.45)$$

$$I_\delta(\text{DC}) = 2\zeta \sqrt{1-P^2} [\cos(2\theta) \cos(2\Re\psi) + J_0(\beta_0) \sin(2\theta) \sin(2\Re\psi)] \quad (6.46)$$

$$I_\delta(\text{AC1}) = 2\zeta \sqrt{2} J_1(\beta_0) P \sin(2\Re\psi) \quad (6.47)$$

$$I_\delta(\text{AC2}) = 2\zeta \sqrt{2} J_2(\beta_0) \sqrt{1-P^2} \sin(2\theta) \sin(2\Re\psi) \quad (6.48)$$

$$2\zeta = \sqrt{\frac{\epsilon}{\mu} \frac{E_0^2}{2}} e^{-l\Im\{k_+ + k_-\}} \quad (6.49)$$

$$\psi = (k_+ - k_-) \frac{l}{2} + 2\phi_h \quad (6.50)$$

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
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

For the case where there is no atomic vapor ($l = 0$):

$$I_\sigma(\text{DC}) = \sqrt{\frac{\epsilon}{\mu} \frac{E_0^2}{2}} \quad (6.51)$$

$$I_\sigma(\text{AC1}) = 0 \quad (6.52)$$

$$I_\sigma(\text{AC2}) = 0 \quad (6.53)$$

$$I_\delta(\text{DC}) = I_\sigma(\text{DC}) \sqrt{1-P^2} [\cos(2\theta) \cos(4\phi_h) + J_0(\beta_0) \sin(2\theta) \sin(4\phi_h)] \quad (6.54)$$

$$I_\delta(\text{AC1}) = I_\sigma(\text{DC}) \sqrt{2} J_1(\beta_0) P \sin(4\phi_h) \quad (6.55)$$

$$I_\delta(\text{AC2}) = I_\sigma(\text{DC}) \sqrt{2} J_2(\beta_0) \sqrt{1-P^2} \sin(2\theta) \sin(4\phi_h) \quad (6.56)$$

- 6.2 Measuring Alkali Number Density with Alkali Polarization
= 0
- 6.3 Measuring Alkali Number Density with Alkali Polarization
 $\neq 0$
- 6.4 Measuring ^3He Density
- 6.5 Measuring ^3He Polarization using EPR

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
\hbar	$6.626\,069 \times 10^{-34}$	$\text{J} \cdot \text{s}$	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).

Element	Ground State	$S_{1/2}$ g_J/g_S	$P_{1/2}$ g_J	$P_{3/2}$ g_J	$\nu_{so}(\text{GHz})$	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.3: 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				
${}^6\text{Li}$	6.015 122 3	0.075 9	1	+0.822 056	+0.822 056
${}^7\text{Li}$	7.016 004 0	0.924 1	3/2	+3.256 44	+2.170 96
Sodium	22.989 770				
${}^{23}\text{Na}$	22.989 769 7	1.0	3/2	+2.217 52	+1.478 35
Potassium	39.098 3				
${}^{39}\text{K}$	38.963 706 9	0.932 58	3/2	+0.391 46	+0.260 97
${}^{40}\text{K}$	39.963 998 7	0.000 117	4	-1.298	-0.324 5
${}^{41}\text{K}$	40.961 826 0	0.067 30	3/2	+0.214 87	+0.143 25
Rubidium	85.467 8				
${}^{85}\text{Rb}$	84.911 789	0.721 7	5/2	+1.353 02	+0.541 208
${}^{87}\text{Rb}$	86.909 184	0.278 3	3/2	+2.751 2	+1.834 1
Cesium	132.905 45				
${}^{133}\text{Cs}$	132.905 447	1.0	7/2	+2.579	+0.736 9
Reference	NIST _d		NIST _e		(1.5)

Table A.4: 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	(1.207)	(1.209)	"	"	"	AIV ₇₇	

Table A.5: Alkali atom ground State and first excited states hyperfine structure.

Appendix B

Irreducible Spherical Vector Basis

In the rectangular basis, a vector is decomposed in the following way:

$$\vec{r} = \sum_{q=1}^3 r_q \hat{\varepsilon}_q \quad (\text{B.1})$$

where 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:

$$\hat{\varepsilon}_p \cdot \hat{\varepsilon}_q = \delta_p^q \quad (\text{B.6})$$

which immediately implies the dot product between two vectors and the modulus square of a vector:

$$\vec{r} \cdot \vec{s} = \sum_{p,q=1}^3 r_p s_q \hat{\varepsilon}_p \cdot \hat{\varepsilon}_q \quad (\text{B.7})$$

$$= \sum_{p,q=1}^3 r_p s_q \delta_p^q \quad (\text{B.8})$$

$$= \sum_{q=1}^3 r_q s_q \quad (\text{B.9})$$

$$|\vec{r}|^2 = \vec{r}^* \cdot \vec{r} \quad (\text{B.10})$$

$$= \sum_{q=1}^3 r_q^* r_q \quad (\text{B.11})$$

$$= x^2 + y^2 + z^2 \quad (\text{B.12})$$

The vector, all dot products, and the modulus squared are all real.

Alternatively, the same vector can be expanded in the spherical basis (Rose, M.E. Elementary Theory of Angular Momentum. New York: John Wiley, 1957. page 105, equation (5.56)): In the rectangular basis, a vector is decomposed in the following way:

$$\vec{r} = \sum_{q=-1}^{+1} (-1)^q r_q \hat{\varepsilon}_{-q} \quad (\text{B.13})$$

where the components r_q and unit vectors ε_q are in general complex and have the following interpretations:

$$r_q^* = (-1)^q r_{-q} \leftrightarrow \hat{\varepsilon}_q^* = (-1)^q \hat{\varepsilon}_{-q} \quad (\text{B.14})$$

$$r_{-1} = -r_{+1}^* = + \left(\frac{x - iy}{\sqrt{2}} \right) \leftrightarrow \hat{\varepsilon}_{-1} = -\hat{\varepsilon}_{+1}^* = + \left(\frac{\hat{x} - i\hat{y}}{\sqrt{2}} \right) \quad (\text{B.15})$$

$$r_0 = r_0^* = z \leftrightarrow \hat{\varepsilon}_0 = \hat{\varepsilon}_0^* = \hat{z} \quad (\text{B.16})$$

$$r_{+1} = -r_{-1}^* = - \left(\frac{x + iy}{\sqrt{2}} \right) \leftrightarrow \hat{\varepsilon}_{+1} = -\hat{\varepsilon}_{-1}^* = - \left(\frac{\hat{x} + i\hat{y}}{\sqrt{2}} \right) \quad (\text{B.17})$$

Orthogonality of the unit vectors is defined the following way:

$$\hat{\varepsilon}_p \cdot \hat{\varepsilon}_q = (-1)^q \delta_p^{-q} \quad (\text{B.18})$$

$$\hat{\varepsilon}_p^* \cdot \hat{\varepsilon}_q = \delta_p^q \quad (\text{B.19})$$

which immediately implies the dot product between two vectors and the modulus square of a vector:

$$\vec{r} \cdot \vec{s} = \sum_{p,q=1}^3 (-1)^{p+q} r_p s_q \hat{\varepsilon}_{-p} \cdot \hat{\varepsilon}_{-q} \quad (\text{B.20})$$

$$= \sum_{p,q=1}^3 (-1)^{p+q-q} r_p s_q \delta_{-p}^q \quad (\text{B.21})$$

$$= \sum_{q=1}^3 (-1)^q r_{-q} s_q \quad (\text{B.22})$$

$$|\vec{r}|^2 = \vec{r}^* \cdot \vec{r} = \sum_{p,q=1}^3 (-1)^{p+q} r_p^* r_q \hat{\varepsilon}_{-p} \cdot \hat{\varepsilon}_{-q} \quad (\text{B.23})$$

$$= \sum_{p,q=1}^3 (-1)^{p+q} r_p^* r_q \delta_{-p}^{-q} \quad (\text{B.24})$$

$$= \sum_{p,q=1}^3 (-1)^{2q} r_q^* r_q \quad (\text{B.25})$$

$$= \sum_{p,q=1}^3 (-1)^q r_{-q} r_q \quad (\text{B.26})$$

$$= r_0^2 - 2r_{-1}r_{+1} \quad (\text{B.27})$$

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

Expansion of Zero Field Eigenbasis

C.1 Clebsch-Gordon Coefficient Formulas

Adapted from equation (17.27) in [Wigner, Eugene, P. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. New York: Academic Press, 1959.] into equation 14³(5) in [Condon, E. U. and G.H. Shortley. *The Theory of Atomic Spectra*. London: CUP, 1967.]:

$$\begin{aligned} \langle (J_1, J_2) m_1, m_2 | J, m \rangle &= \sqrt{\frac{(J + J_1 - J_2)! (J - J_1 + J_2)! (J_1 + J_2 - J)! (J + m)! (J - m)! (2J + 1)}{(J + J_1 + J_2 + 1)! (J_1 - m_1)! (J_1 + m_1)! (J_2 - m_2)! (J_2 + m_2)!}} \\ &\times \delta_m^{(m_1 + m_2)} \sum_{\kappa = \kappa_1}^{\kappa_2} \frac{(-1)^{\kappa + J_2 + m_2} (J + J_2 + m_1 - \kappa)! (J_1 - m_1 + \kappa)!}{(J - J_1 + J_2 - \kappa)! (J + m - \kappa)! \kappa! (\kappa + J_1 - J_2 - m)!} \end{aligned} \quad (\text{C.1})$$

$$\kappa_a = \max [0, J_2 - J_1 + m] \quad (\text{C.2})$$

$$\kappa_b = \min [J + m, J_2 - J_1 + J] \quad (\text{C.3})$$

$$\kappa_1 = \min [\kappa_a, \kappa_b] \quad (\text{C.4})$$

$$\kappa_2 = \max [\kappa_a, \kappa_b] \quad (\text{C.5})$$

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.1.1 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.1.2 For the case $\vec{J}_1 + \vec{1}$

With $m = m_1 \pm 1$:

$$\begin{aligned} \langle (J_1, 1), m_1, \pm 1 | J_1 + 1, m_1 \pm 1 \rangle &= \langle (J - 1, 1), m \mp 1, \pm 1 | J, m \rangle \\ &= \sqrt{\frac{(J_1 \pm m)(J_1 \pm m + 1)}{2[J_1](J_1 + 1)}} \end{aligned} \quad (\text{C.11})$$

$$= \sqrt{\frac{(J_1 \pm m_1 + 1)(J_1 \pm m_1 + 2)}{2[J_1](J_1 + 1)}} \quad (\text{C.12})$$

$$= \sqrt{\frac{(J \pm m - 1)(J \pm m)}{2J(2J - 1)}} \quad (\text{C.13})$$

$$\begin{aligned} \langle (J_1, 1), m_1, \pm 1 | J_1, m_1 \pm 1 \rangle &= \langle (J, 1), m \mp 1, \pm 1 | J, m \rangle \\ &= \mp \sqrt{\frac{(J_1 \pm m)(J_1 \mp m + 1)}{2J_1(J_1 + 1)}} \end{aligned} \quad (\text{C.14})$$

$$= \mp \sqrt{\frac{(J_1 \pm m_1 + 1)(J_1 \mp m_1)}{2J_1(J_1 + 1)}} \quad (\text{C.15})$$

$$= \mp \sqrt{\frac{(J \pm m)(J \mp m + 1)}{2J(J + 1)}} \quad (\text{C.16})$$

$$\begin{aligned} \langle (J_1, 1), m_1, \pm 1 | J_1 - 1, m_1 \pm 1 \rangle &= \langle (J + 1, 1), m \mp 1, \pm 1 | J, m \rangle \\ &= \sqrt{\frac{(J_1 \mp m)(J_1 \mp m + 1)}{2J_1[J_1]}} \end{aligned} \quad (\text{C.17})$$

$$= \sqrt{\frac{(J_1 \mp m_1 - 1)(J_1 \mp m_1)}{2J_1[J_1]}} \quad (\text{C.18})$$

$$= \sqrt{\frac{(J \mp m + 1)(J \mp m + 2)}{2(J + 1)(2J + 3)}} \quad (\text{C.19})$$

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.1.3 For the case $\vec{J}_1 + \frac{3}{2}$

With $m = m_1 \pm \frac{3}{2}$:

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{3}{2} \middle| J_1 + \frac{3}{2}, m_1 \pm \frac{3}{2} \right\rangle &= \left\langle \left(J - \frac{3}{2}, \frac{3}{2} \right), m \mp \frac{3}{2}, \pm \frac{3}{2} \middle| J, m \right\rangle \\ &= \sqrt{\frac{(J_1 \pm m - \frac{1}{2})(J_1 \pm m + \frac{1}{2})(J_1 \pm m + \frac{3}{2})}{2[J_1](J_1 + 1)(2J_1 + 3)}} \end{aligned} \quad (\text{C.24})$$

$$= \sqrt{\frac{(J_1 \pm m_1 + 1)(J_1 \pm m_1 + 2)(J_1 \pm m_1 + 3)}{2[J_1](J_1 + 1)(2J_1 + 3)}} \quad (\text{C.25})$$

$$= \sqrt{\frac{(J \pm m - 2)(J \pm m - 1)(J \pm m)}{4J(J - 1)(2J - 1)}} \quad (\text{C.26})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{3}{2} \middle| J_1 + \frac{1}{2}, m_1 \pm \frac{3}{2} \right\rangle &= \left\langle \left(J - \frac{1}{2}, \frac{3}{2} \right), m \mp \frac{3}{2}, \pm \frac{3}{2} \middle| J, m \right\rangle \\ &= \mp \sqrt{\frac{3(J_1 \pm m - \frac{1}{2})(J_1 \pm m + \frac{1}{2})(J_1 \mp m + \frac{3}{2})}{2J_1[J_1](2J_1 + 3)}} \end{aligned} \quad (\text{C.27})$$

$$= \mp \sqrt{\frac{3(J_1 \pm m_1 + 1)(J_1 \pm m_1 + 2)(J_1 \mp m_1)}{2J_1[J_1](2J_1 + 3)}} \quad (\text{C.28})$$

$$= \mp \sqrt{\frac{3(J \pm m - 1)(J \pm m)(J \mp m + 1)}{4J(2J - 1)(J + 1)}} \quad (\text{C.29})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{3}{2} \middle| J_1 - \frac{1}{2}, m_1 \pm \frac{3}{2} \right\rangle &= \left\langle \left(J + \frac{1}{2}, \frac{3}{2} \right), m \mp \frac{3}{2}, \pm \frac{3}{2} \middle| J, m \right\rangle \\ &= \sqrt{\frac{3(J_1 \pm m - \frac{1}{2})(J_1 \mp m + \frac{1}{2})(J_1 \mp m + \frac{3}{2})}{2[J_1](J_1 + 1)(2J_1 - 1)}} \end{aligned} \quad (\text{C.30})$$

$$= \sqrt{\frac{3(J_1 \pm m_1 + 1)(J_1 \mp m_1 - 1)(J_1 \mp m_1)}{2[J_1](J_1 + 1)(2J_1 - 1)}} \quad (\text{C.31})$$

$$= \sqrt{\frac{3(J \pm m)(J \mp m + 1)(J \mp m + 2)}{4J(J + 1)(2J + 3)}} \quad (\text{C.32})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{3}{2} \middle| J_1 - \frac{3}{2}, m_1 \pm \frac{3}{2} \right\rangle &= \left\langle \left(J + \frac{3}{2}, \frac{3}{2} \right), m \mp \frac{3}{2}, \pm \frac{3}{2} \middle| J, m \right\rangle \\ &= \mp \sqrt{\frac{(J_1 \mp m - \frac{1}{2})(J_1 \mp m + \frac{1}{2})(J_1 \mp m + \frac{3}{2})}{2J_1[J_1](2J_1 - 1)}} \end{aligned} \quad (\text{C.33})$$

$$= \mp \sqrt{\frac{(J_1 \mp m_1 - 2)(J_1 \mp m_1 - 1)(J_1 \mp m_1)}{2J_1[J_1](2J_1 - 1)}} \quad (\text{C.34})$$

$$= \mp \sqrt{\frac{(J \mp m + 1)(J \mp m + 2)(J \mp m + 3)}{4(2J + 3)(J + 2)(J + 1)}} \quad (\text{C.35})$$

With $m = m_1 \pm \frac{1}{2}$:

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 + \frac{3}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J - \frac{3}{2}, \frac{3}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= \sqrt{\frac{3 \left(J_1 \pm m + \frac{1}{2} \right) \left(J_1 + m + \frac{3}{2} \right) \left(J_1 - m + \frac{3}{2} \right)}{2[J_1] (J_1 + 1) (2J_1 + 3)}} \end{aligned} \quad (\text{C.36})$$

$$= \sqrt{\frac{3 \left(J_1 \pm m_1 + 1 \right) \left(J_1 + m_1 + \frac{3 \pm 1}{2} \right) \left(J_1 - m_1 + \frac{3 \mp 1}{2} \right)}{2[J_1] (J_1 + 1) (2J_1 + 3)}} \quad (\text{C.37})$$

$$= \sqrt{\frac{3 (J \pm m - 1) (J + m) (J - m)}{4J (J - 1) (2J - 1)}} \quad (\text{C.38})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 + \frac{1}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J - \frac{1}{2}, \frac{3}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= \mp \left(J_1 \mp 3m + \frac{3}{2} \right) \sqrt{\frac{J_1 \pm m + \frac{1}{2}}{2J_1[J_1] (2J_1 + 3)}} \end{aligned} \quad (\text{C.39})$$

$$= \mp (J_1 \mp 3m_1) \sqrt{\frac{J_1 \pm m_1 + 1}{2J_1[J_1] (2J_1 + 3)}} \quad (\text{C.40})$$

$$= \mp (J \mp 3m + 1) \sqrt{\frac{J \pm m}{4J (2J - 1) (J + 1)}} \quad (\text{C.41})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 - \frac{1}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J + \frac{1}{2}, \frac{3}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= - \left(J_1 \pm 3m - \frac{1}{2} \right) \sqrt{\frac{J_1 \mp m + \frac{1}{2}}{2[J_1] (J_1 + 1) (2J_1 - 1)}} \end{aligned} \quad (\text{C.42})$$

$$= - (J_1 \pm 3m_1 + 1) \sqrt{\frac{J_1 \mp m_1}{2[J_1] (J_1 + 1) (2J_1 - 1)}} \quad (\text{C.43})$$

$$= - (J \pm 3m) \sqrt{\frac{J \mp m + 1}{4J (J + 1) (2J + 3)}} \quad (\text{C.44})$$

$$\begin{aligned} \left\langle \left(J_1, \frac{3}{2} \right), m_1, \pm \frac{1}{2} \middle| J_1 - \frac{3}{2}, m_1 \pm \frac{1}{2} \right\rangle &= \left\langle \left(J + \frac{3}{2}, \frac{3}{2} \right), m \mp \frac{1}{2}, \pm \frac{1}{2} \middle| J, m \right\rangle \\ &= \pm \sqrt{\frac{3 \left(J_1 + m - \frac{1}{2} \right) \left(J_1 - m - \frac{1}{2} \right) \left(J_1 \mp m + \frac{1}{2} \right)}{2J_1[J_1] (2J_1 - 1)}} \end{aligned} \quad (\text{C.45})$$

$$= \pm \sqrt{\frac{3 \left(J_1 + m_1 - \frac{1 \mp 1}{2} \right) \left(J_1 - m_1 - \frac{1 \pm 1}{2} \right) \left(J_1 \mp m_1 \right)}{2J_1[J_1] (2J_1 - 1)}} \quad (\text{C.46})$$

$$= \pm \sqrt{\frac{3 (J + m + 1) (J - m + 1) (J \mp m + 2)}{4 (2J + 3) (J + 2) (J + 1)}} \quad (\text{C.47})$$

C.2 Without Nuclear Spin $I = 0$

$$\left| S_{\frac{1}{2}}, \frac{1}{2}, +\frac{1}{2} \right\rangle = \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.48})$$

$$\left| S_{\frac{1}{2}}, \frac{1}{2}, -\frac{1}{2} \right\rangle = \left| -\frac{1}{2} \right\rangle_S \quad (\text{C.49})$$

$$\left| P_{\frac{1}{2}}, \frac{1}{2}, +\frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} | +1 \rangle_L \left| -\frac{1}{2} \right\rangle_S - \sqrt{\frac{1}{3}} | 0 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.50})$$

$$\left| P_{\frac{1}{2}}, \frac{1}{2}, -\frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} | 0 \rangle_L \left| -\frac{1}{2} \right\rangle_S - \sqrt{\frac{2}{3}} | -1 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.51})$$

$$\left| P_{\frac{3}{2}}, \frac{3}{2}, +\frac{3}{2} \right\rangle = | +1 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.52})$$

$$\left| P_{\frac{3}{2}}, \frac{3}{2}, +\frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} | +1 \rangle_L \left| -\frac{1}{2} \right\rangle_S + \sqrt{\frac{2}{3}} | 0 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.53})$$

$$\left| P_{\frac{3}{2}}, \frac{3}{2}, -\frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} | 0 \rangle_L \left| -\frac{1}{2} \right\rangle_S + \sqrt{\frac{1}{3}} | -1 \rangle_L \left| +\frac{1}{2} \right\rangle_S \quad (\text{C.54})$$

$$\left| P_{\frac{3}{2}}, \frac{3}{2}, -\frac{3}{2} \right\rangle = | -1 \rangle_L \left| -\frac{1}{2} \right\rangle_S \quad (\text{C.55})$$