# Some notes on $^3$He polarimetry using alkali EPR

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### Abstract

It is sometimes profitable to measure the longitudinal nuclear spin polarization of $^3$He. The method described here takes advantage of the vaporized alkali metal already present in a glass target cell. Long range and short range interactions with polarized $^3$He gas result in an "effective" magnetic field felt by the alkali metal atoms. A precisely detectable Zeeman shift in the alkali EPR frequency that is proportional to the $^3$He polarization and density is produced. The EPR frequency is located by exciting the EPR transition and observing the resulting change in the D2 fluorescence. A PI feedback loop is used to lock to the EPR frequency while the direction of the $^3$He spins is reversed via AFP with respect to any baseline magnetic fields. This isolates the $^3$He contribution to the EPR frequency and consequently the $^3$He polarization can be extracted.

# Contents

# 1  Introduction

It is appropriate and obligatory to list the following references in chronological order in which this technique was developed, refined, and "calibrated:"

1. **Effects of rapid spin exchange on the magnetic-resonance spectrum of alkali vapors**
   by W. Happer and A.C. Tam
   *Phys. Rev. A. 16, 1877-1891 (1977)*

2. **Frequency shifts of the magnetic-resonance spectrum of mixtures of nuclear spin-polarized noble gases and vapors of spin-polarized alkali-metal atoms**
   by S. R. Schaefer, G. D. Cates, Ting-Ray Chien, D. Gonatas, W. Happer, and T. G. Walker
   *Phys. Rev. A 39, 56135623 (1989)*

3. **Determination of spin-exchange parameters between optically pumped rubidium and 83Kr**
   by S. R. Schaefer, G. D. Cates, and W. Happer
   *Phys. Rev. A 41, 60636070 (1990)*

4. **Polarization-dependent frequency shifts from Rb-3He collisions**
   by N. R. Newbury, A. S. Barton, P. Bogorad, G. D. Cates, M. Gatzke, H. Mabuchi, and B. Saam
   *Phys. Rev. A 48, 558568 (1993)*

5. **Self-calibrating measurement of polarization-dependent frequency shifts from Rb-3He collisions**
   by A. S. Barton, N. R. Newbury, G. D. Cates, B. Driehuys, H. Middleton, and B. Saam
   *Phys. Rev. A 49, 27662770 (1994)*

6. **Accurate 3He polarimetry using the Rb Zeeman frequency shift due to the Rb-3He spin-exchange collisions**
   by M. V. Romalis and G. D. Cates
   *Phys. Rev. A 58, 30043011 (1998)*

7. **3He polarization-dependent EPR frequency shifts of alkali-metal3He pairs**
   by E. Babcock, I. A. Nelson, S. Kadlecek, T. G. Walker
   *Phys. Rev. A 71, 013414 (2005)*

This document is at best a poor synthesis of the ideas and techniques presented in the aforementioned references and any/all errors and/or mischaracterizations are due solely to the author.

At "low" field, the Zeeman splitting among the hyperfine states of an alkali metal is approximately linear in field. "Low" field is judged by the strength of the Zeeman interaction relative to the hyperfine interaction. For $^{39}$K and $^{85}$Rb, low field therefore is defined to be much less than 165 gauss and 1080 gauss respectively. An approximately linear energy splitting results in transition frequencies that are also approximately linear in field. Traditionally, the target cells are located in a magnetic holding field that is on the order of 10's of gauss. The holding field is produced from an external source such as an electromagnet.

The alkali metal atoms experience a small additional "effective" field due to the presence of polarized $^3$He gas. Under typical operating conditions, about 1/6 of this "effective" field is due to the classical magnetic field produced by the bulk magnetization of the polarized $^3$He gas. The rest of the "effective" field comes from the very short but frequent spin-exchange collisions that occur between the alkali metal atoms and the $^3$He atoms. During these spin-exchange collisions, the alkali valence electron is essentially located within the $^3$He nucleus thus facilitating a hyperfine-like Fermi contact interaction between their spins. These two sources of an additional "effective" field are distinguised in at least three important ways:

1. The size of the classical magnetic field is dependant on the geometry of the target cell; whereas the spin-exchange "effective" field is not.

2. The size of the classical magnetic field is independant of the alkali metal being perturbed; whereas the size of the spin-exchange "effective" field *does* depend on the alkali metal.

3. The classical magnetic field can be, in principle, detected by a sufficiently sensitive external magnetic field probe; whereas the spin-exchange "effective" field can not be.

Because the spin-exchange "effective" field is difficult to calculate precisely from theory, it is usually clumped together with the classical magnetic field and parameterized by a unitless temperature dependant quantity called $\kappa_0$, which must be measured empirically.

The "effective" field produced by the $^3$He is on the order of 10's of milligauss, which causes a frequency shift on the order of 10's of kHz. The EPR transition is probed by sending a frequency modulated excitation into a coil located near the pumping chamber of the target cell. This excitation induces EPR transitions in the alkali metal atoms and therefore depolarizes them. Because of the rapid and efficient spin-exchange between alkali metal atoms, the equilibrium polarization of a volume of alkali vapor near the EPR excitation coil tracks the frequency modulation of the excitation. When the excitation is off resonance, the alkali polarization is high. When the excitation is on resonance, the alkali polarization is lowered. This results in a modulation of the alkali polarization which in turn results in a modulation of the absorption of the incident pump laser light by the alkali vapor.

The modulation of the absorption can be monitored indirectly be observing the size of the fluorescence emitted by the excited alkali atoms as they decay back to the ground state. Although the presence of $N_2$ molecules greatly suppresses the number of radiative decays, a few percent of the transitions back to the ground state still occur radiatively. The amount of D1 and D2 fluorescence is essentially the same because of collisional mixing of the excited states. However, a filter is placed in front of a photodiode to allow

transmission of only the D2 fluorescence. This is because the large D1 background from the pump laser light could potentially saturate the photodiode.

Therefore, the signal detected in the photodiode consists mainly of D2 fluorescence. A strong DC component is present due to the D2 light reaching the photodiode from parts of the cell that are minimally effected by the EPR excitation coil and due to the fact that the EPR excitation is very small and therefore the alkali polarization is not changing much. More important is the AC component that is at the modulation frequency of the EPR excitation coil. A lock-in amplifier is used to detect this small AC signal. Because of the frequency modulation of the EPR excitation, the lineshape that is produced when the lock-in response is plotted against the central frequency of the EPR excitation is the derivative of a lorentzian-like lineshape.

This "FM sweep" lineshape directly determines the behaviour of the feedback loop used to lock to the EPR transition. Modulation and lock-in parameters must be adjusted to produce an optimal "FM sweep" lineshape. The gains of the PI feedback box are then chosen based on the "feedback slope" extracted from the "FM sweep" lineshape. The "feedback slope" is typically in units of $\mu$V per kHz and provides a conversion between the central excitation frequency detuning from EPR frequency and the voltage response of the excitation/sensing electronics. The analog voltage signal from the lock-in is then processed by a PI feedback box and converted into a frequency correction that is applied to the central frequency of the VCO that is generating the EPR excitation.

Once the EPR frequency is locked to by the excitation/sensing electronics, the excitation frequency is recorded by a counter as a function of time. The $^3$He spins are then flipped twice relative to the holding field using NMR frequency sweep AFP. Enough counter data is taken with the $^3$He in either state to result in a high presicion determination of the EPR frequencies of the alkali atoms. The difference in these EPR frequencies is, to first order, proportional to the "effective" field and therefore polarization of the $^3$He.

In the following sections, we will derive the energies and frequencies of the EPR spectrum, attempt to explain the qualiltative features of the FM sweep lineshape, give some guidance on how to obtain the "correct" PI feedback gain parameters, and finally discuss how to extract the $^3$He polarization.

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

## 2.1 Notation & Conventions

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

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

$$\hat{J}_z |J, m_J\rangle = m_J |J, m_J\rangle, m_J = -J..J \tag{2}$$

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \tag{3}$$

$$\hat{J}_\pm |J, m_J\rangle = \sqrt{J(J+1) - m_J(m_J \pm 1)} |J, m_J \pm 1\rangle \tag{4}$$

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

$$\vec{\mu}_S = \frac{\mu_S}{S}\vec{S} \tag{5}$$

$$\frac{\mu_S}{S} = g_S\mu_x \tag{6}$$

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

$$\vec{\mu}_L = \mu_L\vec{L} \tag{7}$$

$$\mu_L = g_L\mu_x \tag{8}$$

$g$ is the unitless Landé factor. Note that the sign of the magnetic moment is carried implicitly in $g$ or alternatively $\mu_J$. 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:

$$-\frac{3}{2}g_S = 3 \underbrace{\left[\frac{-2}{g_S}\right]}_{\approx 1.00116} \approx 3 \tag{9}$$

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, subsection 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 $\mu_x$, which is the Bohr magneton ($\mu_B$) for the electron and the nuclear magneton ($\mu_N$) for nuclei. The different angular momenta will be indentified 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,

- $\vec{J}\left(=\vec{L}+\vec{S}\right)$ is the total electronic angular momentum of the atom,

- $\vec{I}$ is the spin of the nucleus,

- $\vec{F}\left(=\vec{I}+\vec{J}\right)$ 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 $\nu$ (with units of Hz), and angular frequencies $\omega$ (with units of rad·Hz).

## 2.2  A Single Atom in a magnetic field neglecting Nuclear Spin

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:

$$\mathcal{H}_0 = \mathcal{H}_{es} + \mathcal{H}_{so} \tag{10}$$

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

$$\vec{J}^2 \;=\; (\vec{L} + \vec{S})^2 = \vec{L}^2 + 2\vec{L}\cdot\vec{S} + \vec{S}^2 \tag{11}$$

$$\mathcal{H}_{so} \;=\; A_{so}\vec{L}\cdot\vec{S} = \frac{A_{so}}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \tag{12}$$

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

$$n^{2S+1}L_J \tag{13}$$

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

$$\vec{L}_{shell} = \vec{S}_{shell} = 0 \tag{14}$$

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 $n^2P_{\frac{3}{2}}$.

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. Since we're only interested in the ground state RS term for EPR, we'll cut short this discussion of fine structure.

## 2.3 A Single Free Atom with Nuclear Spin in a Magnetic Field

### 2.3.1 Zero Field Eigenbasis

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

$$\mathcal{H}_{hfs} = A_{hfs}\vec{I}\cdot\vec{J} \tag{15}$$

$A_{hfs}$ 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:

$$\vec{F}^2 = (\vec{I} + \vec{J})^2 = \vec{I}^2 + 2\vec{I}\cdot\vec{J} + \vec{J}^2 \tag{16}$$

$$\mathcal{H}_{hfs} = \frac{A_{hfs}}{2}(\vec{F}^2 - \vec{I}^2 - \vec{J}^2) \tag{17}$$

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*. Table (1) depicts the analogy between spin-orbit coupling and the hyperfine interaction.

| 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 |
| $B_{so} \approx 10^7$ gauss | $B_{hf} \approx 10^3$ gauss |

Table 1: Analogy between spin-orbit and hyperfine coupling.

### 2.3.2 Hamiltonian

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

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{hfs} - \vec{\mu}_I \cdot \vec{B} - \vec{\mu}_J \cdot \vec{B} \tag{18}$$

To recap:

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

- The second term is the hyperfine interaction.

- The third and fourth terms are the Zeeman terms for the nuclear spin and the total electronic angular momentum respectively.

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

$$\mathcal{H} = \mathcal{H}_0 + \left( -\frac{A_{hfs}}{2}\left(\vec{I}^2 + \vec{J}^2\right) - g_I\mu_N B F_z \right) + \left( \frac{A_{hfs}}{2}\vec{F}^2 + \left(g_I\mu_N - g_J\mu_B\right)BJ_z \right) \tag{19}$$

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

## 2.4 Energies

### 2.4.1 Derivation of the Breit-Rabi Equation

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 $m_F = \pm F_{max} = \pm\left(I + \frac{1}{2}\right)$, 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 $\mathcal{H}'$,

$$\mathcal{H}' = \frac{A_{hfs}}{2}\vec{F}^2 + \left(g_I\mu_N - g_S\mu_B\right)BJ_z \tag{20}$$

$$\hat{\mathcal{H}}' = \frac{A_{hfs}}{2}\begin{bmatrix} \left(I + \frac{1}{2}\right)\left(I + \frac{3}{2}\right) & 0 \\ 0 & \left(I - \frac{1}{2}\right)\left(I + \frac{1}{2}\right) \end{bmatrix} + \left(g_I\mu_N - g_S\mu_S\right)B\begin{bmatrix} \alpha_+ & \beta_- \\ \beta_+ & \alpha_- \end{bmatrix} \tag{21}$$

$$\alpha_\pm = \left\langle I \pm \frac{1}{2}, m_F \middle| \hat{J}_z \middle| I \pm \frac{1}{2}, m_F \right\rangle \tag{22}$$

$$\beta_\pm = \left\langle I \mp \frac{1}{2}, m_F \middle| \hat{J}_z \middle| I \pm \frac{1}{2}, m_F \right\rangle \tag{23}$$

The first term can be simplified to give:

$$\frac{A_{hfs}}{2}\hat{\vec{F}}^2 = \frac{A_{hfs}}{2}\left(I+\frac{1}{2}\right)\left(I+\frac{1}{2}+\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\right) \tag{24}$$

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

$$|I,m_I\rangle\,|J,m_J\rangle \;=\; |m_I,m_J\rangle \tag{25}$$

$$|F,m_F\rangle \;=\; \sum |m_I,m_J\rangle \underbrace{\langle m_I,m_J|F,m_F\rangle}_{\text{Clebsch-Gordon}} \tag{26}$$

Using the formulas for Clebsch-Gordon coefficients (refer to appendix):

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

$$\tag{27}$$

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

which gives:

$$\alpha_\pm = \pm(\alpha) \;=\; \pm\left(\frac{m_F}{[I]}\right) \tag{28}$$

$$\beta_\pm = -(\beta) \;=\; -\left(\frac{\sqrt{\left(I+\frac{1}{2}\right)^2 - m_F^2}}{[I]}\right) \tag{29}$$

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

$$\mathcal{H}' \;=\; \frac{A_{hfs}}{2}\left(I+\frac{1}{2}\right)^2 + \frac{A_{hfs}}{2}\left(I+\frac{1}{2}\right)\begin{bmatrix} 1+2\alpha x & -2\beta x \\ -2\beta x & -(1+2\alpha x) \end{bmatrix} \tag{30}$$

$$x \;=\; (g_I\mu_N - g_S\mu_B)\frac{2B}{A[I]} \tag{31}$$

This is done by solving the secular equation:

$$0 \;=\; \det\left(\hat{M} - \hat{I}\lambda\right) \tag{32}$$

$$0 \;=\; \begin{vmatrix} 1+2\alpha x - \lambda & -2\beta x \\ -2\beta x & -(1+2\alpha x + \lambda) \end{vmatrix} \tag{33}$$

$$0 \;=\; -(1+2\alpha x - \lambda)(1+2\alpha x + \lambda) - (2\beta x)^2 \tag{34}$$

$$0 \;=\; \lambda^2 - (1+2\alpha x)^2 - (2\beta x)^2 \tag{35}$$

$$\lambda \;=\; \pm\sqrt{(1+2\alpha x)^2 + (2\beta x)^2} \tag{36}$$

$$\;=\; \pm\sqrt{1 + 4\alpha x + 4(\alpha^2 + \beta^2)x^2} \tag{37}$$

Using the eqns. (28) and (29), the following useful relations are derived:

$$\alpha^2 + \beta^2 \;=\; \frac{m_F^2 + \left(I+\frac{1}{2}\right)^2 - m_F^2}{[I]^2} = \frac{\left(I+\frac{1}{2}\right)^2}{2^2\left(I+\frac{1}{2}\right)^2} = \frac{1}{4} \tag{38}$$

$$4\alpha^2 + 4\beta^2 \;=\; 1 \tag{39}$$

We get the eigenvalues:

$$\pm \left( \lambda = \sqrt{1 + 4\alpha x + x^2} \right) \tag{40}$$

The total energy is therefore:

$$E \;=\; E_0 - \frac{A_{hfs}}{2}\left( I(I+1) + \frac{1}{2}\left( \frac{1}{2} + 1 \right) \right) - g_I \mu_N m_F B + E' \tag{41}$$

$$E' \;=\; \frac{A_{hfs}}{2}\left( I + \frac{1}{2} \right)^2 \pm \frac{A_{hfs}}{2}\left( I + \frac{1}{2} \right) \lambda \tag{42}$$

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:

$$\Delta E = \frac{A_{hfs}[I]}{2} = h\nu_{hfs} \tag{43}$$

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

$$E \;=\; -\frac{h\nu_{hfs}}{2[I]} - g_I \mu_N B m_F \pm \frac{h\nu_{hfs}}{2}\sqrt{1 + \frac{4m_F}{[I]} x + x^2} \tag{44}$$

$$x \;=\; (g_I \mu_N - g_S \mu_B)\frac{B}{h\nu_{hfs}} \tag{45}$$

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.

### 2.4.2 Edge States and Low Field Energy Expansions

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:

$$E_{\pm(I+\frac{1}{2})} = \frac{I}{[I]} h\nu_{hfs} \pm \left( \left[ \frac{g_S}{-2} \right] \mu_B - g_I \mu_N I \right) B \tag{46}$$

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:

$$\sqrt{1 + 2ax + x^2} \;=\; 1 + \frac{1}{2}x\,(2a + x) - \frac{1}{2\cdot 4}x^2\,(2a + x)^2 + \frac{1\cdot 3}{2\cdot 4\cdot 6}x^3\,(2a + x)^3 - \frac{1\cdot 3\cdot 5}{2\cdot 4\cdot 6\cdot 8}x^4\,(2a + x)^4$$
$$+\frac{1\cdot 3\cdot 5\cdot 7}{2\cdot 4\cdot 6\cdot 8\cdot 10}x^5\,(2a + x)^5 - \frac{1\cdot 3\cdot 5\cdot 7\cdot 9}{2\cdot 4\cdot 6\cdot 8\cdot 10\cdot 12}x^6\,(2a + x)^6 + \cdots \tag{47}$$

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

$$\sqrt{1 + 2ax + x^2} \;=\; 1 + \frac{1}{2}x\,(2a + x) - \frac{1}{8}x^2\,(4a^2 + x^2 + 4ax) + \frac{1}{16}x^3\,(8a^3 + 12a^2x + 6ax^2 + x^3)$$
$$-\frac{5}{128}x^4\,(16a^4 + 32a^3x + 24a^2x^2 + 8ax^3 + x^4)$$
$$+\frac{7}{256}x^5\,(32a^5 + 80a^4x + 80a^3x^2 + 40a^2x^3 + 10ax^4 + x^5)$$
$$-\frac{21}{1024}x^5\,(64a^6 + 192a^5x + 240a^4x^2 + 160a^3x^3 + 60a^2x^4 + 12ax^5 + x^6)\cdots \tag{48}$$

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

$$\sqrt{1+2ax+x^2} = 1 + \frac{1}{2}x\left(2a+x\right) - \frac{1}{8}x^2\left(4a^2+x^2+4ax\right) + \frac{1}{16}x^3\left(8a^3+12a^2x+6ax^2+x^3\right)$$
$$-\frac{5}{16}x^4\left(2a^4+4a^3x+3a^2x^2\right) + \frac{7}{16}x^5\left(2a^5+5a^4x\right) - \frac{21}{16}x^6a^6 + \mathcal{O}(x^7) \qquad (49)$$

Collecting all the terms order by order:

$$\sqrt{1+2ax+x^2} = 1 + (a)x + \left(\frac{1}{2}-\frac{a^2}{2}\right)x^2 + \left(-\frac{a}{2}+\frac{a^3}{2}\right)x^3 + \left(-\frac{1}{8}+\frac{3a^2}{4}-\frac{5a^4}{8}\right)x^4$$
$$+ \left(\frac{3a}{8}-\frac{5a^3}{4}+\frac{7a^5}{8}\right)x^5 + \left(\frac{1}{16}-\frac{15a^2}{16}-\frac{21a^6}{16}+\frac{35a^4}{16}\right)x^6 + \mathcal{O}(x^7) \qquad (50)$$

Pulling out common factors:

$$\sqrt{1+2ax+x^2} = 1 + ax + \frac{1}{2}\left(1-a^2\right)x^2 - \frac{a}{2}\left(1-a^2\right)x^3 - \frac{1}{8}\left(1-6a^2+5a^4\right)x^4$$
$$+ \frac{3a}{8}\left(1-\frac{10a^2}{3}+\frac{7a^4}{3}\right)x^5 + \frac{1}{16}\left(1-15a^2-21a^6+35a^4\right)x^6 A + \mathcal{O}(x^7) \qquad (51)$$

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

$$\sqrt{1+2ax+x^2} = \sqrt{1\pm 2x+x^2} = \sqrt{(1\pm x)^2} = 1 \pm x \qquad (52)$$

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:

$$\sqrt{1+2ax+x^2} = 1 + ax + \frac{1}{2}\left(1-a^2\right)x^2 - \frac{a}{2}\left(1-a^2\right)x^3 + \frac{1}{8}\left(5a^2-1\right)\left(1-a^2\right)x^4$$
$$+ \frac{3a}{8}\left(1-\frac{7a^2}{3}\right)\left(1-a^2\right)x^5 - \frac{1}{16}\left(14a^2-21a^2-1\right)\left(1-a^2\right)x^6 + \mathcal{O}(x^7) \qquad (53)$$

Making the substitution $a = 2m_F/[I]$, dividing both sides of the Breit-Rabi equation (44) by $h\nu_{hfs}$, and using the sixth order expansion that was just calculated gives:

$$\pm\frac{E_\pm}{h\nu_{hfs}} = a_0 + a_1 x + \left[1-\left(\frac{2m_F}{[I]}\right)^2\right]\left[\sum_{n=2}^{6} a_n x^n\right] \qquad (54)$$

$$x = (g_I\mu_N - g_S\mu_B)\frac{B}{h\nu_{hfs}} \qquad (55)$$

$$[I] = 2I+1 \qquad (56)$$

$$a_0 = \left(\frac{I+\frac{1}{2}\mp\frac{1}{2}}{[I]}\right) \qquad (57)$$

$$a_1 = \frac{m_F}{[I]}\left(\frac{1\pm\frac{g_I\mu_N}{g_S\mu_B}([I]\mp 1)}{1-\frac{g_I\mu_N}{g_S\mu_B}}\right) \approx \frac{m_F}{[I]} + \mathcal{O}(10^{-3}) \qquad (58)$$

$$a_2 = \frac{1}{4} \qquad (59)$$

$$a_3 = -\frac{m_F}{2[I]} \qquad (60)$$

$$a_4 = \frac{1}{16}\left[5\left(\frac{2m_F}{[I]}\right)^2 - 1\right] \qquad (61)$$

$$a_5 = \frac{3m_F}{8[I]}\left[1-\frac{7}{3}\left(\frac{2m_F}{[I]}\right)^2\right] \qquad (62)$$

$$a_6 = -\frac{1}{32}\left[14\left(\frac{2m_F}{[I]}\right)^2 - 21\left(\frac{2m_F}{[I]}\right)^4 - 1\right] \qquad (63)$$

where $\pm$ refers to the $F = I \pm \frac{1}{2}$ manifold. Note that eqn. (46) shows that the energy for the edge states in the upper manifold $\left(F = I + \frac{1}{2} \ \& \ |m_F| = I + \frac{1}{2}\right)$ is linear in field. Therefore, for the edge states, $\left(2m_F/[I]\right)^2 = 1$ and all terms of order two or higher in field in eqn. (54) must disappear order by order. Consequently eqn. (54) is written such that the disappearance of higher order terms is evident.

## 2.5 Eigenstates

### 2.5.1 Labels

At low field, it is useful to label states by $F$ and $m_F$ because $F$ is still almost a good quantum number. Therefore, at low field, we'll refer to two groups of states labeled by $F$ ("manifolds"). 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 groups 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 it's $m_I$, 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) depicts a qualitative energy level diagram for a rubidium atom.

### 2.5.2 Converting between Bases

When considering transitions between these states, it is often useful to work in the $\{|m_I, m_J\rangle\}$ basis. However, we must first represent the mixed hyperfine states $\left\{\left|m_F^{\pm}\right\rangle\right\}$ in the zero field unmixed $\{|F, m_F\rangle\}$ basis. Note that since we are considering the ground state term of an alkali metal atom, there is no fine structure mixing. As mentioned before, the field $B$ does result in hyperfine structure mixing (states with the same $m_F$ but different $F$):

$$\left|m_F^{\pm}\right\rangle = a_1^{\pm}\left|I + \frac{1}{2}, m_F\right\rangle + a_2^{\pm}\left|I - \frac{1}{2}, m_F\right\rangle \tag{64}$$

$$|F, m_F\rangle = \sum_{m_J = -\frac{1}{2}}^{+\frac{1}{2}} |m_F - m_J, m_J\rangle \langle m_F - m_J, m_J \mid F, m_F\rangle \tag{65}$$

$$b_1^{\pm}(m_F) = \left\langle m_F - \frac{1}{2}, +\frac{1}{2}\middle| I \pm \frac{1}{2}, m_F\right\rangle \tag{66}$$

$$b_2^{\pm}(m_F) = \left\langle m_F + \frac{1}{2}, -\frac{1}{2}\middle| I \pm \frac{1}{2}, m_F\right\rangle \tag{67}$$

$$\left|I \pm \frac{1}{2}, m_F\right\rangle = b_1^{\pm}\left|m_F - \frac{1}{2}, +\frac{1}{2}\right\rangle + b_2^{\pm}\left|m_F + \frac{1}{2}, -\frac{1}{2}\right\rangle \tag{68}$$

For clarity, it is emphasized that the $a$ coefficients are due to hyperfine mixing by the field and the $b$ coefficients are due to the hyperfine coupling between the electronic and nuclear spin. The values for $a_{1,2}^{\pm}$ come from the diagonalization of eqn. (30) where $\lambda_{\pm}$ are the eigenvalues given by eqn. (40) and $\alpha$ and $\beta$ are defined by eqns. (28) and (29):

$$a_1^{\pm} = \frac{2\beta x}{\sqrt{(1 + 2\alpha x \mp \lambda)^2 + 4\beta^2 x^2}} \tag{69}$$

$$a_2^{\pm} = \frac{1 + 2\alpha x \mp \lambda}{\sqrt{(1 + 2\alpha x \mp \lambda)^2 + 4\beta^2 x^2}} \tag{70}$$

$$a_1^{\pm} = \pm a_2^{\mp} \tag{71}$$

F=4

P–3/2

mF = –4...4

F=3

mF = –3...3

5p

F=2

mF = –2...2

7.128x10^9 MHz

F=1

mF = –1...1

F=3

mF = –3...3

P–1/2

F=2

mF = –2...2

D1   794.8 nm = 3.775x10^11 MHz

D2   780.0 nm = 3.846x10^11 MHz

10 MHz (~22 gauss)

F=3

mF = –3...3

5s

3035 MHz

S–1/2

F=2

mF = –2...2

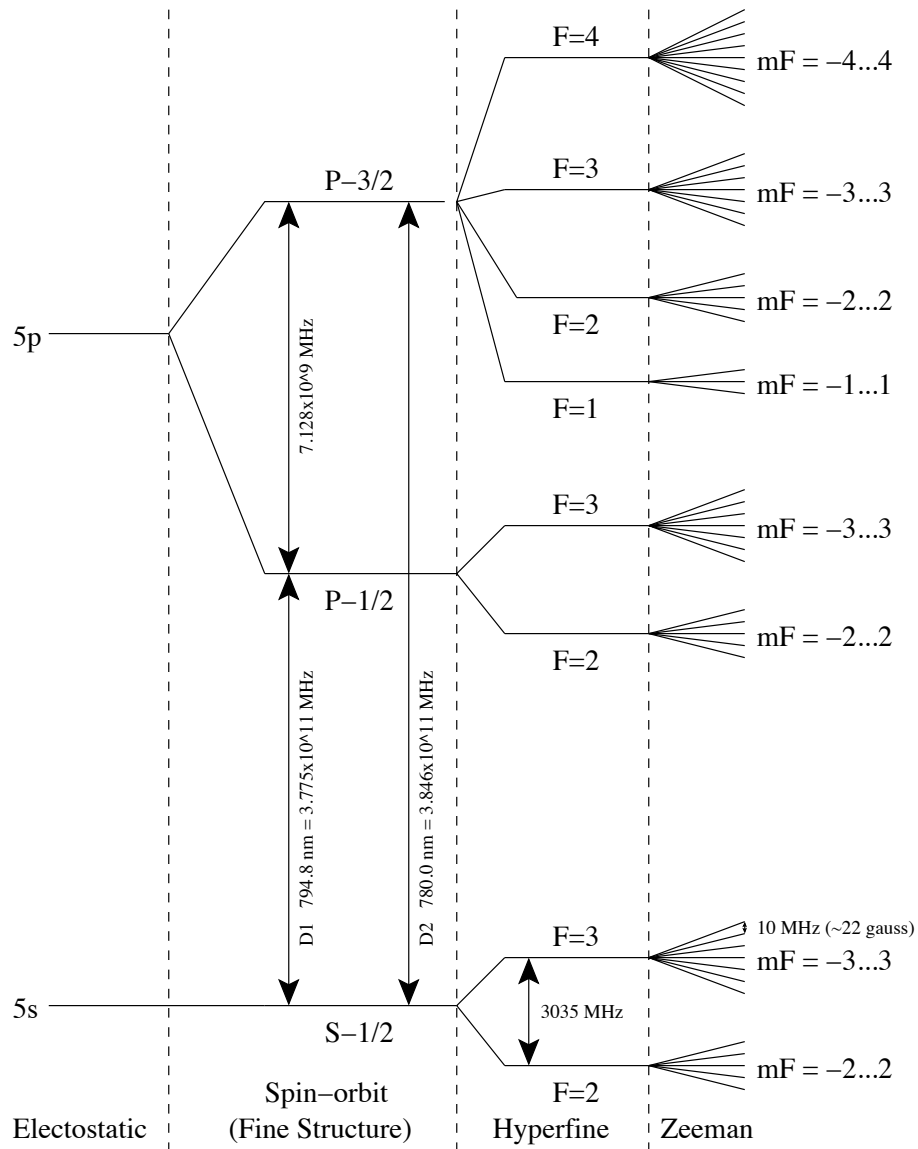Electostatic

Spin–orbit
(Fine Structure)

Hyperfine

Zeeman

Figure 1: Qualitative Energy Level Diagram for Rubidium-85 ($I = 5/2$) in a Weak Field

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

$$a_1 \equiv a_1^+ = a_2^- \tag{72}$$

$$a_2 \equiv a_2^+ = -a_1^- \tag{73}$$

$$b_1 \equiv b_1^+ = b_2^- \tag{74}$$

$$b_2 \equiv b_2^+ = -b_1^- \tag{75}$$

$$\left| I \pm \frac{1}{2}, m_F \right\rangle = b_1 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm b_2 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \tag{76}$$

$$\left| m_F^\pm \right\rangle = a_1 \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 \left| I \mp \frac{1}{2}, m_F \right\rangle \tag{77}$$

Putting this altogether gives:

$$\left| m_F^\pm \right\rangle = a_1 \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 \left| I \mp \frac{1}{2}, m_F \right\rangle \tag{78}$$

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

$$\pm a_2 \left( b_1 \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \mp b_2 \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \right) \tag{79}$$

$$= (a_1 b_1 - a_2 b_2) \underbrace{\left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle}_{|m_I, m_J\rangle} \pm (a_1 b_2 + a_2 b_1) \underbrace{\left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle}_{|m_I, m_J\rangle} \tag{80}$$

### 2.5.3 Populations

### 2.5.4 Populations: 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:

$$\hat{\rho} = \sum_k p_k |\psi_k\rangle \langle \psi_k|$$

$$= \sum_k p_k \sum_{n,m} \langle \psi_k | u_m \rangle \langle u_n | \psi_k \rangle |u_n\rangle \langle u_m| \tag{81}$$

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 $|u_n\rangle$:

$$\rho_{nn} = \sum_k p_k |\langle u_n | \psi_k \rangle|^2 \tag{82}$$

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

$$\left\langle \hat{M} \right\rangle = \mathrm{Tr}(\hat{\rho}\hat{M}) \tag{83}$$

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

$$|u_+\rangle = \left| S_{\frac{1}{2}}, +\frac{1}{2} \right\rangle \tag{84}$$

$$|u_-\rangle = \left| S_{\frac{1}{2}}, -\frac{1}{2} \right\rangle \tag{85}$$

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The state of a single atom labelled by $l$ is:

$$|\psi_l\rangle = c_{l+} e^{i\phi_{l+}} |u_+\rangle + c_{l-} e^{i\phi_{l-}} |u_-\rangle \tag{86}$$

The density matrix for this particular atom is:

$$\hat{\rho}_l = |\psi_l\rangle \langle \psi_l| \tag{87}$$

$$= \left(c_{l+} e^{i\phi_{l+}} |u_+\rangle + c_{l-} e^{i\phi_{l-}} |u_-\rangle\right)\left(c_{l+} e^{-i\phi_{l+}} \langle u_+| + c_{l-} e^{-i\phi_{l-}} \langle u_-|\right) \tag{88}$$

$$= \begin{bmatrix} c_{l+}^2 & c_{l+}c_{l-} e^{i(\phi_{l+}-\phi_{l-})} \\ c_{l+}c_{l-} e^{-i(\phi_{l+}-\phi_{l-})} & c_{l-}^2 \end{bmatrix} \tag{89}$$

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

$$\hat{\rho} = \frac{1}{N}\sum_{l=1}^{N} \hat{\rho}_l \tag{90}$$

$$= \frac{\sum_{l=1}^{N}}{N} \begin{bmatrix} c_{l+}^2 & c_{l+}c_{l-} e^{i(\phi_{l+}-\phi_{l-})} \\ c_{l+}c_{l-} e^{-i(\phi_{l+}-\phi_{l-})} & c_{l-}^2 \end{bmatrix} \tag{91}$$

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:

$$\frac{\sum_{l=1}^{N}}{N} c_{l+}c_{l-} e^{-i(\phi_{l+}-\phi_{l-})} \approx 0 \tag{92}$$

$$\hat{\rho} = \sum_{k} n_k \begin{bmatrix} c_{k+}^2 & 0 \\ 0 & c_{k-}^2 \end{bmatrix} \tag{93}$$

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 $c_k$:

$$\hat{\rho} = \sum_{k} p_k \begin{bmatrix} c_k^2 & 0 \\ 0 & 1-c_k^2 \end{bmatrix} = \begin{bmatrix} \sum_k p_k c_k^2 & 0 \\ 0 & \sum_k p_k \left(1-c_k^2\right) \end{bmatrix} \tag{94}$$

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:

$$P_n = \frac{\exp\left(-\frac{E_n}{kT}\right)}{Z} \tag{95}$$

$$Z = \sum_{n} \exp\left(-\frac{E_n}{kT}\right) \tag{96}$$

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

$$E\left(\left|S_{\frac{1}{2}}, +\frac{1}{2}\right\rangle\right) = E_0^S + \left[\frac{g_S}{-2}\right]\mu_B B \tag{97}$$

$$E\left(\left|S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle\right) = E_0^S - \left[\frac{g_S}{-2}\right]\mu_B B \tag{98}$$

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

$$Z = \exp\left(-\frac{E_+}{kT}\right) + \exp\left(-\frac{E_-}{kT}\right) \tag{99}$$

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$$= \exp\left(-\frac{E_0^S + \left[\frac{g_S}{-2}\right]\mu_B B}{kT}\right) + \exp\left(-\frac{E_0^S - \left[\frac{g_S}{-2}\right]\mu_B B}{kT}\right) \tag{100}$$

$$= \exp\left(-\frac{E_0^S}{kT}\right)\left[\exp\left(-\left[\frac{g_S}{-2}\right]\frac{\mu_B B}{kT}\right) + \exp\left(+\left[\frac{g_S}{-2}\right]\frac{\mu_B B}{kT}\right)\right] \tag{101}$$

$$P_\pm = \frac{\exp\left(-\frac{E_0^S}{kT}\right)\exp\left(\mp\left[\frac{g_S}{-2}\right]\frac{\mu_B B}{kT}\right)}{\exp\left(-\frac{E_0^S}{kT}\right)\left[\exp\left(+\left[\frac{g_S}{-2}\right]\frac{\mu_B B}{kT}\right) + \exp\left(-\left[\frac{g_S}{-2}\right]\frac{\mu_B B}{kT}\right)\right]} \tag{102}$$

$$= \frac{\exp\left(\mp\left[\frac{g_S}{-2}\right]\frac{\mu_B B}{kT}\right)}{\exp\left(+\left[\frac{g_S}{-2}\right]\frac{\mu_B B}{kT}\right) + \exp\left(-\left[\frac{g_S}{-2}\right]\frac{\mu_B B}{kT}\right)} \tag{103}$$

$$P_{m_J} = \frac{\exp\left(m_J \beta\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \tag{104}$$

We have introduced the $\beta$ 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 subsection (2.5.3). For the $S_{\frac{1}{2}}$ ground states at thermal equilibrium, the spin temperature is:

$$\beta = \frac{g_S \mu_B B}{kT} \tag{105}$$

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:

$$P_+ = \frac{\exp\left(+\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} = \sum_k p_k c_k^2 \tag{106}$$

$$P_- = \frac{\exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} = \sum_k p_k \left(1 - c_k^2\right) \tag{107}$$

$$\hat{\rho} = \begin{bmatrix} P_+ & 0 \\ 0 & P_- \end{bmatrix} \tag{108}$$

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

$$P \equiv \frac{\left\langle \hat{J}_z \right\rangle}{J} = \frac{\mathrm{Tr}\left(\hat{\rho}\hat{J}_z\right)}{\frac{1}{2}} \tag{109}$$

$$= 2\,\mathrm{Tr}\left\{\begin{bmatrix} P_+ & 0 \\ 0 & P_- \end{bmatrix}\begin{bmatrix} +\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix}\right\} \tag{110}$$

$$= 2\,\mathrm{Tr}\left\{\begin{bmatrix} +\frac{P_+}{2} & 0 \\ 0 & -\frac{P_-}{2} \end{bmatrix}\right\} \tag{111}$$

$$= 2\left(+\frac{P_+}{2} - \frac{P_-}{2}\right) \tag{112}$$

$$= P_+ - P_- \tag{113}$$

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:

$$P = \frac{\exp\left(+\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} - \frac{\exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \tag{114}$$

$$= \frac{\exp\left(+\frac{\beta}{2}\right) - \exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} \tag{115}$$

$$P = \tanh\left(\frac{\beta}{2}\right) \tag{116}$$

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:

$$P = \frac{\exp\left(+\frac{\beta}{2}\right) - \exp\left(-\frac{\beta}{2}\right)}{\exp\left(+\frac{\beta}{2}\right) + \exp\left(-\frac{\beta}{2}\right)} = \frac{x - \frac{1}{x}}{x + \frac{1}{x}} = \frac{x^2 - 1}{x^2 + 1} \tag{117}$$

$$Px^2 + P = x^2 - 1 \tag{118}$$

$$(P - 1)x^2 = -P - 1 \tag{119}$$

$$x^2 = \left[\exp\left(+\frac{\beta}{2}\right)\right]^2 = \frac{1 + P}{1 - P} \tag{120}$$

$$\beta = \log\left(\frac{1 + P}{1 - P}\right) \tag{121}$$

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:

$$\rho_{m_F} = \frac{e^{\beta m_F}}{Z_F} = \frac{e^{\beta m_J}}{Z_J} \frac{e^{\beta m_I}}{Z_I} \tag{122}$$

$$Z_F = \sum_{m_F=-F}^{+F} e^{\beta m_F} \tag{123}$$

$$Z_J = \sum_{m_J=-J}^{+J} e^{\beta m_J} \tag{124}$$

$$Z_I = \sum_{m_I=-I}^{+I} e^{\beta m_I} \tag{125}$$

$$m_F = m_J + m_I \tag{126}$$

The meaning of $\beta$, 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

$$a_{\frac{3}{2}} : a_{\frac{1}{2}} : a_{-\frac{1}{2}} : a_{-\frac{3}{2}} = \alpha^3 : \alpha^2 : \alpha : 1$$
$$b_{\frac{1}{2}} : b_{-\frac{1}{2}} = \alpha : 1$$

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

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

Table 2: Transitions are labelled by the higher $m_F$ state.

is a constant. This implies that the density matrix for a system of Na and N in spin-exchange equilibrium is given by

$$\rho = \frac{\exp\left[-\left(I_{1z} + S_{1z}\right)\beta\right]\exp\left[-\left(I_{2z} + S_{2z}\right)\beta\right]}{\text{Tr}\left\{\exp\left[-\left(I_{1z} + S_{1z}\right)\beta\right]\exp\left[-\left(I_{2z} + S_{2z}\right)\beta\right]\right\}},$$

where $\beta$ is such that the total $z$ component of the angular momentum of the system is given by $Tr[(I_{1s} + S_{1z} + I_{2z} + S_{2z})\rho]$. The parameter $\beta$ might be called an angular momentum spin temperature.

They were discussing spin-exchange between sodium and nitrogen, but it is perfectably applicable to other spin-exchange systems including "pure" and "hybrid" cells. This gives the relative population of the $\left|m_F - \frac{1}{2} \mp \frac{1}{2}\right\rangle$ state:

$$\rho_\pm = \frac{e^{\beta\left(m_F - \frac{1}{2} \mp \frac{1}{2}\right)}}{Z_F} \tag{127}$$

from which the relative population difference is easily obtained:

$$\rho_+ - \rho_- = \frac{e^{\beta(m_F - 1)}}{Z_F} - \frac{e^{\beta m_F}}{Z_F} = \frac{e^{\beta m_F}}{Z_F}\left(e^{-\beta} - 1\right) \tag{128}$$

## 2.6 Transition Frequencies

### 2.6.1 EPR Spectrum

EPR stands for *Electron Paramagnetic Resonance*. At low field, it refers to the transitions between adjacent states within a particular manifold. Transitions between $m_F \leftrightarrow m_F - 1$ will be labeled by the higher state $m_F$. For example, refer to table (2) for the applicable transitions within the ground state for potassium-39 and rubidium-85. Recall that:

$$g_S = -2\left[1 + \mathcal{O}(10^{-3})\right] \tag{129}$$

$$x = \left(g_I \mu_N - g_S \mu_B\right)\frac{B}{h\nu_{hfs}} \tag{130}$$

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

$$\nu_\pm = \frac{\nu_{hfs}}{2}\left(\sqrt{1 + \frac{4m_F}{[I]}x + x^2} - \sqrt{1 + \frac{4\left(m_F - 1\right)}{[I]}x + x^2}\right) \mp \frac{g_I \mu_N B}{h} \tag{131}$$

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

### 2.6.2 End Transition Frequencies

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

$$m_F = \pm\left(I + \frac{1}{2}\right) \to 4m_F = \pm 2[I] \to \sqrt{1 + \frac{4m_F}{[I]}x + x^2} = 1 \pm x \tag{132}$$

$$\nu_{\pm} = \pm\frac{\nu_{hfs}}{2}\left[1 \pm x - \sqrt{1 \pm 2\left(\frac{2I-1}{[I]}\right)x + x^2}\right] - \frac{g_I \mu_N B}{h} \tag{133}$$

$$= \pm\frac{\nu_{hfs}}{2}\left[1 - \sqrt{1 \pm 2\left(\frac{2I-1}{[I]}\right)x + x^2}\right] + \frac{\nu_{hfs}}{2}(g_I\mu_N - g_S\mu_B)\frac{B}{h\nu_{hfs}} - \frac{g_I\mu_N B}{h} \tag{134}$$

$$= \left(\left[\frac{g_S}{-2}\right]\mu_B - \frac{1}{2}g_I\mu_N\right)\frac{B}{h} \pm \frac{\nu_{hfs}}{2}\left[1 - \sqrt{1 \pm 2\left(\frac{2I-1}{[I]}\right)x + x^2}\right] \tag{135}$$

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

### 2.6.3 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. (135) in terms of $x$ and isolating the square root term:

$$\nu_{\pm} = \frac{(-g_S\mu_B - g_I\mu_N)}{(-g_S\mu_B + g_I\mu_N)}\left(\frac{\nu_{hfs}}{2}\right)x \pm \frac{\nu_{hfs}}{2}\left[1 - \sqrt{1 \pm 2\left(\frac{2I-1}{[I]}\right)x + x^2}\right] \tag{136}$$

$$= \frac{\nu_{hfs}}{2}\left(\left[\frac{-g_S\mu_B - g_I\mu_N}{-g_S\mu_B + g_I\mu_N}\right]x \pm 1 \mp \sqrt{1 \pm 2\left(\frac{2I-1}{[I]}\right)x + x^2}\right) \tag{137}$$

$$= \frac{\nu_{hfs}}{2}\left(\underbrace{\left[\frac{-g_S\mu_B - g_I\mu_N}{-g_S\mu_B + g_I\mu_N}\right]}_{a}x \pm 1 \mp \sqrt{1 \pm 2\underbrace{\left[\frac{2I-1}{[I]}\right]}_{b}x + x^2}\right) \tag{138}$$

$$\nu = \frac{\nu_{hfs}}{2}\left(ax + s - s\sqrt{1 + 2sbx + x^2}\right) \tag{139}$$

$$s = \pm 1 \to s^2 = 1 \tag{140}$$

$$n = 2\frac{\nu}{\nu_{hfs}} = ax + s - s\sqrt{1 + 2sbx + x^2} \tag{141}$$

$$n - ax - s = s\sqrt{1 + 2sbx + x^2} \tag{142}$$

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

$$(n - ax - s)^2 = \left(-s\sqrt{1 + 2sbx + x^2}\right)^2 \tag{143}$$

$$n^2 + a^2x^2 + 1 - 2nax - 2sn + 2sax = 1 + 2sbx + x^2 \tag{144}$$

$$0 = 1 + 2sbx + x^2 - n^2 - a^2x^2 - 1 + 2nax + 2sn - 2sax \tag{145}$$

$$0 = \left(1 - a^2\right)x^2 + 2\left(sb - sa + na\right)x + 2sn - n^2 \tag{146}$$

$$0 = x^2 + 2\left(\frac{sb - sa + na}{1 - a^2}\right)x + \frac{2sn - n^2}{1 - a^2} \tag{147}$$

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, subsection 5.5):

$$\mathcal{A}x^2 + \mathcal{B}x + \mathcal{C} \;=\; 0 \tag{148}$$

$$q \;\equiv\; -\frac{1}{2}\left[\mathcal{B} + \text{sgn}(\mathcal{B})\sqrt{\mathcal{B}^2 - 4\mathcal{A}\mathcal{C}}\right] \tag{149}$$

$$x_1 = \frac{q}{\mathcal{A}} \quad \& \quad x_2 = \frac{\mathcal{C}}{q} \tag{150}$$

*In principle, the "traditional" quadratic formula is formally equivalent to the solutions (150). 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, $\nu$. 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:

$$a \;=\; \frac{a_1}{a_2} = \frac{a_x - a_y}{a_x + a_y} = \frac{-g_S\mu_B - g_I\mu_N}{-g_S\mu_B + g_I\mu_N} \tag{151}$$

$$1 - a^2 \;=\; 1 - \frac{a_1^1}{a_2^2} = \frac{a_2^2 - a_1^2}{a_2^2} = \frac{(a_x + a_y)^2 - (a_x - a_y)^2}{a_2^2} = \frac{4a_x a_y}{a_2^2} \tag{152}$$

$$b - 1 \;=\; \frac{2I - 1}{[I]} - 1 = \frac{2I - 1 - 2I - 1}{[I]} = -\frac{2}{[I]} \tag{153}$$

$$b + 1 \;=\; \frac{2I - 1}{[I]} + 1 = \frac{2I - 1 + 2I + 1}{[I]} = +\frac{4I}{[I]} \tag{154}$$

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

$$\mathcal{A} \;=\; 1 \tag{155}$$

$$\mathcal{B} \;=\; 2\left(\frac{sb - sa + na}{1 - a^2}\right) = 2a_2\left(\frac{sba_2 - sa_1 + na_1}{4a_x a_y}\right) \tag{156}$$

$$=\; 2(a_x + a_y)\left(\frac{sba_x + sba_y - sa_x + sa_y + na_x - na_y}{4a_x a_y}\right) \tag{157}$$

$$=\; \left(\frac{a_x + a_y}{2sa_x a_y}\right)[a_x(b - 1 + sn) + a_y(b + 1 - sn)] \tag{158}$$

$$\mathcal{C} \;=\; \frac{2sn - n^2}{1 - a^2} = n\frac{(a_x + a_y)^2}{4a_x a_y}(2s - n) = n(2 - sn)\frac{(a_x + a_y)^2}{4sa_x a_y} \tag{159}$$

The discriminant is:

$$\mathcal{B}^2 - 4\mathcal{A}\mathcal{C} \;=\; \left(\frac{a_x + a_y}{2sa_x a_y}\right)^2[a_x(b - 1 + sn) + a_y(b + 1 - sn)]^2 - 4n(2 - sn)\frac{(a_x + a_y)^2}{4sa_x a_y} \tag{160}$$

$$=\; (a_x + a_y)^2\left(\frac{[a_x(b - 1 + sn) + a_y(b + 1 - sn)]^2}{4a_x^2 a_y^2} - \frac{n(2 - sn)}{sa_x a_y}\right) \tag{161}$$

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

$$=\; \left(\frac{a_x + a_y}{2a_x a_y}\right)^2[a_x^2(b - 1 + sn)^2 + a_y^2(b + 1 - sn)^2 \tag{162}$$

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

$$=\; \left(\frac{a_x + a_y}{2a_x a_y}\right)^2$$

$$\times\left[a_x^2(b - 1 + sn)^2 + a_y^2(b + 1 - sn)^2 + 2a_x a_y(b^2 - 1 - 2sn + n^2)\right] \tag{163}$$

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

$$-a_x(b-1-n) - a_y(b+1+n) \quad > \quad 0$$

$$n \quad > \quad \frac{a_x(b-1)+a_y(b+1)}{a_x-a_y}$$

$$\nu \quad > \quad \frac{\nu_{hfs}}{[I]}\left(\frac{-1+g'}{1-\frac{g'}{2I}}\right) \leftrightarrow \mathrm{sgn}(\mathcal{B}) = +1 \tag{164}$$

$$g' \quad = \quad \frac{a_y}{a_x} = \left[\frac{-2}{g_S}\right]\frac{g_I\mu_N I}{\mu_B} \approx 10^{-3} \tag{165}$$

Since $g'$ is very small, $\nu$ always satisfies (164) and consequently for $s = -1$, $\mathcal{B} > 0$. For $s = +1$:

$$a_x(b-1+n) + a_y(b+1-n) \quad > \quad 0$$

$$n \quad > \quad \frac{a_x(1-b)-a_y(b+1)}{a_x-a_y}$$

$$\nu \quad > \quad \frac{\nu_{hfs}}{[I]}\left(\frac{1+g'}{1+\frac{g'}{2I}}\right) \leftrightarrow \mathrm{sgn}(\mathcal{B}) = +1 \tag{166}$$

$$\nu \quad < \quad \frac{\nu_{hfs}}{[I]}\left(\frac{1+g'}{1+\frac{g'}{2I}}\right) \leftrightarrow \mathrm{sgn}(\mathcal{B}) = -1 \tag{167}$$

$$g' \quad = \quad \frac{a_y}{a_x} = \left[\frac{-2}{g_S}\right]\frac{g_I\mu_N I}{\mu_B} \approx 10^{-3} \tag{168}$$

For low field, $\nu$ satisfies (167) 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 $x_2$:

$$q \quad = \quad \left(\frac{a_x+a_y}{-4sa_xa_y}\right)\left[a_x\left(b-1+sn\right)+a_y\left(b+1-sn\right)\right] - \left(\frac{a_x+a_y}{-4sa_xa_y}\right) \times$$

$$\sqrt{\left[a_x^2\left(b-1+sn\right)^2+a_y^2\left(b+1-sn\right)^2+2a_xa_y\left(b^2-1-2sn+n^2\right)\right]} \tag{168}$$

$$x_2 \quad = \quad \frac{\mathcal{C}}{q} = \frac{n(2-sn)(a_x+a_y)^2}{4sa_xa_yq} = \frac{n(2-sn)(a_x+a_y)}{a_x(1-b-sn)+a_y(sn-1-b)+\sqrt{\cdots}} \tag{169}$$

$$x \quad = \quad (a_x+a_y)\frac{B}{h\nu_{hfs}} = x_2 \tag{170}$$

$$B(\nu) \quad = \quad \frac{h\nu_{hfs}n(2-sn)}{a_x(1-b-sn)+a_y(sn-1-b)+\sqrt{\cdots}} \tag{171}$$

Relabelling and rearranging things:

$$B(\nu) \quad = \quad \left[\frac{-2}{g_S}\right]\left(\frac{h\nu_{hfs}}{\mu_B}\right)\frac{\nu_0\left(1-s\nu_0/[I]\right)}{(1-s\nu_0)-g'\left(1-\frac{s}{2I}\nu_0\right)+\sqrt{\cdots}} \tag{172}$$

$$\cdots \quad = \quad (1-s\nu_0)^2 - 2g'\left(1+\frac{s[I]}{2I}\nu_0-\frac{\nu_0^2}{2I}\right)+g'^2\left(1-\frac{s}{2I}\nu_0\right)^2 \tag{173}$$

$$\nu_0 \quad = \quad [I]\frac{\nu}{\nu_{hfs}}\left(=\frac{n}{1-b}\right) \tag{174}$$

$$g' \quad = \quad \left[\frac{-2}{g_S}\right]\frac{g_I\mu_N I}{\mu_B}\left(=2I\frac{a_y}{a_x}\right) \tag{175}$$

Equation (172) gives the field $B$ given the end transition frequency $\nu$ 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 (172) is applicable to the alkali metal

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

Table 3: Upper Manifold End Transitions for which Equation (172) is valid with $s = \pm$

transitions listed in table (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 $m_F \leftrightarrow m_F - 1$.

### 2.6.4 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 (2). The difference in frequencies between twin transitions depends only on the magnitude of the field:

$$\Delta\nu_{\text{twin}} = \nu_{\text{lower}} - \nu_{\text{upper}} = +2g_I \frac{\mu_N}{h} B \tag{176}$$

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:

$$^{39}\text{K} \quad : \quad \nu\left(F = 1, m_F = \pm 1 \leftrightarrow 0\right) - \nu\left(F = 2, m_F = \pm 1 \leftrightarrow 0\right) = 3.98 \text{ kHz} \tag{177}$$

$$^{85}\text{Rb} \quad : \quad \nu\left(F = 2, m_F = \pm 2 \leftrightarrow \pm 1 \leftrightarrow 0\right) - \nu\left(F = 3, m_F = \pm 2 \leftrightarrow \pm 1 \leftrightarrow 0\right) = 8.25 \text{ kHz} \tag{178}$$

### 2.6.5 Low Field Frequency Expansion

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

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

$$+ \left( 3\frac{a - a'}{8} - 5\frac{a^3 - a'^3}{4} + 7\frac{a^5 - a'^5}{8} \right) x^5$$

$$+ \left( -15\frac{a^2 - a'^2}{16} - 21\frac{a^6 - a'^6}{16} + 35\frac{a^4 - a'^4}{16} \right) x^6 \tag{179}$$

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

$$a^n - a'^n = \left( \frac{2m_F}{[I]} \right)^n - \left( \frac{2(m_F - 1)}{[I]} \right)^n = \left[ \frac{2}{b} \right]^n [m_F^n - (m_F - 1)^n] \tag{180}$$

Factoring out $b^n$ from each term:

$$\begin{aligned}
\frac{\Delta}{2} =\ & \frac{x}{b} + [1 - 2m_F]\frac{x^2}{b^2} + 2\left[ 1 - 3m_F + 3m_F^2 - \frac{b^2}{4} \right]\frac{x^3}{b^3} \\
& + \left[ 5\left( 1 - 4m_F + 6m_F^2 - 4m_F^3 \right) - \frac{3b^2}{2}(1 - 2m_F) \right]\frac{x^4}{b^4} \\
& + \left[ 14\left( 1 - 5m_F + 10m_F^2 - 10m_F^3 + 5m_F^4 \right) - 5b^2\left( 1 - 3m_F + 3m_F^2 \right) + \frac{3b^4}{8} \right]\frac{x^5}{b^5} \\
& + \left[ 42\left( 1 - 6m_F + 15m_F^2 - 20m_F^3 + 15m_F^4 - 6m_F^5 \right) \right]\frac{x^6}{b^6} \\
& + \left[ -\frac{35b^2}{2}\left( 1 - 4m_F + 6m_F^2 - 4m_F^3 \right) + \frac{15b^4}{8}(1 - 2m_F) \right]\frac{x^6}{b^6} \tag{181}
\end{aligned}$$

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

$$\frac{\nu_\pm}{\nu_{hfs}} = \sum_{n=1}^{6} c_n \frac{x^n}{[I]^n} \tag{182}$$

$$x = (g_I\mu_N - g_S\mu_B)\frac{B}{h\nu_{hfs}} \tag{183}$$

$$[I] = 2I + 1 \tag{184}$$

$$c_1 = \frac{1 \pm \frac{g_I\mu_N}{g_S\mu_B}([I] \mp 1)}{1 - \frac{g_I\mu_N}{g_S\mu_B}} = 1 \pm \mathcal{O}(10^{-3}) \tag{185}$$

$$c_2 = 1 - 2m_F \tag{186}$$

$$c_3 = 2\left( 1 - 3m_F + 3m_F^2 - \frac{[I]^2}{4} \right) \tag{187}$$

$$c_4 = 5\left( 1 - 4m_F + 6m_F^2 - 4m_F^3 \right) - \frac{3[I]^2}{2}(1 - 2m_F) \tag{188}$$

$$c_5 = 14\left( 1 - 5m_F + 10m_F^2 - 10m_F^3 + 5m_F^4 \right) - 5[I]^2\left( 1 - 3m_F + 3m_F^2 \right) + \frac{3[I]^4}{8} \tag{189}$$

$$\begin{aligned}
c_6 =\ & 42\left( 1 - 6m_F + 15m_F^2 - 20m_F^3 + 15m_F^4 - 6m_F^5 \right) \\
& - \frac{35[I]^2}{2}\left( 1 - 4m_F + 6m_F^2 - 4m_F^3 \right) + \frac{15[I]^4}{8}(1 - 2m_F) \tag{190}
\end{aligned}$$

where $\pm$ refers to the manifold.

### 2.6.6   Low Field Frequency Inversion Formula

If we drop all terms higher than second order, then we can get an inversion formula for equation (182) for *any* transition at low field. Thus applying the quadratic formula (150) 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:

$$B \approx \left( \frac{h\nu}{\mu_B} \right)\frac{[I]}{1 + \sqrt{1 + 4(1 - 2m_F)\nu/\nu_{hfs}}} \tag{191}$$

### 2.6.7 Low Field Adjacent Transition Frequency Difference

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

$$\left| \frac{\nu\left(m_F + 1 \leftrightarrow m_F\right) - \nu\left(m_F \leftrightarrow m_F - 1\right)}{\nu_{hfs}} \right| = 2\frac{x^2}{[I]^2} = 2\left[\left(g_I\mu_N - g_S\mu_B\right)\frac{B}{[I]h\nu_{hfs}}\right]^2 \tag{192}$$

### 2.6.8 Low Field Frequency Derivative with respect to Field Expansion

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

$$\frac{d\nu}{dB} = \mp\frac{g_I\mu_N}{h} + \frac{\left(g_I\mu_N - g_S\mu_B\right)}{2h[I]}\left(\frac{2m_F + [I]x}{\sqrt{1 + \frac{4m_F}{[I]}x + x^2}} - \frac{2m_F - 2 + [I]x}{\sqrt{1 + \frac{4(m_F-1)}{[I]}x + x^2}}\right) \tag{193}$$

The derivative can be "expanded" in $x$ at low field by taking the derivative of equation (182) term by term. To fifth order in field, the derivative of the frequency with respect to the field is:

$$\frac{d\nu_\pm}{dB} = \frac{\left(g_I\mu_N - g_S\mu_B\right)}{h[I]}\sum_{n=0}^{5} b_n\frac{x^n}{[I]^n} \tag{194}$$

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

$$[I] = 2I + 1 \tag{196}$$

$$b_0 = \frac{1 \pm \frac{g_I\mu_N}{g_S\mu_B}\left([I] \mp 1\right)}{1 - \frac{g_I\mu_N}{g_S\mu_B}} = 1 \pm \mathcal{O}(10^{-3}) \tag{197}$$

$$b_1 = 2\left(1 - 2m_F\right) \tag{198}$$

$$b_2 = 6\left(1 - 3m_F + 3m_F^2 - \frac{[I]^2}{4}\right) \tag{199}$$

$$b_3 = 20\left(1 - 4m_F + 6m_F^2 - 4m_F^3\right) - 6[I]^2\left(1 - 2m_F\right) \tag{200}$$

$$b_4 = 70\left(1 - 5m_F + 10m_F^2 - 10m_F^3 + 5m_F^4\right) - 25[I]^2\left(1 - 3m_F + 3m_F^2\right) + \frac{15[I]^4}{8} \tag{201}$$

$$b_5 = 252\left(1 - 6m_F + 15m_F^2 - 20m_F^3 + 15m_F^4 - 6m_F^5\right)$$
$$- 105[I]^2\left(1 - 4m_F + 6m_F^2 - 4m_F^3\right) + \frac{45[I]^4}{4}\left(1 - 2m_F\right) \tag{202}$$

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

$$b_0 = \frac{1 + \frac{g_I\mu_N}{g_S\mu_B}(2I)}{1 - \frac{g_I\mu_N}{g_S\mu_B}} = 1 \pm \mathcal{O}(10^{-3}) \tag{203}$$

$$b_1 = \mp 4I \tag{204}$$

$$b_2 = 6I\left(2I - 1\right) \tag{205}$$

$$b_3 = \mp 8I\left(4I^2 - 6I + 1\right) \tag{206}$$

$$b_4 = 10I\left(2I - 1\right)\left(4I^2 - 10I + 1\right) \tag{207}$$

$$b_5 = \mp 12I\left(16I^4 - 80I^3 + 80I^2 - 20I + 1\right) \tag{208}$$

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

## 2.7 EPR Transition Lineshape

### 2.7.1 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. subsection 23, page 2, equation 13):

$$\frac{d\Gamma_{\pm}}{dE} = \frac{2\pi}{\hbar} \left| \left\langle m_F - \frac{1}{2} \pm \frac{1}{2} \right| \hat{W} \left| m_F - \frac{1}{2} \mp \frac{1}{2} \right\rangle \right|^2 \frac{d\rho_{\pm}}{dE} \tag{209}$$

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:

$$\left| \langle m_F | \hat{W} | m_F - 1 \rangle \right|^2 = \left| \langle m_F - 1 | \hat{W} | m_F \rangle \right|^2 \tag{210}$$

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 domintates lifetime of the each hyperfine level is spin-exchange between (alike or unalike) 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:

$$\Gamma = \int \left( \frac{d\Gamma_+}{dE} - \frac{d\Gamma_-}{dE} \right) dE \tag{211}$$

$$= \frac{2\pi}{\hbar} \left| \langle m_F - 1 | \hat{W} | m_F \rangle \right|^2 \int \left( \frac{d\rho_+}{dE} - \frac{d\rho_-}{dE} \right) dE \tag{212}$$

Therefore the area is the net transition probability rate:

$$\Gamma = \frac{2\pi}{\hbar} \left| \langle m_F - 1 | \hat{W} | m_F \rangle \right|^2 [\rho_+ - \rho_-] \tag{213}$$

where $\rho_{\pm}$ is relative population of the state that is absorbing (emitting). First we will derive the the matrix element in $\Gamma$ and then we will discuss the relative populations $\rho_{\pm}$.

### 2.7.2 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 3.9 $\Omega$ & an inductance of 0.5 $\mu$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:

$$\mathcal{H}_{EPR} = \mathcal{H} + \mathcal{W} \tag{214}$$

$$\mathcal{W} = -\vec{\mu_I} \cdot \vec{B}_{rf} - \vec{\mu_J} \cdot \vec{B}_{rf} \tag{215}$$

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

$$W_{fi} = \frac{\hbar}{2} \langle m_F - 1 | \omega_I \hat{I}_- + \omega_J \hat{J}_- | m_F \rangle \tag{216}$$

$$= \frac{\hbar}{2} \langle m_F - 1 | \omega_I \hat{F}_- + (\omega_J - \omega_I) \hat{J}_- | m_F \rangle \tag{217}$$

$$= \frac{\hbar}{2} \langle f | \omega_I \hat{F}_- + (\omega_J - \omega_I) \hat{J}_- | i \rangle \tag{218}$$

$$\omega_I = -\frac{g_I \mu_N B_{RF}}{\hbar} \tag{219}$$

$$\omega_J = -\frac{g_S \mu_B B_{RF}}{\hbar} \tag{220}$$

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

$$\left\langle \hat{F}_- \right\rangle = \left\langle m_F^{\pm} - 1 \right| \hat{F}_- \left| m_F^{\pm} \right\rangle \tag{221}$$

$$= \left[ a_1 (m_F - 1) \left\langle I \pm \frac{1}{2}, m_F - 1 \right| \pm a_2 (m_F - 1) \left\langle I \mp \frac{1}{2}, m_F - 1 \right| \right]$$
$$\hat{F}_- \left[ a_1 (m_F) \left| I \pm \frac{1}{2}, m_F \right\rangle \pm a_2 (m_F) \left| I \mp \frac{1}{2}, m_F \right\rangle \right] \tag{222}$$

$$= \left[ a_1 (m_F - 1) \left\langle I \pm \frac{1}{2}, m_F - 1 \right| \pm a_2 (m_F - 1) \left\langle I \mp \frac{1}{2}, m_F - 1 \right| \right]$$
$$\left[ f_\pm a_1 (m_F) \left| I \pm \frac{1}{2}, m_F - 1 \right\rangle \pm f_\mp a_2 (m_F) \left| I \mp \frac{1}{2}, m_F - 1 \right\rangle \right] \tag{223}$$

$$= f_\pm a_1 (m_F) a_1 (m_F - 1) + f_\mp a_2 (m_F) a_2 (m_F - 1) \tag{224}$$

$$= f_\pm a_{1f} a_{1i} + f_\mp a_{2f} a_{2i} \tag{225}$$

$$f_\pm = \sqrt{\left( I + \frac{1}{2} \right) \left( I + \frac{1}{2} \pm 1 \right) - m_F (m_F - 1)} \tag{226}$$

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

$$\left\langle \hat{J}_- \right\rangle^{\pm} = \left\langle m_F^{\pm} - 1 \right| \hat{J}_- \left| m_F^{\pm} \right\rangle \tag{227}$$

$$= (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - 1 \mp \frac{1}{2}, \pm \frac{1}{2} \right| \pm (a_{1f} b_{2f} + a_{2f} b_{1f})$$
$$\times \left\langle m_F - 1 \pm \frac{1}{2}, \mp \frac{1}{2} \right| \right] \hat{J}_- \left[ (a_{1i} b_{1i} - a_{2i} b_{2i}) \right.$$
$$\times \left| m_F \mp \frac{1}{2}, \pm \frac{1}{2} \right\rangle \pm (a_{1i} b_{2i} + a_{2i} b_{1i}) \left| m_F \pm \frac{1}{2}, \mp \frac{1}{2} \right\rangle \tag{228}$$

$$\left\langle \hat{J}_- \right\rangle^{+} = (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - \frac{3}{2}, +\frac{1}{2} \right| + (a_{1f} b_{2f} + a_{2f} b_{1f})$$
$$\times \left\langle m_F - \frac{1}{2}, -\frac{1}{2} \right| \right] \sqrt{\frac{1}{2} \frac{3}{2} + \frac{1}{2} \frac{1}{2}} \left[ (a_{1i} b_{1i} - a_{2i} b_{2i}) \left| m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \tag{229}$$

$$= [a_{1f} b_{2f} + a_{2f} b_{1f}] \times [a_{1i} b_{1i} - a_{2i} b_{2i}] \tag{230}$$

$$\left\langle \hat{J}_- \right\rangle^{-} = (a_{1f} b_{1f} - a_{2f} b_{2f}) \left\langle m_F - \frac{1}{2}, -\frac{1}{2} \right| - (a_{1f} b_{2f} + a_{2f} b_{1f})$$
$$\times \left\langle m_F - \frac{3}{2}, +\frac{1}{2} \right| \right] \sqrt{\frac{1}{2} \frac{3}{2} + \frac{1}{2} \frac{1}{2}} \left[ - (a_{1i} b_{2i} + a_{2i} b_{1i}) \left| m_F - \frac{1}{2}, -\frac{1}{2} \right\rangle \tag{231}$$

$$= [a_{2f} b_{2f} - a_{1f} b_{1f}] \times [a_{1i} b_{2i} + a_{2i} b_{1i}] \tag{232}$$

Note the following relations:

$$b_{2f} b_{1i} = \frac{\sqrt{\left( I + \frac{1}{2} \right) \left( I + \frac{3}{2} \right) - m_F (m_F - 1)}}{2I + 1} = \frac{f_+}{2I + 1} \tag{233}$$

$$b_{1f}b_{2i} = \frac{\sqrt{\left(I+\frac{1}{2}\right)\left(I-\frac{1}{2}\right)-m_F\left(m_F-1\right)}}{2I+1} = \frac{f_-}{2I+1} \tag{234}$$

$$b_{1f}b_{1i} = \frac{\sqrt{\left(I+\frac{1}{2}\right)\left(I-\frac{1}{2}\right)+m_F\left(m_F-1\right)+2m_F\left(I+\frac{1}{2}\right)}}{2I+1} = \frac{g_-}{2I+1} \tag{235}$$

$$b_{2f}b_{2i} = \frac{\sqrt{\left(I+\frac{1}{2}\right)\left(I+\frac{3}{2}\right)+m_F\left(m_F-1\right)-2m_F\left(I+\frac{1}{2}\right)}}{2I+1} = \frac{g_+}{2I+1} \tag{236}$$

$$g_\pm = \sqrt{\left(I+\frac{1}{2}\right)\left(I+\frac{1}{2}\pm 1\right)+m_F\left(m_F-1\right)\mp 2m_F\left(I+\frac{1}{2}\right)} \tag{237}$$

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

$$\left\langle \hat{J}_-\right\rangle^+ = [a_{1f}b_{2f}+a_{2f}b_{1f}]\times[a_{1i}b_{1i}-a_{2i}b_{2i}] \tag{238}$$

$$= a_{1f}a_{1i}\frac{f_+}{2I+1}+a_{2f}a_{1i}\frac{g_-}{2I+1}-a_{1f}a_{2i}\frac{g_+}{2I+1}-a_{2f}a_{2i}\frac{f_-}{2I+1} \tag{239}$$

$$\left\langle \hat{J}_-\right\rangle^- = [a_{2f}b_{2f}-a_{1f}b_{1f}]\times[a_{1i}b_{2i}+a_{2i}b_{1i}] \tag{240}$$

$$= a_{2f}a_{1i}\frac{g_+}{2I+1}-a_{1f}a_{1i}\frac{f_-}{2I+1}+a_{2f}a_{2i}\frac{f_+}{2I+1}-a_{1f}a_{2i}\frac{g_-}{2I+1} \tag{241}$$

$$\left\langle \hat{J}_-\right\rangle^\pm = \pm a_{1f}a_{1i}\frac{f_\pm}{2I+1}+a_{2f}a_{1i}\frac{g_\mp}{2I+1}-a_{1f}a_{2i}\frac{g_\pm}{2I+1}\mp a_{2f}a_{2i}\frac{f_\mp}{2I+1} \tag{242}$$

Putting this altoghether,

$$W_{fi} = \frac{\hbar}{2}\omega_I\left(f_\pm a_{1f}a_{1i}+f_\mp a_{2f}a_{2i}\right)+\frac{\hbar}{2}\left(\omega_J-\omega_I\right)$$
$$\times\left(\pm a_{1f}a_{1i}\frac{f_\pm}{2I+1}+a_{2f}a_{1i}\frac{g_\mp}{2I+1}-a_{1f}a_{2i}\frac{g_\pm}{2I+1}\mp a_{2f}a_{2i}\frac{f_\mp}{2I+1}\right) \tag{243}$$
$$= \frac{\hbar}{2}\left(\frac{2I\omega_I+(1\mp 1)\omega_I\pm\omega_J}{2I+1}\right)f_\pm a_{1f}a_{1i}+\frac{\hbar}{2}\left(\frac{2I\omega_I+(1\pm 1)\omega_I\mp\omega_J}{2I+1}\right)$$
$$\times f_\mp a_{2f}a_{2i}+\frac{\hbar}{2}\left(\frac{\omega_J-\omega_I}{2I+1}\right)\left(g_\mp a_{2f}a_{1i}-g_\pm a_{1f}a_{2i}\right) \tag{244}$$

Using the small field approximations from before:

$$a_1 = 1-\frac{\beta^2}{2}x^2 \tag{245}$$

$$a_2 = -\beta x+2\alpha\beta x^2 \tag{246}$$

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

$$|W_{fi}|^2 \simeq \frac{\hbar^2}{4}\left(\frac{2I\omega_I+(1\mp 1)\omega_I\pm\omega_J}{2I+1}\right)^2 f_\pm^2-\frac{\hbar^2}{4}\left(\frac{2I\omega_I+(1\mp 1)\omega_I\pm\omega_J}{2I+1}\right)$$
$$\times\left(\frac{\omega_J-\omega_I}{2I+1}\right)f_\pm\left(g_\mp\beta_f-g_\pm\beta_i\right)x+\mathcal{O}(x^2) \tag{247}$$

### 2.7.3   Area Under Curve

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

$$\rho_\pm = \frac{e^{\beta\left(m_F-\frac{1}{2}\mp\frac{1}{2}\right)}}{Z_F} \tag{248}$$

from which the relative population difference is easily obtained:

$$\rho_+ - \rho_- = \frac{e^{\beta(m_F-1)}}{Z_F} - \frac{e^{\beta m_F}}{Z_F} = \frac{e^{\beta m_F}}{Z_F}\left(e^{-\beta} - 1\right) \tag{249}$$

Putting together all of these results, we get

$$|\Gamma| = \frac{2\pi}{\hbar}|W_{fi}|^2 e^{\beta m_F}\left(\frac{1 - e^{-\beta}}{Z_F}\right) \tag{250}$$

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

$$A_{m_F} \simeq A_0\left(\frac{2\pi}{\hbar}\right)\left[\frac{\hbar^2}{4}\left(\frac{\omega_J}{2I+1}\right)^2 f_\pm^2\right] e^{\beta m_F}\left(\frac{1 - e^{-\beta}}{Z_F}\right) + \mathcal{O}(x) \tag{251}$$

$$\simeq A_0\frac{2\pi}{\hbar}\left(\frac{B_{RF}}{2I+1}\right)^2 [F(F+1) - m_F(m_F-1)] e^{\beta m_F} \tag{252}$$

where $A$ is a common factor for all transitions. Note that this $\beta$ is the spin temperature and not the $\beta$ defined in eqn. (29).

# 3    FM Sweep Lineshape

The signal from the photodiode to the lockin is:

$$L(\omega(t)) = A\frac{\Gamma}{\left(\omega(t) - \omega_{EPR}\right)^2 + \frac{\Gamma^2}{4}} \tag{253}$$

$$\int_{-\infty}^{+\infty} L(\omega)\,d\nu = \frac{1}{2\pi}\int_{-\infty}^{+\infty} L(\omega)\,d\omega = A \tag{254}$$

the lockin does:

$$S(t) = \int_{-\infty}^{t} L(\omega(u))\exp\left[-\frac{t-u}{\tau}\right]\cos(\omega_0 u)\,\frac{du}{\tau} \tag{255}$$

$$= L(\omega(u))\exp\left[-\frac{t-u}{\tau}\right]\frac{\sin(\omega_0 u)}{\tau\omega_0}\Big|_{-\infty}^{t} \tag{256}$$

$$-\int_{-\infty}^{t}\left(\frac{1}{\tau}L(\omega(u))\exp\left[-\frac{t-u}{\tau}\right] + L'(\omega(u))\exp\left[-\frac{t-u}{\tau}\right]\right)\frac{\sin(\omega_0 u)}{\omega_0}\frac{du}{\tau} \tag{257}$$

$$= L(\omega(t))\frac{\sin(\omega_0 t)}{\tau\omega_0} - \int_{-\infty}^{t} L'(\omega(u))\exp\left[-\frac{t-u}{\tau}\right]\frac{\sin(\omega_0 u)}{\omega_0}\frac{du}{\tau} \tag{258}$$

$$-\int_{-\infty}^{t} L(\omega(u))\exp\left[-\frac{t-u}{\tau}\right]\frac{\sin(\omega_0 u)}{\tau\omega_0}\frac{du}{\tau} \tag{259}$$

$$= L(\omega(t))\frac{\sin(\omega_0 t)}{\tau\omega_0} - \int_{-\infty}^{t} L'(\omega(u))\exp\left[-\frac{t-u}{\tau}\right]\frac{\sin(\omega_0 u)}{\omega_0}\frac{du}{\tau} \tag{260}$$

$$+L(\omega(t))\frac{\cos(\omega_0 t)}{\tau^2\omega_0^2} \tag{261}$$

$$-\int_{-\infty}^{t}\left(\frac{1}{\tau}L(\omega(u))\exp\left[-\frac{t-u}{\tau}\right] + L'(\omega(u))\exp\left[-\frac{t-u}{\tau}\right]\right)\frac{\cos(\omega_0 u)}{\tau\omega_0^2}\frac{du}{\tau} \tag{262}$$

$$= L(\omega(t))\frac{\sin(\omega_0 t)}{\tau\omega_0} + L(\omega(t))\frac{\cos(\omega_0 t)}{\tau^2\omega_0^2} \tag{263}$$

$$-\int_{-\infty}^{t} L'(\omega(u))\exp\left[-\frac{t-u}{\tau}\right]\frac{\sin(\omega_0 u)}{\omega_0}\frac{du}{\tau} \tag{264}$$

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$$-\int_{-\infty}^{t} L(\omega(u)) \exp\left[-\frac{t-u}{\tau}\right] \frac{\cos(\omega_0 u)}{\tau^2 \omega_0^2} \frac{du}{\tau} \tag{265}$$

$$-\int_{-\infty}^{t} L'(\omega(u)) \exp\left[-\frac{t-u}{\tau}\right] \frac{\cos(\omega_0 u)}{\tau \omega_0^2} \frac{du}{\tau} \tag{266}$$

$$= \ L(\omega(t))\frac{\sin(\omega_0 t)}{\tau \omega_0} + L(\omega(t))\frac{\cos(\omega_0 t)}{\tau^2 \omega_0^2} - \frac{S(t)}{\tau^2 \omega_0^2} \tag{267}$$

$$-\int_{-\infty}^{t} L'(\omega(u)) \exp\left[-\frac{t-u}{\tau}\right] \left(\frac{\sin(\omega_0 u)}{\tau \omega_0} + \frac{\cos(\omega_0 u)}{\tau^2 \omega_0^2}\right)\ du \tag{268}$$

$$\left[1 + \tau^2 \omega_0^2\right] S(t) \ = \ \left[\tau \omega_0 \sin(\omega_0 t) + \cos(\omega_0 t)\right] L(\omega(t)) \tag{269}$$

$$-\int_{-\infty}^{t} L'(\omega(u)) \exp\left[-\frac{t-u}{\tau}\right] \left(\tau \omega_0 \sin(\omega_0 u) + \cos(\omega_0 u)\right)\ du \tag{270}$$

$$= \ \int_{-\infty}^{t} \frac{dL}{d\omega}\Omega_0 \omega_0 \sin(\omega_0 t + \phi) \exp\left[-\frac{t-u}{\tau}\right] \left(\tau \omega_0 \sin(\omega_0 u) + \cos(\omega_0 u)\right)\ du \tag{271}$$

$$= \ \int_{-\infty}^{t} \frac{dL}{d\omega} \frac{\Omega_0 \omega_0}{2} \exp\left[-\frac{t-u}{\tau}\right] \left[\tau \omega_0 \left(\cos(\phi) - \cos(2\omega_0 u + \phi)\right) + \sin(\phi) + \sin(2\omega_0 u + \phi)\right]\ du \tag{272}$$

high freq stuff gets integrated out and cos and cos squared are replaced with time averages:

$$stuff \ = \ \left\langle \frac{dL}{d\omega} \right\rangle_t \frac{\Omega_0 \omega_0}{2} \left[\tau \omega_0 \cos(\phi) + \sin(\phi)\right] \int_{-\infty}^{t} \exp\left[-\frac{t-u}{\tau}\right]\ du \tag{273}$$

$$= \ \left\langle \frac{dL}{d\omega} \right\rangle_t \frac{\Omega_0 \tau \omega_0}{2} \left[\tau \omega_0 \cos(\phi) + \sin(\phi)\right] \tag{274}$$

all together, this gives:

$$S(t) \ = \ \left[\frac{\tau \omega_0 \sin(\omega_0 t) + \cos(\omega_0 t)}{1 + \tau^2 \omega_0^2}\right] L(\omega) + \left\langle \frac{dL}{d\omega} \right\rangle_t \frac{\Omega_0 \tau \omega_0}{2} \left[\frac{\tau \omega_0 \cos(\phi) + \sin(\phi)}{1 + \tau^2 \omega_0^2}\right] \tag{275}$$

if $\tau \omega_0 \gg 1$ then:

$$S(t) \ = \ \left\langle \frac{dL}{d\omega} \right\rangle_t \frac{\Omega_0}{2} \left[\cos(\phi) + \frac{\sin(\phi)}{\tau \omega_0}\right] + \left[\frac{\sin(\omega_0 t)}{\tau \omega_0} + \frac{\cos(\omega_0 t)}{\tau^2 \omega_0^2}\right] L(\omega) \tag{276}$$

If the lock in is in phase with the signal or nearly in phase $\phi \approx \pi$, then:

$$S(t) \ = \ -\left\langle \frac{dL}{d\omega} \right\rangle_t \frac{\Omega_0}{2} + \left[\frac{\sin(\omega_0 t)}{\tau \omega_0} + \frac{\cos(\omega_0 t)}{\tau^2 \omega_0^2}\right] L(\omega) \tag{277}$$

and filtering out the high freqencuy crap:

$$\left\langle (\omega(t) - \omega_{EPR})^2 \right\rangle_t \ = \ \left\langle (\omega_{set} + \Omega_0 \cos(\omega_0 t) - \omega_{EPR})^2 \right\rangle_t \tag{278}$$

$$= \ \left\langle (\delta\omega + \Omega_0 \cos(\omega_0 t))^2 \right\rangle_t \tag{279}$$

$$= \ \left\langle \delta\omega^2 + \Omega_0^2 \cos^2(\omega_0 t) + \delta\omega \Omega_0 \cos(\omega_0 t) \right\rangle_t \tag{280}$$

$$= \ \delta\omega^2 + \pi \Omega_0^2 \tag{281}$$

$$S(t) \ = \ -\left\langle \frac{dL}{d\omega} \right\rangle_t \frac{\Omega_0}{2} \tag{282}$$

$$= \ A\Gamma \delta\omega \Omega_0 \left[\delta\omega^2 + \pi \Omega_0^2 + \frac{\Gamma^2}{4}\right]^{-2} \tag{283}$$

where the slope at zero detuning $\delta\omega = 0$:

$$m_F \ = \ A\Gamma \Omega_0 \left[\pi \Omega_0^2 + \frac{\Gamma^2}{4}\right]^{-2} \tag{284}$$

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$$m_F(\Omega_0 \gg \Gamma) \quad \approx \quad \frac{A\Gamma}{\pi^2 \Omega_0^3} \tag{285}$$

$$m_F(\Omega_0 \ll \Gamma) \quad \approx \quad \frac{16 A\Omega_0}{\Gamma^3} \tag{286}$$

the feedback pk to pk width is:

$$\Delta\omega_{ppw} \quad = \quad \sqrt{\frac{4\pi}{3}\Omega_0^2 + \frac{1}{3}\Gamma^2} \tag{287}$$

the feedback pk to pk height is:

$$\Delta\omega_{pph} \quad = \quad \frac{9A\Gamma\Omega_0}{16}\left[\pi\Omega_0^2 + \frac{\Gamma^2}{4}\right]^{-\frac{3}{2}} \tag{288}$$

# 4 PI Feedback

## 4.1 Introduction

## 4.2 Proportional Gain

## 4.3 Integral Gain

# 5 Extracting the Polarization

## 5.1 Field produced by a Uniformly Magnetized Sample

## 5.2 Traditional Method

## 5.3 Exact Frequency Inversion Method

# 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

- RS$_{85}$  Radzig, A.A. and B.M. Smirnov. *Reference Data on Atoms, Molecules, and Ions.* Berlin: Springer-Verlag, 1985.

- AIV$_{77}$  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 $\pm9$ on the last digit, but is usually $\pm2$. 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.

| Symbol | Value | Units | Description |
|---|---|---|---|
| $c$ | 299 792 458 | $\mathrm{m \cdot s^{-1}}$ | definition of the speed of light |
| $\epsilon_0$ | $8.854\,187\,817 \times 10^{-12}$ | $\mathrm{C^2 \cdot N^{-1} \cdot m^{-2}}$ | permittivity of free space |
| $\mu_0$ | $4\pi \times 10^{-7}$ | $\mathrm{N \cdot A^{-2}}$ | 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 |
| $\mu_B$ | $9.274\,000\,95 \times 10^{-24}$ | $\mathrm{J \cdot T^{-1}}$ | Bohr magneton |
| $\mu_N$ | $5.050\,783\,4 \times 10^{-27}$ | $\mathrm{J \cdot T^{-1}}$ | Nuclear magneton |
| $h$ | $6.626\,069 \times 10^{-34}$ | $\mathrm{J \cdot s}$ | Planck constant |
| $\alpha^{-1}$ | 137.035 999 | unitless | fine structure constant |
| amu | $1.660\,538\,9 \times 10^{-27}$ | kg | $12\cdot$(atomic mass unit) = mass $^{12}$C |

Table 4: Fundamental Physical Constants [CODATA 2002]. These values are found at [NIST$_\mathrm{a}$].

| Element | D1 | | | | | D2 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda(\mathrm{nm, air})$ | $\tau(\mathrm{ns})$ | $f$ | $\tau(\mathrm{ns})$ | $f$ | $\lambda(\mathrm{nm, air})$ | $\tau(\mathrm{ns})$ | $f$ | $\tau(\mathrm{ns})$ | $f$ |
| 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$_\mathrm{b}$ | | | RS$_{85}$ | | NIST$_\mathrm{b}$ | | | RS$_{85}$ | |

Table 5: Alkali atom D1 and D2 transition wavelengths ($\lambda$), lifetimes ($\tau$), and oscillator strengths ($f$).

| Isotope | Mass (amu) | Natural Abundance | Nuclear Spin, $I$ | Magnetic Moment $(\mu_N)$ | g-factor $g_I(\mu_N)$ |
|---|---|---|---|---|---|
| Lithium | 6.941 | | | | |
| $^6$Li | 6.015 122 3 | 0.075 9 | 1 | +0.822 056 | +0.822 056 |
| $^7$Li | 7.016 004 0 | 0.924 1 | 3/2 | +3.256 44 | +2.170 96 |
| Sodium | 22.989 770 | | | | |
| $^{23}$Na | 22.989 769 7 | 1.0 | 3/2 | +2.217 52 | +1.478 35 |
| Potassium | 39.098 3 | | | | |
| $^{39}$K | 38.963 706 9 | 0.932 58 | 3/2 | +0.391 46 | +0.260 97 |
| $^{40}$K | 39.963 998 7 | 0.000 117 | 4 | −1.298 | −0.324 5 |
| $^{41}$K | 40.961 826 0 | 0.067 30 | 3/2 | +0.214 87 | +0.143 25 |
| Rubidium | 85.467 8 | | | | |
| $^{85}$Rb | 84.911 789 | 0.721 7 | 5/2 | +1.353 02 | +0.541 208 |
| $^{87}$Rb | 86.909 184 | 0.278 3 | 3/2 | +2.751 2 | +1.834 1 |
| Cesium | 132.905 45 | | | | |
| $^{133}$Cs | 132.905 447 | 1.0 | 7/2 | +2.579 | +0.736 9 |
| Reference | NIST$_d$ | | NIST$_e$ | | (5) |

Table 6: Alkali atom isotopic and nuclear data.

| Iso. | $S_{1/2}$ | | | $P_{1/2}$ | | | $P_{3/2}$ | |
|---|---|---|---|---|---|---|---|---|
| | $A$ (MHz) | $\nu_{hfs}$ (MHz) | $x=1$ (gauss) | $A$ (MHz) | $\nu_{hfs}$ (MHz) | $x=1$ (gauss) | $A$ (MHz) | $B$ (MHz) |
| $^6$Li | 152.136 841 | 228.205 261 | 81.4 | 17.38 | 26.06 | 27.9 | −1.155 | −0.1 |
| $^7$Li | 401.752 043 3 | 803.504 086 6 | 287 | 45.92 | 91.83 | 98.4 | −3.055 | −0.22 |
| $^{23}$Na | 885.813 064 4 | 1 771.626 128 | 632 | 94.3 | 188.6 | 202 | 18.69 | 2.9 |
| $^{39}$K | 230.859 860 1 | 461.719 720 2 | 165 | 28.85 | 57.7 | 61.8 | 6.06 | 2.8 |
| $^{40}$K | −285.731 | −1 142.92 | −405 | | | | −7.59 | −3.5 |
| $^{41}$K | 127.006 935 2 | 254.013 870 4 | 90.6 | | | | 3.40 | 3.3 |
| $^{85}$Rb | 1 011.910 813 | 3 035.732 439 | 1 080 | 120.72 | 362.16 | 388 | 25.01 | 25.88 |
| $^{87}$Rb | 3 417.341 306 4 | 6 834.682 612 8 | 2 440 | 406.2 | 812.4 | 870 | 84.845 | 12.52 |
| $^{133}$Cs | 2 298.157 942 5 | 9 192.631 770 | 3 280 | 291.9 | 1 167 | 1 250 | 50.34 | −0.4 |
| Ref. | AIV$_{77}$ | (43) | (45) | ” | ” | ” | AIV$_{77}$ | |

Table 7: Alkali atom ground State and first excited states hyperfine structure.

# B  Expansion of Zero Field Eigenbasis

## B.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 $14^3(5)$ in [Condon, E. U. and G.H. Shortley. *The Theory of Atomic Spectra.* London: CUP, 1967.]:

$$\langle (J_1, J_2)\, m_1, m_2 | J, m \rangle = \sqrt{\frac{(J + J_1 - J_2)!\,(J - J_1 + J_2)!\,(J_1 + J_2 - J)!\,(J + m)!\,(J - m)!\,(2J + 1)}{(J + J_1 + J_2 + 1)!\,(J_1 - m_1)!\,(J_1 + m_1)!\,(J_2 - m_2)!\,(J_2 + m_2)!}}$$

$$\times \delta_m^{(m_1 + m_2)} \sum_{\kappa = \kappa_1}^{\kappa_2} \frac{(-1)^{\kappa + J_2 + m_2}\,(J + J_2 + m_1 - \kappa)!\,(J_1 - m_1 + \kappa)!}{(J - J_1 + J_2 - \kappa)!\,(J + m - \kappa)!\,\kappa!\,(\kappa + J_1 - J_2 - m)!} \quad (289)$$

$$\kappa_a = \max[0, J_2 - J_1 + m] \quad (290)$$
$$\kappa_b = \min[J + m, J_2 - J_1 + J] \quad (291)$$
$$\kappa_1 = \min[\kappa_a, \kappa_b] \quad (292)$$
$$\kappa_2 = \max[\kappa_a, \kappa_b] \quad (293)$$

where $\kappa$ is summed over all non-negative integers between $\kappa_1$ and $\kappa_2$. Note the usual rules:

$$\langle (J_1, J_2)\, m_1, m_2 | J, m \rangle = (-1)^{J - J_1 - J_2} \langle (J_2, J_1)\, m_2, m_1 | J, m \rangle \quad (294)$$

$$J_1, J_2, J \geq 0 \qquad J = |J_1 - J_2| \ldots (J_1 + J_2) \quad (295)$$

$$m_1 = -J_1 \ldots + J_1 \qquad m_2 = -J_2 \ldots + J_2 \qquad m = m_1 + m_2 = -J \ldots + J \quad (296)$$

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 $1^3, 2^3, \& \, 3^3$.

## B.2  For the case $\vec{J}_1 + \frac{\vec{1}}{2}$

$$\left\langle \left(J_1, \frac{1}{2}\right), m_1, \pm\frac{1}{2} \middle| J_1 + \frac{1}{2}, m_1 \pm \frac{1}{2} \right\rangle = \left\langle \left(J - \frac{1}{2}, \frac{1}{2}\right), m \mp \frac{1}{2}, \pm\frac{1}{2} \middle| J, m \right\rangle$$

$$= \sqrt{\frac{J_1 \pm m + \frac{1}{2}}{[J_1]}} = \sqrt{\frac{J_1 \pm m_1 + 1}{[J_1]}} = \sqrt{\frac{J \pm m}{2J}} \quad (297)$$

$$\left\langle \left(J_1, \frac{1}{2}\right), m_1, \pm\frac{1}{2} \middle| J_1 - \frac{1}{2}, m_1 \pm \frac{1}{2} \right\rangle = \left\langle \left(J + \frac{1}{2}, \frac{1}{2}\right), m \mp \frac{1}{2}, \pm\frac{1}{2} \middle| J, m \right\rangle$$

$$= \mp\sqrt{\frac{J_1 \mp m + \frac{1}{2}}{[J_1]}} = \mp\sqrt{\frac{J_1 \mp m_1}{[J_1]}} = \mp\sqrt{\frac{J \mp m + 1}{2(J + 1)}} \quad (298)$$

## B.3 For the case $\vec{J}_1 + \vec{1}$

### B.3.1 With $m = m_1 \pm 1$:

$$\langle (J_1, 1), m_1, \pm 1 | J_1 + 1, m_1 \pm 1 \rangle = \langle (J-1, 1), m \mp 1, \pm 1 | J, m \rangle$$

$$= \sqrt{\frac{(J_1 \pm m)(J_1 \pm m + 1)}{2[J_1](J_1 + 1)}} \tag{299}$$

$$= \sqrt{\frac{(J_1 \pm m_1 + 1)(J_1 \pm m_1 + 2)}{2[J_1](J_1 + 1)}} \tag{300}$$

$$= \sqrt{\frac{(J \pm m - 1)(J \pm m)}{2J(2J - 1)}} \tag{301}$$

$$\langle (J_1, 1), m_1, \pm 1 | J_1, m_1 \pm 1 \rangle = \langle (J, 1), m \mp 1, \pm 1 | J, m \rangle$$

$$= \mp \sqrt{\frac{(J_1 \pm m)(J_1 \mp m + 1)}{2J_1(J_1 + 1)}} \tag{302}$$

$$= \mp \sqrt{\frac{(J_1 \pm m_1 + 1)(J_1 \mp m_1)}{2J_1(J_1 + 1)}} \tag{303}$$

$$= \mp \sqrt{\frac{(J \pm m)(J \mp m + 1)}{2J(J + 1)}} \tag{304}$$

$$\langle (J_1, 1), m_1, \pm 1 | J_1 - 1, m_1 \pm 1 \rangle = \langle (J+1, 1), m \mp 1, \pm 1 | J, m \rangle$$

$$= \sqrt{\frac{(J_1 \mp m)(J_1 \mp m + 1)}{2J_1[J_1]}} \tag{305}$$

$$= \sqrt{\frac{(J_1 \mp m_1 - 1)(J_1 \mp m_1)}{2J_1[J_1]}} \tag{306}$$

$$= \sqrt{\frac{(J \mp m + 1)(J \mp m + 2)}{2(J+1)(2J + 3)}} \tag{307}$$

### B.3.2 With $m = m_1$:

$$\langle (J_1, 1), m_1, 0 | J_1 \pm 1, m_1 \rangle = \langle (J \mp 1, 1), m, 0 | J, m \rangle$$

$$= \pm \sqrt{\frac{\left(J_1 - m + \frac{1}{2} \pm \frac{1}{2}\right)\left(J_1 + m + \frac{1}{2} \pm \frac{1}{2}\right)}{[J_1]\left(J_1 + \frac{1}{2} \pm \frac{1}{2}\right)}} \tag{308}$$

$$= \pm \sqrt{\frac{\left(J_1 - m_1 + \frac{1}{2} \pm \frac{1}{2}\right)\left(J_1 + m_1 + \frac{1}{2} \pm \frac{1}{2}\right)}{[J_1]\left(J_1 + \frac{1}{2} \pm \frac{1}{2}\right)}} \tag{309}$$

$$= \pm \sqrt{\frac{\left(J - m + \frac{1}{2} \mp \frac{1}{2}\right)\left(J + m + \frac{1}{2} \mp \frac{1}{2}\right)}{(2J + 1 \mp 2)\left(J + \frac{1}{2} \mp \frac{1}{2}\right)}} \tag{310}$$

$$\langle (J_1, 1), m_1, 0 | J_1, m_1 \rangle = \langle (J, 1), m, 0 | J, m \rangle$$

$$= \frac{m_1}{\sqrt{J_1(J_1 + 1)}} = \frac{m}{\sqrt{J(J + 1)}} \tag{311}$$

## B.4 For the case $\vec{J}_1 + \frac{\vec{3}}{2}$

### B.4.1 With $m = m_1 \pm \frac{3}{2}$:

$$\left\langle \left(J_1, \frac{3}{2}\right), m_1, \pm\frac{3}{2} \middle| J_1 + \frac{3}{2}, m_1 \pm \frac{3}{2} \right\rangle = \left\langle \left(J - \frac{3}{2}, \frac{3}{2}\right), m \mp \frac{3}{2}, \pm\frac{3}{2} \middle| J, m \right\rangle$$

$$= \sqrt{\frac{\left(J_1 \pm m - \frac{1}{2}\right)\left(J_1 \pm m + \frac{1}{2}\right)\left(J_1 \pm m + \frac{3}{2}\right)}{2[J_1]\left(J_1 + 1\right)\left(2J_1 + 3\right)}} \tag{312}$$

$$= \sqrt{\frac{\left(J_1 \pm m_1 + 1\right)\left(J_1 \pm m_1 + 2\right)\left(J_1 \pm m_1 + 3\right)}{2[J_1]\left(J_1 + 1\right)\left(2J_1 + 3\right)}} \tag{313}$$

$$= \sqrt{\frac{\left(J \pm m - 2\right)\left(J \pm m - 1\right)\left(J \pm m\right)}{4J\left(J - 1\right)\left(2J - 1\right)}} \tag{314}$$

$$\left\langle \left(J_1, \frac{3}{2}\right), m_1, \pm\frac{3}{2} \middle| J_1 + \frac{1}{2}, m_1 \pm \frac{3}{2} \right\rangle = \left\langle \left(J - \frac{1}{2}, \frac{3}{2}\right), m \mp \frac{3}{2}, \pm\frac{3}{2} \middle| J, m \right\rangle$$

$$= \mp\sqrt{\frac{3\left(J_1 \pm m - \frac{1}{2}\right)\left(J_1 \pm m + \frac{1}{2}\right)\left(J_1 \mp m + \frac{3}{2}\right)}{2J_1[J_1]\left(2J_1 + 3\right)}} \tag{315}$$

$$= \mp\sqrt{\frac{3\left(J_1 \pm m_1 + 1\right)\left(J_1 \pm m_1 + 2\right)\left(J_1 \mp m_1\right)}{2J_1[J_1]\left(2J_1 + 3\right)}} \tag{316}$$

$$= \mp\sqrt{\frac{3\left(J \pm m - 1\right)\left(J \pm m\right)\left(J \mp m + 1\right)}{4J\left(2J - 1\right)\left(J + 1\right)}} \tag{317}$$

$$\left\langle \left(J_1, \frac{3}{2}\right), m_1, \pm\frac{3}{2} \middle| J_1 - \frac{1}{2}, m_1 \pm \frac{3}{2} \right\rangle = \left\langle \left(J + \frac{1}{2}, \frac{3}{2}\right), m \mp \frac{3}{2}, \pm\frac{3}{2} \middle| J, m \right\rangle$$

$$= \sqrt{\frac{3\left(J_1 \pm m - \frac{1}{2}\right)\left(J_1 \mp m + \frac{1}{2}\right)\left(J_1 \mp m + \frac{3}{2}\right)}{2[J_1]\left(J_1 + 1\right)\left(2J_1 - 1\right)}} \tag{318}$$

$$= \sqrt{\frac{3\left(J_1 \pm m_1 + 1\right)\left(J_1 \mp m_1 - 1\right)\left(J_1 \mp m_1\right)}{2[J_1]\left(J_1 + 1\right)\left(2J_1 - 1\right)}} \tag{319}$$

$$= \sqrt{\frac{3\left(J \pm m\right)\left(J \mp m + 1\right)\left(J \mp m + 2\right)}{4J\left(J + 1\right)\left(2J + 3\right)}} \tag{320}$$

$$\left\langle \left(J_1, \frac{3}{2}\right), m_1, \pm\frac{3}{2} \middle| J_1 - \frac{3}{2}, m_1 \pm \frac{3}{2} \right\rangle = \left\langle \left(J + \frac{3}{2}, \frac{3}{2}\right), m \mp \frac{3}{2}, \pm\frac{3}{2} \middle| J, m \right\rangle$$

$$= \mp\sqrt{\frac{\left(J_1 \mp m - \frac{1}{2}\right)\left(J_1 \mp m + \frac{1}{2}\right)\left(J_1 \mp m + \frac{3}{2}\right)}{2J_1[J_1]\left(2J_1 - 1\right)}} \tag{321}$$

$$= \mp\sqrt{\frac{\left(J_1 \mp m_1 - 2\right)\left(J_1 \mp m_1 - 1\right)\left(J_1 \mp m_1\right)}{2J_1[J_1]\left(2J_1 - 1\right)}} \tag{322}$$

$$= \mp\sqrt{\frac{\left(J \mp m + 1\right)\left(J \mp m + 2\right)\left(J \mp m + 3\right)}{4\left(2J + 3\right)\left(J + 2\right)\left(J + 1\right)}} \tag{323}$$

**B.4.2  With $m = m_1 \pm \frac{1}{2}$:**

$$\left\langle \left(J_1, \frac{3}{2}\right), m_1, \pm\frac{1}{2} \middle| J_1 + \frac{3}{2}, m_1 \pm \frac{1}{2}\right\rangle = \left\langle \left(J - \frac{3}{2}, \frac{3}{2}\right), m \mp \frac{1}{2}, \pm\frac{1}{2} \middle| J, m\right\rangle$$

$$= \sqrt{\frac{3\left(J_1 \pm m + \frac{1}{2}\right)\left(J_1 + m + \frac{3}{2}\right)\left(J_1 - m + \frac{3}{2}\right)}{2[J_1]\left(J_1 + 1\right)\left(2J_1 + 3\right)}} \tag{324}$$

$$= \sqrt{\frac{3\left(J_1 \pm m_1 + 1\right)\left(J_1 + m_1 + \frac{3\pm1}{2}\right)\left(J_1 - m_1 + \frac{3\mp1}{2}\right)}{2[J_1]\left(J_1 + 1\right)\left(2J_1 + 3\right)}} \tag{325}$$

$$= \sqrt{\frac{3\left(J \pm m - 1\right)\left(J + m\right)\left(J - m\right)}{4J\left(J - 1\right)\left(2J - 1\right)}} \tag{326}$$

$$\left\langle \left(J_1, \frac{3}{2}\right), m_1, \pm\frac{1}{2} \middle| J_1 + \frac{1}{2}, m_1 \pm \frac{1}{2}\right\rangle = \left\langle \left(J - \frac{1}{2}, \frac{3}{2}\right), m \mp \frac{1}{2}, \pm\frac{1}{2} \middle| J, m\right\rangle$$

$$= \mp\left(J_1 \mp 3m + \frac{3}{2}\right)\sqrt{\frac{J_1 \pm m + \frac{1}{2}}{2J_1[J_1]\left(2J_1 + 3\right)}} \tag{327}$$

$$= \mp\left(J_1 \mp 3m_1\right)\sqrt{\frac{J_1 \pm m_1 + 1}{2J_1[J_1]\left(2J_1 + 3\right)}} \tag{328}$$

$$= \mp\left(J \mp 3m + 1\right)\sqrt{\frac{J \pm m}{4J\left(2J - 1\right)\left(J + 1\right)}} \tag{329}$$

$$\left\langle \left(J_1, \frac{3}{2}\right), m_1, \pm\frac{1}{2} \middle| J_1 - \frac{1}{2}, m_1 \pm \frac{1}{2}\right\rangle = \left\langle \left(J + \frac{1}{2}, \frac{3}{2}\right), m \mp \frac{1}{2}, \pm\frac{1}{2} \middle| J, m\right\rangle$$

$$= -\left(J_1 \pm 3m - \frac{1}{2}\right)\sqrt{\frac{J_1 \mp m + \frac{1}{2}}{2[J_1]\left(J_1 + 1\right)\left(2J_1 - 1\right)}} \tag{330}$$

$$= -\left(J_1 \pm 3m_1 + 1\right)\sqrt{\frac{J_1 \mp m_1}{2[J_1]\left(J_1 + 1\right)\left(2J_1 - 1\right)}} \tag{331}$$

$$= -\left(J \pm 3m\right)\sqrt{\frac{J \mp m + 1}{4J\left(J + 1\right)\left(2J + 3\right)}} \tag{332}$$

$$\left\langle \left(J_1, \frac{3}{2}\right), m_1, \pm\frac{1}{2} \middle| J_1 - \frac{3}{2}, m_1 \pm \frac{1}{2}\right\rangle = \left\langle \left(J + \frac{3}{2}, \frac{3}{2}\right), m \mp \frac{1}{2}, \pm\frac{1}{2} \middle| J, m\right\rangle$$

$$= \pm\sqrt{\frac{3\left(J_1 + m - \frac{1}{2}\right)\left(J_1 - m - \frac{1}{2}\right)\left(J_1 \mp m + \frac{1}{2}\right)}{2J_1[J_1]\left(2J_1 - 1\right)}} \tag{333}$$

$$= \pm\sqrt{\frac{3\left(J_1 + m_1 - \frac{1\mp1}{2}\right)\left(J_1 - m_1 - \frac{1\pm1}{2}\right)\left(J_1 \mp m_1\right)}{2J_1[J_1]\left(2J_1 - 1\right)}} \tag{334}$$

$$= \pm\sqrt{\frac{3\left(J + m + 1\right)\left(J - m + 1\right)\left(J \mp m + 2\right)}{4\left(2J + 3\right)\left(J + 2\right)\left(J + 1\right)}} \tag{335}$$

## B.5   Ground State With Nuclear Spin $I = \frac{3}{2}, \frac{5}{2}$

The following is the notation, where $c_{1,2}$ are Clebsch-Gordon coefficients:

$$|L_J, F, m_F\rangle = c_1 \left|S = \frac{1}{2}, +\frac{1}{2}\right\rangle_S \left|I, m_F - \frac{1}{2}\right\rangle_I + c_2 \left|S = \frac{1}{2}, -\frac{1}{2}\right\rangle_S \left|I, m_F + \frac{1}{2}\right\rangle_I \tag{336}$$

For the Case $I = \frac{3}{2}$:

$$\left|S_{\frac{1}{2}}, 2, \pm 2\right\rangle = \left|\pm\frac{1}{2}\right\rangle_S \left|\pm\frac{3}{2}\right\rangle_I \tag{337}$$

$$\left|S_{\frac{1}{2}}, 2, +1\right\rangle = \sqrt{\frac{3}{4}}\left|+\frac{1}{2}\right\rangle_S \left|+\frac{1}{2}\right\rangle_I + \sqrt{\frac{1}{4}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{3}{2}\right\rangle_I \tag{338}$$

$$\left|S_{\frac{1}{2}}, 2, 0\right\rangle = \sqrt{\frac{1}{2}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{1}{2}\right\rangle_I + \sqrt{\frac{1}{2}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{1}{2}\right\rangle_I \tag{339}$$

$$\left|S_{\frac{1}{2}}, 2, -1\right\rangle = \sqrt{\frac{1}{4}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{3}{2}\right\rangle_I + \sqrt{\frac{3}{4}}\left|-\frac{1}{2}\right\rangle_S \left|-\frac{1}{2}\right\rangle_I \tag{340}$$

$$\left|S_{\frac{1}{2}}, 1, +1\right\rangle = \sqrt{\frac{1}{4}}\left|+\frac{1}{2}\right\rangle_S \left|+\frac{1}{2}\right\rangle_I - \sqrt{\frac{3}{4}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{3}{2}\right\rangle_I \tag{341}$$

$$\left|S_{\frac{1}{2}}, 1, 0\right\rangle = \sqrt{\frac{1}{2}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{1}{2}\right\rangle_I - \sqrt{\frac{1}{2}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{1}{2}\right\rangle_I \tag{342}$$

$$\left|S_{\frac{1}{2}}, 1, -1\right\rangle = \sqrt{\frac{3}{4}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{3}{2}\right\rangle_I - \sqrt{\frac{1}{4}}\left|-\frac{1}{2}\right\rangle_S \left|-\frac{1}{2}\right\rangle_I \tag{343}$$

For the Case $I = \frac{5}{2}$:

$$\left|S_{\frac{1}{2}}, 3, \pm 3\right\rangle = \left|\pm\frac{1}{2}\right\rangle_S \left|\pm\frac{5}{2}\right\rangle_I \tag{344}$$

$$\left|S_{\frac{1}{2}}, 3, +2\right\rangle = \sqrt{\frac{5}{6}}\left|+\frac{1}{2}\right\rangle_S \left|+\frac{3}{2}\right\rangle_I + \sqrt{\frac{1}{6}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{5}{2}\right\rangle_I \tag{345}$$

$$\left|S_{\frac{1}{2}}, 3, +1\right\rangle = \sqrt{\frac{2}{3}}\left|+\frac{1}{2}\right\rangle_S \left|+\frac{1}{2}\right\rangle_I + \sqrt{\frac{1}{3}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{3}{2}\right\rangle_I \tag{346}$$

$$\left|S_{\frac{1}{2}}, 3, 0\right\rangle = \sqrt{\frac{1}{2}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{1}{2}\right\rangle_I + \sqrt{\frac{1}{2}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{1}{2}\right\rangle_I \tag{347}$$

$$\left|S_{\frac{1}{2}}, 3, -1\right\rangle = \sqrt{\frac{1}{3}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{3}{2}\right\rangle_I + \sqrt{\frac{2}{3}}\left|-\frac{1}{2}\right\rangle_S \left|-\frac{1}{2}\right\rangle_I \tag{348}$$

$$\left|S_{\frac{1}{2}}, 3, -2\right\rangle = \sqrt{\frac{1}{6}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{5}{2}\right\rangle_I + \sqrt{\frac{5}{6}}\left|-\frac{1}{2}\right\rangle_S \left|-\frac{3}{2}\right\rangle_I \tag{349}$$

$$\left|S_{\frac{1}{2}}, 2, +2\right\rangle = \sqrt{\frac{1}{6}}\left|+\frac{1}{2}\right\rangle_S \left|+\frac{3}{2}\right\rangle_I - \sqrt{\frac{5}{6}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{5}{2}\right\rangle_I \tag{350}$$

$$\left|S_{\frac{1}{2}}, 2, +1\right\rangle = \sqrt{\frac{1}{3}}\left|+\frac{1}{2}\right\rangle_S \left|+\frac{1}{2}\right\rangle_I - \sqrt{\frac{2}{3}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{3}{2}\right\rangle_I \tag{351}$$

$$\left|S_{\frac{1}{2}}, 2, 0\right\rangle = \sqrt{\frac{1}{2}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{1}{2}\right\rangle_I - \sqrt{\frac{1}{2}}\left|-\frac{1}{2}\right\rangle_S \left|+\frac{1}{2}\right\rangle_I \tag{352}$$

$$\left|S_{\frac{1}{2}}, 2, -1\right\rangle = \sqrt{\frac{2}{3}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{3}{2}\right\rangle_I - \sqrt{\frac{1}{3}}\left|-\frac{1}{2}\right\rangle_S \left|-\frac{1}{2}\right\rangle_I \tag{353}$$

$$\left|S_{\frac{1}{2}}, 2, -2\right\rangle = \sqrt{\frac{5}{6}}\left|+\frac{1}{2}\right\rangle_S \left|-\frac{5}{2}\right\rangle_I - \sqrt{\frac{1}{6}}\left|-\frac{1}{2}\right\rangle_S \left|-\frac{3}{2}\right\rangle_I \tag{354}$$

# C  Spherical Basis

In the rectangular basis, a vector is decomposed in the following way:

$$\vec{r} = \sum_{q=1}^{3} r_q \hat{\varepsilon}_q \tag{355}$$

where the components $r_q$ and unit vectors $\varepsilon_q$ are real and have the following interpretations:

$$r_q^* = r_q \quad \leftrightarrow \quad \hat{\varepsilon}_q^* = \hat{\varepsilon}_q \tag{356}$$

$$r_1 = r_1^* = x \quad \leftrightarrow \quad \hat{\varepsilon}_1 = \hat{\varepsilon}_1^* = \hat{x} \tag{357}$$

$$r_2 = r_2^* = y \quad \leftrightarrow \quad \hat{\varepsilon}_2 = \hat{\varepsilon}_2^* = \hat{y} \tag{358}$$

$$r_3 = r_3^* = z \quad \leftrightarrow \quad \hat{\varepsilon}_3 = \hat{\varepsilon}_3^* = \hat{z} \tag{359}$$

Orthogonality of the unit vectors is defined the following way:

$$\hat{\varepsilon}_p \cdot \hat{\varepsilon}_q = \delta_p^q \tag{360}$$

which immediately implies the dot product between two vectors and the modulus square of a vector:

$$\vec{r} \cdot \vec{s} = \sum_{p,q=1}^{3} r_p s_q \hat{\varepsilon}_p \cdot \hat{\varepsilon}_q \tag{361}$$

$$= \sum_{p,q=1}^{3} r_p s_q \delta_p^q \tag{362}$$

$$= \sum_{q=1}^{3} r_q s_q \tag{363}$$

$$|\vec{r}|^2 = \vec{r}^* \vec{r} \tag{364}$$

$$= \sum_{q=1}^{3} r_q^* r_q \tag{365}$$

$$= x^2 + y^2 + z^2 \tag{366}$$

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:

$$\vec{r} = \sum_{q=-1}^{+1} (-1)^q r_q \hat{\varepsilon}_{-q} \tag{367}$$

where the components $r_q$ and unit vectors $\varepsilon_q$ are in general complex and have the following interpretations:

$$r_q^* = (-1)^q r_{-q} \quad \leftrightarrow \quad \hat{\varepsilon}_q^* = (-1)^q \hat{\varepsilon}_{-q} \tag{368}$$

$$r_{-1} = -r_{+1}^* = + \left( \frac{x - iy}{\sqrt{2}} \right) \quad \leftrightarrow \quad \hat{\varepsilon}_{-1} = -\hat{\varepsilon}_{+1}^* = + \left( \frac{\hat{x} - i\hat{y}}{\sqrt{2}} \right) \tag{369}$$

$$r_0 = r_0^* = z \quad \leftrightarrow \quad \hat{\varepsilon}_0 = \hat{\varepsilon}_0^* = \hat{z} \tag{370}$$

$$r_{+1} = -r_{-1}^* = - \left( \frac{x + iy}{\sqrt{2}} \right) \quad \leftrightarrow \quad \hat{\varepsilon}_{+1} = -\hat{\varepsilon}_{-1}^* = - \left( \frac{\hat{x} + i\hat{y}}{\sqrt{2}} \right) \tag{371}$$

Orthogonality of the unit vectors is defined the following way:

$$\hat{\varepsilon}_p \cdot \hat{\varepsilon}_q = (-1)^q \delta_p^{-q} \tag{372}$$

$$\hat{\varepsilon}_p^* \cdot \hat{\varepsilon}_q = \delta_p^q \tag{373}$$

which immediately implies the dot product between two vectors and the modulus square of a vector:

$$\vec{r} \cdot \vec{s} = \sum_{p,q=1}^{3} (-1)^{p+q} r_p s_q \hat{\varepsilon}_{-p} \cdot \hat{\varepsilon}_{-q} \tag{374}$$

$$= \sum_{p,q=1}^{3} (-1)^{p+q-q} r_p s_q \delta_{-p}^{q} \tag{375}$$

$$= \sum_{q=1}^{3} (-1)^{q} r_{-q} s_q \tag{376}$$

$$|\vec{r}|^2 = \vec{r}^* \cdot \vec{r} = \sum_{p,q=1}^{3} (-1)^{p+q} r_p^* r_q \hat{\varepsilon}_{-p}^* \cdot \hat{\varepsilon}_{-q} \tag{377}$$

$$= \sum_{p,q=1}^{3} (-1)^{p+q} r_p^* r_q \delta_{-p}^{-q} \tag{378}$$

$$= \sum_{p,q=1}^{3} (-1)^{2q} r_q^* r_q \tag{379}$$

$$= \sum_{p,q=1}^{3} (-1)^{q} r_{-q} r_q \tag{380}$$

$$= r_0^2 - 2r_{-1} r_{+1} \tag{381}$$