Chapter 2

Theory of Nuclear Magnetic Resonance

To understand the techniques of nuclear magnetic resonance spectroscopy which I will discuss throughout this thesis, I will first need to introduce some of the fundamentals of quantum mechanics which will be used to describe the application of static and rotating frame magnetic fields to a system composed of a large number of spins. There are a large number of good fundamental and more advanced texts on quantum mechanics.\textsuperscript{1-5} Also I would direct the reader to additional books written specifically about nuclear magnetic resonance which provide the basis for much of the theory presented in this chapter.\textsuperscript{6-13} Finally the doctoral theses of Sun, Mueller and Chmelka all provide additional detailed information about the techniques presented here.\textsuperscript{14-16} Before doing a complete description of NMR in terms of quantum mechanics, I will first introduce the classical magnetization vector picture.

Classical Magnetization Description

The magnetization picture assumes that an ensemble of spins may be treated as an overall macroscopic magnetization which rotates about the axis of the applied magnetic field at a characteristic Larmor frequency. This description may adequately characterize some simple single- and multiple-pulse experiments. The Larmor energy splitting is given by the formula

$$\Delta E_j = h\gamma B_0 = h\omega_j$$ (2.1)

where $\hbar$ is Planck's constant, $\gamma$ is the gyromagnetic ratio and $B_0$ is the static magnetic field. A useful concept in describing NMR experiments is the rotating frame of the Larmor frequency. Mathematically we transform from a fixed laboratory frame to a frame which is rotating at the Larmor frequency about the $z_{lab}$ axis defined by the static mag-
netic field. In this frame the Cartesian coordinates \((x_{lab}, y_{lab}, z_{lab})\) will be transformed according to the following relationships:

\[
\begin{align*}
x_{rot} &= x_{lab} \cos \omega_l t + y_{lab} \sin \omega_l t \\
y_{rot} &= y_{lab} \cos \omega_l t - x_{lab} \sin \omega_l t \\
z_{rot} &= z_{lab}
\end{align*}
\]  

(2.2)

where \((x_{rot}, y_{rot}, z_{rot})\) are the rotating frame coordinates and \(\omega_l\) is the Larmor frequency.

First, in this frame the effective \(z_{rot}\) axis magnetic field is exactly canceled for off-resonance spins and appears as a much smaller field \(B_{offset} = B_0 - \left(\frac{\omega_c - \delta}{\gamma}\right)\) to spins off resonance by \(\delta\). Second, in the rotating frame a magnetic field oscillating about the laboratory \(x\)-axis (i.e. the applied radio frequency pulse) will appear as the sum of two oscillating magnetic fields. One oscillates at a frequency \(\omega_{\text{effective}} = \omega_{\text{applied}} - \omega_l\) and the other at a frequency \(\omega_{\text{effective}} = -\omega_{\text{applied}} - \omega_l\). Only the former, low frequency, rotating frame magnetic field can affect the net magnetization of the sample. In the presence of a strong radio frequency (RF) pulse, the net \(z\) magnetization will begin to process about the effective magnetic field which is the vector sum of the \(B_{offset}\) along the \(z_{rot}\) axis and \(B_1\) along the \(x_{rot}\) axis. For on-resonance spins, a \(\pi/2\) pulse consists of RF field applied for a time such that \(\frac{\pi}{2} = \gamma B_{\text{effective}} t\). For spins which are only slightly off resonance \((B_1 > B_{offset})\), this RF pulse will effectively be a "90° pulse" to a good approximation and the \(z_{rot}\) magnetization will rotate about the \(x_{rot}\) axes to generate a large \(y_{rot}\) magnetization. When the strong RF pulse is turned off, the effective magnetic field returns to the purely \(B_{offset}\) state along the \(z_{rot}\) axis. At this point, the net \(y_{rot}\) magnetization will begin to process about the \(z_{rot}\) axis. This rotating magnetization will appear as an oscillating magnetic field in the laboratory frame and can be detected with the same coil used to generate the RF pulse. The detected signal called a free induction decay (FID) contains the Fourier sum of all the frequencies present in the sample. The rotating frame Bloch equations describe this magnetization evolution in classical terms and are shown below.
\[
\begin{align*}
\frac{dM_z}{dt} &= -\gamma M_y B_1 + \frac{M_0 - M_z}{T_1} \\
\frac{dM_x}{dt} &= \gamma M_y B_{\text{offset}} - \frac{M_x}{T_2} \\
\frac{dM_y}{dt} &= \gamma \left( M_z B_1 - M_x B_{\text{offset}} \right) - \frac{M_y}{T_2}
\end{align*}
\]

These equations show the excitation and free induction decay behavior described. In addition, they include relaxation terms not yet discussed. The \(T_1\) (longitudinal) and \(T_2\) (transverse) relaxation rates are described more completely in some of the basic NMR texts. For the purpose of this thesis, they will always be treated classically, meaning, an irreversible exponential loss of coherence of both transverse \((M_x\) and \(M_y\)) and longitudinal \((M_z)\) magnetization components. In quantum mechanical terms, they will lead to an overall exponential damping of density matrix elements (such as \(I_x, I_y\) or \(I_z\)) to equilibrium \((I_z)\).

Quantum Mechanical Description

Any discussion of NMR will ultimately be limited if only the Bloch equations are used to describe the system. To this end, the quantum mechanical fundamentals will be discussed in the next section.

Rotations and Tensors

One of the most fundamental concepts in NMR is that of rotations. Many rather complex problems in NMR spectroscopy (and other physical sciences) are greatly simplified by judicious choice of reference frame. The use of Wigner rotation matrices to simplify the mathematics of rotations has been well described in books by Rose\(^{17}\), Edmonds\(^{18}\) and Zare\(^{19}\). Figure 2.1 shows the definition of the three Euler angles \((\alpha, \beta, \gamma)\) as used in Wigner rotation matrices \(D_{m,n}^{(i)}(\alpha, \beta, \gamma)\). One use of Wigner rotation matrices is to rotate an object with tensor properties between frames of reference.
Suppose we have a tensor $A$ of rank $l$ with elements $A_{lm}$ which we wish to rotate into a new frame. In this new frame, the resulting tensor $R_l$ will have elements $R_{lm}$ given by the following expression.

$$R_{lm} = \sum_{n=-l}^{l} D^{(l)}_{nm}(\alpha, \beta, \gamma) A_{ln} \quad (2.4)$$

This expression may be numerically simplified by expressing $D^{(l)}_{nm}(\alpha, \beta, \gamma)$ in terms of exponentials and reduced Wigner rotation matrix elements, $d^{(l)}_{nm}(\beta)$.

$$D^{(l)}_{nm}(\alpha, \beta, \gamma) = e^{-i(m\alpha + n\beta)} d^{(l)}_{nm}(\beta) \quad (2.5)$$

The expressions for each of the reduced Wigner rotation matrices can be found in any of the previously mentioned sources. For most of the work in this thesis, I will deal primarily with second rank tensors in both spin and spatial coordinates. Therefore, for refer-
ence, I include a table (2.1) of second-rank reduced Wigner matrices, but this is by no means a complete set of matrices for all possible applications.

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<td>2</td>
<td>$\left(\frac{1+\cos\beta}{2}\right)^2$</td>
<td>$-\frac{1+\cos\beta}{2}\sin\beta$</td>
<td>$\sqrt{\frac{3}{5}}\sin^2\beta$</td>
<td>$-\frac{1-\cos\beta}{2}\sin\beta$</td>
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<tr>
<td>1</td>
<td>$\frac{1+\cos\beta}{2}\sin\beta$</td>
<td>$\cos^2\beta - \frac{1-\cos\beta}{2}$</td>
<td>$-\sqrt{\frac{3}{5}}\sin2\beta$</td>
<td>$\frac{1+\cos\beta}{2} - \cos^2\beta$</td>
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<tr>
<td>0</td>
<td>$\sqrt{\frac{3}{5}}\sin^2\beta$</td>
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<td>$\frac{3\cos^2\beta - 1}{2}$</td>
<td>$-\sqrt{\frac{3}{5}}\sin2\beta$</td>
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<td>-1</td>
<td>$\frac{1-\cos\beta}{2}\sin\beta$</td>
<td>$\frac{1+\cos\beta}{2} - \cos^2\beta$</td>
<td>$\sqrt{\frac{3}{5}}\sin2\beta$</td>
<td>$\cos^2\beta - \frac{1-\cos\beta}{2}$</td>
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<td>$\left(\frac{1-\cos\beta}{2}\right)^2$</td>
<td>$\frac{1-\cos\beta}{2}\sin\beta$</td>
<td>$\sqrt{\frac{3}{5}}\sin^2\beta$</td>
<td>$\frac{1+\cos\beta}{2}\sin\beta$</td>
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Table 2.1 Second-rank reduced Wigner rotation matrix elements $d^{(2)}_{nm}(\beta)$. These elements may be used in conjunction with equation 2.4 and 2.5 to facilitate rotation of tensors.

**Perturbation Theory**

To analyze the effect of adding a small internal Hamiltonian, like chemical shift, to the overall system described by a large external Hamiltonian, I will use standard static perturbation theory. Perturbation theory has been described previously in a large number of locations; any good quantum mechanics text will include a section on this topic. Briefly, I will sketch the basics and their application to NMR. Given an arbitrary Hamiltonian which is the sum of two parts, one large (for example the Zeeman interaction) and the other small (the chemical shift or quadrupolar interactions), a starting point is to assume that the eigenvalues and eigenstates are those of the large Hamiltonian only and then add correction terms, as in a Taylor series expansion. Shown below is the derivation of the correction to both the eigenvalues and eigenstates for a general Hamiltonian (equation 2.6) which is very similar to that found in Baym.¹

\[ H = H_0 + V \]  \hspace{1cm} (2.6)
where the eigenstates $|n\rangle$ and eigenvalues $\epsilon_n$ of $H_0$, the dominant interaction, are known exactly

$$H_0|n\rangle = \epsilon_n|n\rangle. \quad (2.7)$$

It is assumed that the actual eigenvalues and eigenstates will be very similar to those of the large $H_0$ Hamiltonian. This assumption will be analytically true as the size of the perturbation $V$ goes to zero. Therefore, we will arbitrarily redefine our Hamiltonian with a parameter which may be varied between 0 and 1 (ultimately we will let $\lambda$ go to 1).

$$H = H_0 + \lambda V \quad (2.8)$$

Now we can confidently expand the actual eigenvalues $E_N$ and eigenstates $|N\rangle$ below.

$$|N\rangle = |n\rangle + \lambda |N^{(1)}\rangle + \lambda^2 |N^{(2)}\rangle + \lambda^3 |N^{(3)}\rangle + \cdots$$

$$E_N = \epsilon_n + \lambda E_N^{(1)} + \lambda^2 E_N^{(2)} + \lambda^3 E_N^{(3)} + \cdots \quad (2.9)$$

Now we assume that the eigenstates of $H_0$ are normalized to 1 $\langle n|n\rangle = 1$ and we will choose the normalization of $|N\rangle$ so that $\langle n|N\rangle = 1$ also.

$$\langle n|N\rangle = 1 = \langle n|n\rangle + \lambda \langle n|N^{(1)}\rangle + \lambda^2 \langle n|N^{(2)}\rangle + \lambda^3 \langle n|N^{(3)}\rangle + \cdots \quad (2.10)$$

This implies that for an arbitrary $\lambda$, each correction term $|N^{(i)}\rangle$ is orthogonal to the original basis state $|n\rangle$.

$$\langle n|N^{(i)}\rangle = 0 \quad \text{for} \quad i = 1,2,3,\ldots \quad (2.11)$$

Now we can write the Schrödinger equation for the complete Hamiltonian.

$$H|N\rangle = (H_0 + \lambda V)|N\rangle = E_N|N\rangle \quad (2.12)$$

Collecting terms on both sides of the equation with the same power of $\lambda$ yields the following set of equations.
\[ \lambda^0 \rightarrow H_0 |n\rangle = \varepsilon_n |n\rangle \]

\[ \lambda^1 \rightarrow H_0 \left[ |N^{(1)}\rangle + V |n\rangle \right] = E_N^{(1)} |n\rangle + \varepsilon_n |N^{(1)}\rangle \]

\[ \lambda^2 \rightarrow H_0 \left[ |N^{(2)}\rangle + V |N^{(1)}\rangle \right] = E_N^{(2)} |n\rangle + E_N^{(1)} |N^{(1)}\rangle + \varepsilon_n |N^{(2)}\rangle \]

\[
\vdots
\]

\[ \lambda^k \rightarrow H_0 \left[ |N^{(k)}\rangle + V |N^{(k-1)}\rangle \right] = E_N^{(k)} |n\rangle + E_N^{(k-1)} |N^{(1)}\rangle + \cdots + \varepsilon_n |N^{(k)}\rangle \quad (2.13) \]

To determine the first order eigenvalue correction \( E_N^{(1)} \), we need to take the scalar product of the second equation with \( \langle n | \). By our previously defined orthogonality and normalization equations, this produces the eigenvalue correction term.

\[ \langle n | H_0 | N^{(1)} \rangle + \langle n | V | n \rangle = \langle n | E_N^{(1)} | n \rangle + \langle n | \varepsilon_n | N^{(1)} \rangle \]

\[ \varepsilon_n \langle n | N^{(1)} \rangle + \langle n | V | n \rangle = E_N^{(1)} \langle n | n \rangle + \varepsilon_n \langle n | N^{(1)} \rangle \]

\[ \langle n | V | n \rangle = E_N^{(1)} \quad (2.14) \]

This result states that to first-order in perturbation theory, we need merely to calculate the eigenvalues using the original basis set. This is equivalent to simply ignoring the non-diagonal matrix elements of \( V \). For most NMR calculations we perform, this rather crude approximation is sufficient. In some cases where \( V \) is large, however, higher order terms may be needed (for example the second-order quadrupolar shift). To calculate the higher order eigenvalue corrections, we take the scalar product of the \( \lambda^k \) equation with \( \langle n | \). This produces the following result.

\[ E_N^{(k)} = \langle n | V | N^{(k-1)} \rangle \quad (2.15) \]

This expression shows that once we know the \((k-1)\)th correction to the eigenstate, we can calculate the \( k \)th correction to the eigenvalue. The first step in calculating the correction to the eigenstates is to expand the \( k \)th correction eigenstate in terms of the complete basis set of \( H_0 \). Note that the sum excludes the \( m = n \) state but includes all other possible eigenstates of \( H_0 \), as this state is defined as orthogonal to the correction eigenstate.

\[ |N^{(k)}\rangle = \sum_{m \neq n} |m\rangle \langle m | N^{(k)} \rangle \quad (2.16) \]
Now to calculate the second order correction (higher-orders are calculated in a similar fashion) we take the scalar product of the $\lambda^1$ equation with a basis state $\langle m \rangle$ (but not $\langle n \rangle$).

$$\langle m | H_0 | N^{(1)} \rangle + \langle m | V | n \rangle = \langle m | E_N^{(1)} | n \rangle + \langle m | \epsilon_n | N^{(1)} \rangle$$

$$\epsilon_m \langle m | N^{(1)} \rangle + \langle m | V | n \rangle = E_N^{(1)} \langle m | n \rangle + \epsilon_n \langle m | N^{(1)} \rangle$$

$$\langle m | V | n \rangle = (\epsilon_n - \epsilon_m) \langle m | N^{(1)} \rangle$$

(2.17)

$$\frac{\langle m | V | n \rangle}{\epsilon_n - \epsilon_m} = \langle m | N^{(1)} \rangle$$

Finally, we insert this result into equation 2.16 and take the scalar product with $\langle n | V \rangle$.

$$E_N^{(2)} = \langle n | V | N^{(1)} \rangle = \sum_{m \neq n} \frac{\langle n | V | m \rangle \langle m | V | n \rangle}{\epsilon_n - \epsilon_m}$$

(2.18)

At this point, a word of warning in general, accidental degeneracy in the $\epsilon_m$ eigenvalues can lead to problems and special precautions must be taken under those conditions (this actually happens when this type of theory is applied to nuclear quadrupole resonance (NQR) experiments$^{13}$). However, for most NMR problems, this will not present any difficulties. An alternative way of writing our result is that the original Hamiltonian ($H_0 + V$) may be approximated by a diagonal Hamiltonian, in which the higher order energy correction terms appear on the diagonal.

$$H = \sum_n (\epsilon_n + E_N^{(1)} + E_N^{(2)} + \ldots | n \rangle \langle n |$$

(2.19)

In summary, the results of perturbation theory show that to first-order it is correct to truncate Hamiltonians, such as the chemical shift Hamiltonian in the presence of the Zeeman interaction, by ignoring all terms which do not commute with the basis (Zeeman) Hamiltonian (this is often referred to as dropping the non-secular terms). In cases where the first-order correction is very large, second-order (and possibly higher) corrections must be considered, but these must be considered using the entire perturbing Hamiltonian (as the truncated first-order Hamiltonian would actually give a zero result for any higher order correction, as it is entirely diagonal in the unperturbed basis set).
Zeeman Interaction

In nuclear magnetic resonance, the single most important Hamiltonian is the nuclear Zeeman Hamiltonian. This is expressed in the laboratory frame below in equation 2.20.

\[ H_Z = -\hbar \gamma B_0 I_0 = -\hbar \omega I_0 \]  

(2.20)

The magnetic field, \( B_0 \), defines the \( z_{lab} \) axis, \( \hbar \) is Planck's constant, \( \gamma \) is the gyromagnetic ratio of the nucleus of interest and \( \omega I \) is the Larmor frequency. The spin operator, \( I_0 \), is defined below, as well as the two other spherical operators which make up the complete Zeeman spin operator set.

\[ I_0 = I_z \]

\[ I_{\pm 1} = \pm \frac{1}{\sqrt{2}} (I_x \pm iI_y) \]  

(2.21)

The most fundamental aspect of the Zeeman interaction in high magnetic field is that it is always (for the purposes of this dissertation) the largest nuclear spin interaction present in a system. This effectively means that the eigenvalues and eigenstates of the Zeeman Hamiltonian will act as a basis set for the perturbative expansion of the other important interactions. The \( m \) spin states (the Zeeman eigenstates) for an isolated \( I \) spin nucleus are \( |I, m\rangle \). The matrix elements in this basis set for the various operators are given below.

\[ I_0 |I, m\rangle = m |I, m\rangle \]

\[ I_{\pm 1} |I, m\rangle = \frac{\pm 1}{\sqrt{2}} \sqrt{(I \mp m)(I \pm m + 1)} |I, m \pm 1\rangle \]  

(2.22)

In this description any state with \( |m| > I \) is equivalent to the null state. For many of our applications, however, we will also use a density matrix formulation of quantum mechanics. In this formalism, operators can be represented as matrices which operate on a density matrix which describes the system. Matrices which represent operators are defined below.
\[ I_k = \sum_{m,n=-I}^{I} |I,m\rangle\langle I,m| |I_k\rangle L_{I,n}\langle I,n| \]

\[ = \sum_{m,n=-I}^{I} c_{m,n} |I,m\rangle\langle I,n| \]  

(2.23)

\[ c_{m,n} = \langle I,m| I_k | I,n\rangle \]

A brief description of the density matrix formulation of quantum mechanics is merited here. Suppose we have a linear superposition state \( \psi(t) \) (in Hilbert space) of the Zeeman Hamiltonian given below with complex coefficients \( a_m(t) \).

\[ \psi(t) = \sum_{m=-I}^{I} a_m(t)|I,m\rangle \]  

(2.24)

This state will evolve under a time-independent Hamiltonian according to the Schrödinger equation.

\[ i\hbar \frac{d\psi(t)}{dt} = H\psi(t) \]

\[ \Downarrow \]

\[ \psi(t) = e^{-iH\hbar t}\psi(0) \]  

(2.25)

Alternatively, the same information may be presented in a density matrix formulation (Liouville space), where the density matrix which defines the system is given in equation 2.26.

\[ \rho(t) = \psi(t)\psi^\dagger(t) = \sum_{m,n=-I}^{I} a_m(t)a_n^\dagger(t)|I,m\rangle\langle I,n| \]

\[ = e^{-iH\hbar t}\psi(0)\psi^\dagger(0)e^{iH\hbar t} = e^{-iH\hbar t}\rho(0)e^{iH\hbar t} \]  

(2.26)

It is in this form that most NMR experiments will be described throughout this and other works.

The initial density matrix at thermal equilibrium in a high magnetic field can be shown to be

\[ \rho_0 = \frac{1}{Z} \exp\{-H_Z/kT\} \approx \frac{1}{(2I+1)} \left\{ 1 + H_Z/kT \right\} \]

\[ Z = \text{tr}\{\exp\{-H_Z/kT\}\} = (2I+1) \]  

(2.27)
where \( k \) is Boltzmann’s constant, \( \mathbf{1} \) is a \((2I + 1 \times 2I + 1)\) unit matrix, and \( T \) is the spin temperature. It can be shown that only the second term is observable in an NMR experiment and therefore the unit matrix may be dropped from the expression leaving the reduced density matrix \( \rho_r \) that will be used throughout this work. (It may be noted that this represents a very small net population difference of only about \( 10^{-4} \).)

\[
\rho_0 \approx \frac{\hbar t B_0}{(2I + 1)kT} I_0 \rightarrow \rho_r = I_0 
\] (2.28)

The evolution of a density matrix under a time-dependent Hamiltonian will be governed by the Liouville-von Neumann equation, which may easily be derived from the Schrödinger equation 2.25.

\[
\frac{d\rho_r(t)}{dt} = -\frac{i}{\hbar} [H(t), \rho_r(t)]
\] (2.29)

This may be solved analytically, where \( T \) is the Dyson time-ordering operator.\(^{20,21}\)

\[
\rho_r(t) = U(t)\rho_0 U^\dagger(t) \\
U(t) = T \exp\left\{-\frac{i}{\hbar} \int_0^t H(s) \, ds\right\}
\] (2.30)

Throughout the remainder of this work, the subscript \( r \) will be dropped from the reduced density matrix and the reader should assume that all density matrices are in the reduced form.

The final element needed to look at NMR problems is the transformation to a frame which is rotating at the frequency \(-\omega_{rot}\), as in the classical case. This may be accomplished by the following transformations. First, the rotating frame wavefunction may be related to the laboratory frame wavefunction below and may be inserted into the Schrödinger equation.

\[
\psi(t) = e^{i\omega_{rot}t_0} \psi_{rot}(t) \\
i\hbar \frac{d\psi(t)}{dt} = H_Z \psi(t) \\
i\hbar \frac{d\left\{e^{i\omega_{rot}t_0} \psi_{rot}(t)\right\}}{dt} = -\hbar \omega t_0 e^{i\omega_{rot}t_0} \psi_{rot}(t)
\] (2.31a)
Expanding the various derivatives and simplifying yields the effective Hamiltonian, \( \tilde{H}_Z \), below.

\[
i\hbar e^{i\omega_{\text{rot}} I_0 t} \frac{d\psi_{\text{rot}}(t)}{dt} - \hbar \omega_{\text{rot}} I_0 e^{i\omega_{\text{rot}} I_0 t} \psi_{\text{rot}}(t) = -\hbar \omega I_0 e^{i\omega_{\text{rot}} I_0 t} \psi_{\text{rot}}(t)
\]

\[
i\hbar \frac{d\psi_{\text{rot}}(t)}{dt} = -\hbar (\omega_I - \omega_{\text{rot}}) I_0 \psi_{\text{rot}}(t) \quad (2.31b)
\]

\[
\tilde{H}_Z = -\hbar (\omega_I - \omega_{\text{rot}}) I_0
\]

\[
\rho_{\text{rot}}(t) = e^{i\omega_{\text{rot}} I_0 t} \rho(t) e^{-i\omega_{\text{rot}} I_0 t}
\]

Since the Zeeman Hamiltonian commutes with \( I_0 \), we have merely an offset Hamiltonian in the rotating frame, just as in the classical case. The concept of transforming Hamiltonians into an interaction frame will prove essential to simplify calculations later. In this rotating frame, the Zeeman energy splitting has been effectively removed, however it will show up as an energy offset on all rotating frame measurements or calculations, since these must always be performed in the stationary laboratory frame. In practice, spectra are usually collected over a narrow bandwidth centered at the rotating frame energy and therefore the actual Zeeman splitting energy doesn't appear in most spectra.

**Radio frequency irradiation**

The application of radio frequency pulses to a spin system was discussed earlier in the classical description. The quantum mechanical description is very similar in all respects. We express the oscillating magnetic field created at the \( \omega_{\text{rot}} \) frequency with intensity \( B_1 \) in the Hamiltonian, \( H_{RF} \). Here, the RF is applied to the system through a coil which defines the \( x_{\text{lab}} \) axis perpendicular to the static magnetic field \( B_0 \).

\[
H_{RF} = -\hbar \gamma B_1 \cos(\omega_{\text{rot}} t + \phi) I_{x}^{\text{lab}}
\]

This Hamiltonian may then be transformed into the rotating frame, as in equation 2.31 and the new RF Hamiltonian is shown below.
The single oscillating RF field is converted into two RF fields, one at zero frequency and the other at $2\omega_{rot}$. In addition, this shows that by using a standard single coil in the laboratory frame, fully one half of the useful RF power is lost in the rotating frame. This second field averages to zero in the interaction frame and cannot affect the density matrix, just as a high frequency oscillating magnetic field cannot pick up a piece of iron in the laboratory frame. The rotating frame RF Hamiltonian is now the dominant Hamiltonian in the interaction frame, as long as the offset, $\left(\omega_{rot} - \omega_l\right)$, is small compared to $\frac{\gamma B_1}{2}$. Now suppose we allow the equilibrium density matrix to evolve for a time $\tau$ under the RF Hamiltonian (assuming no offset and $\phi = 0$). In this case, the density matrix after a pulse will be described by the following equation.

$$\rho(\tau) = e^{-i\omega_1\tau I_x} \rho(0) e^{i\omega_1\tau I_x}$$

This shows the same features as the classical description. In fact, including a phase or offset term leads to identical results as the classical results. As a final note on the RF Hamiltonian, by controlling the phase $\phi$ of the RF, the researcher can effectively apply fields along both the $x_{rot}$ and $y_{rot}$ axes, which proves essential in the case of multiple pulse experiments.

**Chemical Shift Anisotropy**

The chemical shift interaction is a good starting point to look at the major features of the internal NMR Hamiltonians. Chemical shifts arise from the interaction of the magnetic dipole moment of the nucleus and local magnetic fields generated by both the
motion of electrons in the large magnetic field (diamagnetic effects) and paramagnetic effects due to excited state electrons. I will not discuss the theoretical schemes used to calculate these shifts and will suffice it to say that they exist and are often anisotropic (dependent on orientation of the molecule). The form of the chemical shift Hamiltonian is given below in equation 2.35a.

\[
H_{CSA} = h\gamma\delta_{\text{iso,cs}}B_0 I_0 + h\omega_{\text{csa}} \sum_{m=-2}^{2} (-1)^m A_{2,m}^{\text{CS}} T_{2,m}^{\text{CS}}
\]

\[
\omega_{\text{csa}} = \sqrt{\frac{2}{3}} \gamma \delta_{\text{CS}}
\]

\[
T_{2,0}^{\text{CS}} = B_0 I_0
\]

\[
T_{2,\pm 1}^{\text{CS}} = B_0 I_{\pm 1}
\]

\[
T_{2,\pm 2}^{\text{CS}} = 0
\]

(2.35a)

Where \( A_{2,m}^{\text{CS}} \) is defined below.

\[
A_{2,m}^{\text{CS}} = \sum_{m'=-2}^{2} D_{m'm}^{(2)} (\alpha^{CS}, \beta^{CS}, \gamma^{CS}) \rho_{2,m'}^{CS}
\]

\[
\delta^{CS} = (\delta_{zz} - \delta_{\text{iso,cs}})
\]

\[
\rho_{2,0}^{CS} = \sqrt{\frac{2}{3}}
\]

\[
\rho_{2,\pm 1}^{CS} = 0
\]

\[
\rho_{2,\pm 2}^{CS} = \frac{1}{2} \eta_{CS} = \frac{(\delta_{xx} - \delta_{yy})}{2(\delta_{zz} - \delta_{\text{iso,cs}})}
\]

(2.35b)

The principal values of the chemical shift tensor (sometimes reported instead of \( \delta_{\text{iso,cs}}, \delta^{CS} \) and \( \eta_{CS} \)) are arranged such that \( |\delta_{zz} - \delta_{\text{iso,cs}}| \geq |\delta_{yy} - \delta_{\text{iso,cs}}| \geq |\delta_{xx} - \delta_{\text{iso,cs}}| \).

The values of these principal values are very small and are usually reported in units of parts per million (ppm). For \(^{13}\text{C}\), for instance, the range of possible chemical shifts is from about -20 to 250 ppm which is about 27 kHz at a Larmor frequency of 100 MHz. The Euler angles, \( (\alpha^{CS}, \beta^{CS}, \gamma^{CS}) \), refer to the orientation of the principal axis system of the chemical shift tensor relative to the laboratory frame (see definition of Euler angles in
This Hamiltonian, while appearing quite complex on the outside, actually can be greatly reduced when transformed to the rotating frame.  

$$\tilde{H}_{CSA} = \hbar \gamma \delta_{isacs} B_0 I_0 + \hbar \omega_{csa} \sum_{m=-2}^{2} (-1)^m A^C_{2,-m} \tilde{T}^{CS}_{2,m}$$

$$\tilde{T}^{CS}_{2,0} = B_0 I_0$$

$$\tilde{T}^{CS}_{2,+1} = B_0 (I_{+1} \cos \omega_{rot} t - i I_{-1} \sin \omega_{rot} t)$$

$$\tilde{T}^{CS}_{2,-1} = B_0 (I_{-1} \cos \omega_{rot} t - i I_{+1} \sin \omega_{rot} t)$$

(2.36)

In the rotating frame Hamiltonian, all of the oscillating terms, $\tilde{T}^{CS}_{2,\pm 1}$, may be ignored (alternatively an identical result comes from first-order perturbation theory), leaving the simple chemical shift Hamiltonian.

$$\tilde{H}_{CSA} = \hbar \delta_{isacs} \omega I_0 + \hbar \omega_{csa} B_0 A^C_{2,0} I_0$$

(2.37)

Another way of thinking about the truncating effect of transforming to the rotating frame is to say that any terms in any Hamiltonian which do not commute with the Zeeman Hamiltonian will oscillate rapidly in the rotating frame and average to zero. In terms of energy level splittings, the chemical shift may be expressed below.

$$\Delta E_{m \rightarrow m-1}^{CSA} = \langle I, m | \tilde{H}_{CSA} | I, m \rangle - \langle I, m-1 | \tilde{H}_{CSA} | I, m-1 \rangle$$

$$= \hbar \omega I \left( \delta_{isacs} + \sqrt{3} \delta^C A^C_{2,0} \right)$$

(2.38)

Quadrupolar Interaction

The first discussion of the quadrupolar interaction was by Casimir in an essay on the nuclear-electric hyperfine interaction in 1936. Additionally, one of the more complete early treatments of the quadrupolar interaction is the work by Cohen and Reif. More modern information on this subject may be found in additional sources. The basic Hamiltonian has the same form as the chemical shift anisotropy Hamiltonian.
\[ H_Q = \hbar \omega_Q \sum_{m=-2}^{2} (-1)^m A_{2,m}^Q T_{2,m}^Q \]

\[ \omega_Q = \frac{e^2 q Q}{2 I (2 I - 1) \hbar} \]

\[ T_{2,0}^Q = \frac{1}{\sqrt{6}} \left( 3 I_0^2 - I^2 \right) \]

\[ T_{2,\pm 1}^Q = \frac{1}{\sqrt{2}} \left( I_0 I_{\pm 1} + I_{\pm 1} I_0 \right) \]

\[ T_{2,\pm 2}^Q = I_{\pm 1}^2 \]

Where \( A_{2,m}^Q \) is defined below.

\[ A_{2,m}^Q = \sum_{m'=-2}^{2} D_{m,m'}^{(2)}(\alpha^Q, \beta^Q, \gamma^Q) \rho_{2,m'}^Q \]

\[ eq = V_{zz} \]

\[ \rho_{2,0}^Q = \sqrt{\frac{3}{2}} \]

\[ \rho_{2,\pm 1}^Q = 0 \]

\[ \rho_{2,\pm 2}^Q = \frac{1}{2} \eta_Q = \frac{(V_{xx} - V_{yy})}{2 V_{zz}} \]

Again, as in the previous section, the values of the electric field gradient (EFG) in the principal axis frame are defined such that \( |V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \) and the Euler angles refer to the orientation of the EFG axis system relative to the laboratory frame. Additionally, since the quadrupolar tensor is traceless, there is no net isotropic shift due to this interaction (at least to first order in perturbation theory). As before, we can truncate this Hamiltonian by eliminating the non-commuting \( \tilde{T}_{2,\pm 1}^Q, \tilde{T}_{2,\pm 2}^Q \) terms. The remaining Hamiltonian is expressed in equation 2.41.

\[ \tilde{H}_Q = \frac{\hbar \eta_Q}{\sqrt{6}} A_{2,0}^Q \left( 3 I_0^2 - I(I+1) \right) \]

This first-order perturbation result illustrates an example where higher order corrections are needed. To show the necessity, we look at the eigenvalues for the \( 2I+1 \) energy levels of the Zeeman basis states.
\[ \langle I, m | \hat{H}_Q | I, m \rangle = E_m^{(1Q)} = \frac{\hbar \omega_Q}{\sqrt{6}} A_{2,0}^Q \langle I, m \mid (3I_0^2 - I(I+1)) \mid I, m \rangle \]

\[ E_m^{(1Q)} = \frac{\hbar \omega_Q}{\sqrt{6}} A_{2,0}^Q (3m^2 - I(I+1)) \]

\[ \vdots \]

\[ E_0^{(1Q)} = -\frac{\hbar \omega_Q}{\sqrt{6}} A_{2,0}^Q (I(I+1)) \]

\[ \text{or} \]

\[ E_{\pm \frac{1}{2}}^{(1Q)} = \frac{\hbar \omega_Q}{\sqrt{6}} A_{2,0}^Q \left( \frac{3}{4} - I(I+1) \right) \]

(2.42)

The last two energies are for the two distinct cases where the spin is either an integer \((I = 1, 2, 3, \ldots)\) or half-odd integer \((I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots)\). Also, it is notable that in the spin 1/2 case, only the final \(E_{\pm \frac{1}{2}}^{(1Q)}\) energy levels exist and are analytically zero, as is expected since a spin 1/2 has no quadrupolar moment of the nucleus. At this point it is valuable to calculate the energy splittings between a variety of single quantum \((\Delta m = \pm 1)\) transitions.

\[ \Delta E_{m \rightarrow m-1}^{(1Q)} = E_m^{(1Q)} - E_{m-1}^{(1Q)} = \frac{3\hbar \omega_Q}{\sqrt{6}} A_{2,0}^Q (2m - 1) \]

(2.43)

The first feature which is immediately visible is that for \(m = \frac{1}{2}\), the splitting is analytically zero. In fact for any other value of \(m\), this splitting will depend on both the size of the quadrupolar coupling and the orientation of a given crystallite. Only half-odd integer spins have a central transition \(\left( \frac{1}{2} \leftrightarrow -\frac{1}{2} \right)\) which is unaffected by the quadrupolar interaction to first order. In addition, if we calculate the energy splitting for a multiple quantum \((m \leftrightarrow -m)\) transition (for both integer and half-odd integer spins), we find that these also have no first-order quadrupolar energy splitting correction. For both the central transition and multiple quantum transition, it is crucial to calculate the second-order contribution to the energy splitting since this becomes the dominant energy splitting correction. Additionally, when the quadrupolar coupling is large, the second-order quadrupolar correction will make significant changes to the satellite transition energy splittings. For the remainder of this thesis, I will describe experiments and theory pertaining primarily to the central transition of half-odd integer spins. For more information on the study of multi-
ple-quantum overtone spectroscopy or integer spin spectroscopy, I direct the reader to the
original NMR references and references therein.\textsuperscript{6,7,12,25-28}

To calculate the second order correction to the energy splittings in a quadrupolar
system, we need to return to equation 2.18 where now the sum is over the additional 2\(I\)
Zeeman states (all except for the \(m\) state) for a quadrupolar spin \(I\).

\[
E_m^{(Q)} = \sum_{n \neq m} \frac{\langle I, m | H_Q | I, n \rangle \langle I, n | H_Q | I, m \rangle}{\hbar \omega_I (m - n)}
\]

(2.44)

Rather than calculate this for a general \(m\), I will instead look only at the central transition
second-order quadrupolar energy splitting expression.

\[
\Delta E_{\frac{1}{2} \rightarrow -\frac{1}{2}}^{(Q)} = \sum_{n \neq \frac{1}{2}} \frac{\|\langle I, n | H_Q | I, \frac{1}{2} \rangle\|^2}{\hbar \omega_I (\frac{1}{2} - n)} - \sum_{n \neq -\frac{1}{2}} \frac{\|\langle I, n | H_Q | I, -\frac{1}{2} \rangle\|^2}{\hbar \omega_I (-\frac{1}{2} - n)}
\]

\[
= \frac{\hbar \omega_Q^2}{\omega_I} \left[ \sum_{n \neq \frac{1}{2}} \frac{\|\langle I, n | \sum_{k=-2}^{2} (-1)^k A_{2-k}^{Q} T_{2k}^{Q} | I, \frac{1}{2} \rangle\|^2}{(\frac{1}{2} - n)} - \right]
\]

\[
\left[ \sum_{n \neq -\frac{1}{2}} \frac{\|\langle I, n | \sum_{k=-2}^{2} (-1)^k A_{2-k}^{Q} T_{2k}^{Q} | I, -\frac{1}{2} \rangle\|^2}{(-\frac{1}{2} - n)} \right]
\]

(2.45)

These sums may be simplified by realizing that the \(T_{2k}^{Q}\) spin operators produce non-zero
results for only very specific bra-ket pairs. For example, \(\langle I, j | T_{20}^{Q} | I, m \rangle \neq 0\) only when \(j\)
and \(m\) are the same. In fact, below are shown the only non-zero matrix elements involving
the \(|\pm \frac{1}{2}\rangle\) ket, which will be used to simplify equation 2.45.

\[
\langle I, \pm \frac{1}{2} | T_{20}^{Q} | I, \pm \frac{1}{2} \rangle = \frac{1}{\sqrt{2}} (\frac{3}{4} - I(I + 1))
\]

\[
\langle I, \pm \frac{1}{2} | T_{2\pm 1}^{Q} | I, \pm \frac{1}{2} \rangle = 0
\]

\[
\langle I, \pm \frac{3}{2} | T_{2\pm 1}^{Q} | I, \pm \frac{1}{2} \rangle = \sqrt{(I - \frac{3}{2})(I + \frac{3}{2})}
\]

(2.46)

\[
\langle I, \pm \frac{1}{2} | T_{2\pm 2}^{Q} | I, \pm \frac{3}{2} \rangle = \frac{(I+\frac{1}{2})}{2} \sqrt{(I - \frac{1}{2})(I + \frac{3}{2})}
\]

\[
\langle I, \pm \frac{3}{2} | T_{2\pm 2}^{Q} | I, \pm \frac{1}{2} \rangle = \frac{1}{2} \sqrt{(I - \frac{1}{2})(I - \frac{3}{2})(I + \frac{3}{2})(I + \frac{5}{2})}
\]
Also, because the sums over \( n \) are limited to \( n \neq \pm \frac{1}{2} \) and \( n \neq -\frac{1}{2} \) respectively, the first of these relationships will not be used at all. The second shows that in fact all \( n \neq \pm \frac{1}{2} \) may be ignored. Additionally, if the spin is \( I = 3/2 \), then the final relationship will also disappear (as evident in the fourth formula of 2.46 and in the fact that there is no 5/2 state for a spin 3/2 nucleus). Now performing the sums in equation 2.45 we arrive at the following formula for the second-order central transition energy splitting correction. Equation 2.47 was simplified using the complex conjugate relationship \( (A_{2, m}^{Q})^\dagger = (-1)^m A_{2, -m}^{Q} \) which is correct in this case, while not generally true for all tensors.

\[
\Delta E_{1/2 \rightarrow -1/2}^{(2Q)} = \frac{\hbar \omega}{\omega_i} \left( I(I + 1) - \frac{3}{4} \left(2 A_{2,1}^{Q} A_{2,-1}^{Q} + A_{2,2}^{Q} A_{2,-2}^{Q} \right) \right) \quad (2.47)
\]

This result is now in a form which may be used to calculate actual NMR line positions, which we will do in the next section.

**Dipole-Dipole Interaction**

The homonuclear and heteronuclear dipolar coupling Hamiltonians are some of the most well studied in NMR. The basic form for a Hamiltonian describing the coupling between two spins \( i \) and \( j \) is given in equation 2.48.

\[
H_D = -\sum_{j \neq i} \hbar \omega_{D_{ij}} \sum_{m=-2}^{2} (-1)^m A_{2, -m}^{D_{ij}} T_{2, m}^{D_{ij}}
\]

\[
\omega_{D_{ij}} = \gamma_i \gamma_j \frac{1}{r_{i,j}^3}
\]

\[
T_{2, 0}^{D_{ij}} = \frac{1}{\sqrt{6}} \left(3 I_{i,0} I_{j,0} - I_i \cdot I_j \right)
\]

\[
T_{2, \pm 1}^{D_{ij}} = \frac{1}{\sqrt{2}} \left(I_{i,0} I_{j, \pm 1} + I_{i, \pm 1} I_{j, 0} \right)
\]

\[
T_{2, \pm 2}^{D_{ij}} = I_{i, \pm 1} I_{j, \pm 1}
\]

Where \( A_{2, m}^{D_{ij}} \) is defined below.
As usual, the Euler angles refer to the orientation of the principal axis of the dipolar coupling (corresponding to the vector connecting the two nuclei) relative to the laboratory frame. It is immediately apparent upon substitution of the principal axis components into the formula for the spatial tensor \(A^{D_{ij}}_{2,m}\), that only \(\beta_{ij}^D\), which corresponds to the angle between the internuclear vector and the static magnetic field, affects the overall Hamiltonian. Secondly, truncation of this Hamiltonian by the Zeeman Hamiltonian is more difficult because there are two cases, the homonuclear \((i\text{ and } j\text{ have similar Larmor frequencies})\) and the heteronuclear \((i\text{ and } j\text{ have different Larmor frequencies})\). In any case, only the \(m = 0\) term will remain, giving the following Hamiltonian.

\[
H_D = -\sum_{j \neq i} h \omega_{D_{ij}} \frac{1}{2} \left( 3 I_{i,0} I_{j,0} - I_i \cdot I_j \right) d_0^{(2)}(\beta_{ij}^D) 
\]

I will return to this formula in chapter 3 when discussing the homonuclear dipolar coupling contribution to dynamic-angle spinning linewidth. In addition, I will use this Hamiltonian when discussing the theory of cross-polarization in chapter 5. In all other cases, the dipolar coupling may be thought of as an irreversible relaxation mechanism which leads to a Gaussian decay.

**Truncation of RF Hamiltonian by the Quadrupolar Hamiltonian**

The quadrupolar Hamiltonian is often times the second largest interaction present in a system (in most cases only the Zeeman is larger) even in the presence of RF irradiation. As such, when both radio frequency irradiation and quadrupolar Hamiltonians are present, it is important to evaluate the relative sizes of these two parts,\(^{29-34}\) just as the Zeeman offset term affects the RF effectiveness. To compare the RF and quadrupolar...
Hamiltonians, we need only examine the first-order contributions, since the second-order quadrupolar interaction will rarely be larger than 100 kHz in the systems we study. The total RF and quadrupolar Hamiltonian which is present in the rotating frame is given below.

\[ \tilde{H} = \tilde{H}_Z + \tilde{H}_Q + \tilde{H}_{RF} \]

\[ = \hbar (\omega_I - \omega_{rot}) I_0 + \frac{\hbar \alpha Q}{6} A_{2,0} \left( 3 I_0^2 - I(I + 1) \right) \]

\[ + \frac{\hbar \gamma B_i}{2} \left[ I_x \cos \phi - I_y \sin \phi \right] \]

(2.51)

In order to simplify this Hamiltonian, we may rewrite it in terms of fictitious spin 1/2 operators. These are spin operators which involve only two states and look like the traditional spin 1/2 operators. Given below are the basic definitions which have been outlined previously.\(^{25,26,35}\)

\[ I^{jk}_z = \frac{1}{2} (|j\rangle\langle j| - |k\rangle\langle k|) \quad I^{jk}_z = -I^{kj}_z \]

\[ I^{jk}_x = \frac{1}{2} (|j\rangle\langle j| + |k\rangle\langle k|) \quad I^{jk}_x = I^{kj}_x \]

\[ I^{jk}_y = \frac{i}{2} (-|j\rangle\langle k| + |k\rangle\langle j|) \quad I^{jk}_y = -I^{kj}_y \]

(2.52)

Within the \(jk\) manifold, these operators obey the usual spin 1/2 commutation rules

\[ \left[ I_{\alpha}^{jk}, I_{\beta}^{jk} \right] = i I_{\gamma}^{jk} \]

(2.53)

where \(\alpha, \beta, \gamma = x, y, z\) and cyclic permutations. For commutators between different submanifolds, the following commutation rules apply.

\[ \left[ I_{x}^{jk}, I_{x}^{ik} \right] = \left[ I_{y}^{jk}, I_{y}^{ik} \right] = \frac{i}{2} I_{y}^{ji} \]

\[ \left[ I_{z}^{jk}, I_{z}^{ik} \right] = 0 \]

\[ \left[ I_{y}^{jk}, I_{z}^{ik} \right] = -\frac{i}{2} I_{x}^{jk} \]

\[ \left[ I_{x}^{jk}, I_{z}^{ik} \right] = \frac{i}{2} I_{x}^{jk} \]

(2.54)

The last is the most important, since this states that all fictitious spin-1/2 operators commute between unconnected manifolds. Using these relationships, the normal \(I_z, I_x\) and \(I_y\)
may be redefined in the Hamiltonian given by equation 2.48 (where the spin \( I \) is a half-odd integer spin) using the following relationships.

\[
\begin{align*}
I_z &= 2I \left( I_z^{1,2} + I_z^{2I+1} \right) + 2(2I - 1) \left( I_z^{2,3} + I_z^{2I-1,2I} \right) + \\
&\quad + n(2I - (n-1)) \left( I_z^{n,n+1} + I_z^{2I+1-n,2I+2-n} \right) + \\
&\quad + \left( I + \frac{1}{2} \right) \left( I_z^{2I+1,2I+3} \right) \\
I_x &= \sqrt{2I} \left( I_x^{1,2} + I_x^{2I+1} \right) + \sqrt{2(2I - 1)} \left( I_x^{2,3} + I_x^{2I-1,2I} \right) + \\
&\quad + \sqrt{n(2I - (n-1))} \left( I_x^{n,n+1} + I_x^{2I+1-n,2I+2-n} \right) + \\
&\quad + \left( I + \frac{1}{2} \right) \left( I_x^{2I+1,2I+3} \right) \\
I_y &= \sqrt{2I} \left( I_y^{1,2} + I_y^{2I+1} \right) + \sqrt{2(2I - 1)} \left( I_y^{2,3} + I_y^{2I-1,2I} \right) + \\
&\quad + \sqrt{n(2I - (n-1))} \left( I_y^{n,n+1} + I_y^{2I+1-n,2I+2-n} \right) + \\
&\quad + \left( I + \frac{1}{2} \right) \left( I_y^{2I+1,2I+3} \right)
\end{align*}
\] (2.55a, 2.55b, 2.55c)

Additionally, the \((3I_0^2 - I(I+1))\) term may also be reduced.

\[
(3I_0^2 - I(I+1)) = \frac{1}{2} \left( 2I^2 - I \right) \left( I_z^{1,2} - I_z^{2I+1} \right) + \frac{1}{2} \left( 4I^2 - 8I + 3 \right) \left( I_z^{2,3} - I_z^{2I-1,2I} \right) + \\
\quad + \cdots + \frac{1}{2} \left( 2nI^2 - \sum_{i=0}^{n-1} (6i + 1)I + 3 \sum_{i=0}^{n-1} i^2 \right) \left( I_z^{n,n+1} - I_z^{2I+1-n,2I+2-n} \right) + \\
\quad + \cdots + \left( 0 \right) \left( I_z^{2I+1,2I+3} \right)
\] (2.56)

The last term is of particular importance, as this is the central transition contribution of the first-order quadrupolar Hamiltonian. As expected, this is zero and this makes the central transition manifold different from all of the other fictitious spin 1/2 manifolds for this Hamiltonian. The Hamiltonian from equation 2.51 may be divided into a sum of \(jk\) sub-manifold Hamiltonians \(\tilde{H}_{jk}\) below with all other Hamiltonian elements \((j-k \neq \pm 1)\) zero.
\[ \tilde{H}_{j,j+1} + \tilde{H}_{n,n+1} = \hbar j (\omega_l - \omega_{rot}) (2I - j + 1) \left( I_{z,j}^{j+1} + I_{z,n}^{n+1} \right) + \]
\[ + \frac{\hbar \omega_Q A^Q_2,0}{2J^0} \left( 2jI^2 + \sum_{i=0}^{j-1} (3i^2 - (6i + 1)I) \left( I_{z,j}^{j+1} - I_{z,n}^{n+1} \right) \right) \]
\[ + \frac{\hbar B_1}{J} \sqrt{j(2I - j + 1)} \left[ \left( I_{y,j}^{j+1} + I_{y,n}^{n+1} \right) \cos \phi - \left( I_{y,j}^{j+1} + I_{y,n}^{n+1} \right) \sin \phi \right] \]  

(2.57)

where we define \( n = 2I + 1 - j \). These Hamiltonians may be truncated to first-order using our knowledge about the size of the interactions, \( (\omega_l - \omega_{rot}) < \frac{\gamma B_1}{2} \ll \frac{\omega_Q A^Q_2,0}{2J^0} \).

\[ \tilde{H}_{j,j+1} + \tilde{H}_{n,n+1} = \hbar j (\omega_l - \omega_{rot}) (2I - J + 1) \left( I_{z,j}^{j+1} + I_{z,n}^{n+1} \right) + \]
\[ + \frac{\hbar \omega_Q A^Q_2,0}{2J^0} \left( 2jI^2 + \sum_{i=0}^{j-1} (3i^2 - (6i + 1)I) \left( I_{z,j}^{j+1} - I_{z,n}^{n+1} \right) \right) \]  

(2.58)

This shows that the application of an RF pulse to a quadrupolar system produces distinctively different results that when applied to a spin 1/2 system. First, the Hamiltonians under RF irradiation for the outer transition sub-manifolds (the upper equation in 2.55) are all identical and are equivalent to free precession without RF irradiation. Second, the Hamiltonian for the central transition (the lower equation in 2.55) corresponds to the same Hamiltonian as a spin 1/2 under RF irradiation, with the change by a factor of \( I + \frac{1}{2} \) in the effective rotating frame magnetic field. Thus, a 90° pulse for a quadrupolar nucleus will be shorter than for a comparable spin 1/2 system by a factor of \( I + \frac{1}{2} \) since the RF precession frequency is scaled by this factor. The effect of quadrupolar truncation of the RF Hamiltonian will be more thoroughly discussed later when we look at cross-polarization of quadrupolar nuclei under Hartmann-Hahn matching conditions (see Chapter 5).
Coherence Pathways

Having briefly described both the Hamiltonians present in most solid systems and the effect of truncation, it may now be useful to describe evolution and detection of NMR signals. For most of the experiments in this thesis, I will look at simple two level systems (either spin 1/2 or the central transition of a half-odd integer quadrupolar nucleus). In the absence of dipolar coupling, there are only three different coherent states that the density matrix can evolve into or from; they are $I_z$, $I_y$ and $I_x$ (for quadrupolar nuclei, the central transition superscripts have been dropped). Alternatively, the density matrix may be expressed in terms of spherical tensor operators $I_0$, $I_{+1}$, and $I_{-1}$. Our detector will always be a single coil capable of collecting data in quadrature (both the real and imaginary components in the induced FID). Therefore the observable in our experiments will be $I_{+1}$ (or $I_{-1}$ but never both). However, the phase of the receiver ($\phi_r$) may be controlled (by adding the real and imaginary data from each scan differently in the computer acquisition system to form the FID) to arbitrary accuracy in the computer. That is to say our observable may be written in equation 2.59 as

$$S(t) = \text{tr} \left[ \rho(t) I_{+1} e^{-i\phi_r} \right].$$ (2.59)

This has the property of extracting only the $L_{-1}$ components from the density matrix; all other components will have a zero trace. The response of the system to pulses and free evolution can be characterized by the Hamiltonians below (where the pulse is applied with phase $\phi$).

$$\tilde{H}_{fid} = \hbar \omega_{fid} I_z$$
$$\tilde{H}_{RF} = \hbar \omega_{RF} \left[ I_x \cos \phi - I_y \sin \phi \right]$$

$$\omega_{fid} = \frac{\Delta E_{fid}}{\hbar}$$
$$\omega_{RF} = \frac{\gamma B}{2} \left( I + \frac{1}{2} \right)$$ (2.60)

The response of each of the possible states of the density matrix to each Hamiltonian is given below.
\[ U_{RF} = \exp\left[-i \hat{H}_{RF} t/\hbar\right] = \exp\left[-i \omega_{RF} t \left( I_x \cos \phi - I_y \sin \phi \right)\right] \]

\[ U_{fid} = \exp\left[-i \omega_{fid} I_z\right] \]  

\[ U_{RF} I_z U_{RF}^\dagger = I_z \cos \omega_{RF} t + \sin \omega_{RF} t \left[ I_x \sin \phi - I_y \cos \phi \right] \]

\[ U_{RF} I_x U_{RF}^\dagger = I_x \left( \cos^2 \phi + \sin^2 \phi \cos \omega_{RF} t \right) + I_y \frac{\sin \phi}{2} \left( 1 - \cos \omega_{RF} t \right) - I_z \sin \phi \sin \omega_{RF} t \]  

\[ U_{RF} I_y U_{RF}^\dagger = I_y \left( \sin^2 \phi + \cos^2 \phi \cos \omega_{RF} t \right) + I_x \frac{\sin \phi}{2} \left( 1 - \cos \omega_{RF} t \right) + I_z \cos \phi \sin \omega_{RF} t \]  

\[ U_{fid} I_z U_{fid}^\dagger = I_z \]

\[ U_{fid} I_x U_{fid}^\dagger = I_x \cos \omega_{fid} t + I_y \sin \omega_{fid} t \]

\[ U_{fid} I_y U_{fid}^\dagger = I_y \cos \omega_{fid} t - I_x \sin \omega_{fid} t \]  

These equations are more useful when expressed in the spherical operator basis set.

\[ U_{RF} I_0 U_{RF}^\dagger = I_0 \cos \omega_{RF} t + \frac{i \sin \omega_{RF} t}{\sqrt{2}} \left[ I_{\pm 1} e^{-i \phi} + I_{1} e^{i \phi} \right] \]

\[ U_{RF} I_{\pm 1} U_{RF}^\dagger = \frac{1}{2} I_{\pm 1} \left( 1 + \cos \omega_{RF} t \right) - \frac{1}{2} I_1 \left( 1 - \cos \omega_{RF} t \right) e^{\pm \phi} + \frac{i}{\sqrt{2}} I_0 e^{\pm i \phi} \sin \omega_{RF} t \]  

\[ U_{fid} I_0 U_{fid}^\dagger = I_0 \]

\[ U_{fid} I_{\pm 1} U_{fid}^\dagger = I_{\pm 1} e^{\mp i \phi_{fid}} \]  

These equations may now be used to show the importance of coherence pathways in NMR. As an initial example, we will look at an experiment consisting of a 90° pulse with phase \( \phi_1 \) followed by a delay \( t_1 \) followed by a 90° pulse with phase \( \phi_2 \) followed by a delay \( t_1 \) and then acquisition with phase \( \phi_r \). The observed signal may then be calculated using the above equations (2.62). Our initial density matrix will be \( I_0 \). This evolves during the first pulse into the following coherences (or states).

\[ I_0 \xrightarrow{90^\circ, \phi_1} \frac{i}{\sqrt{2}} \left( I_{\pm 1} e^{-i \phi_1} + I_{-1} e^{i \phi_1} \right) \]  

This state will continue to evolve under the FID Hamiltonian for a period \( t_1 \) giving the following result.
\[
\frac{i}{\sqrt{2}} \left( I_{+1} e^{-i\phi_1} + I_{-1} e^{i\phi_1} \right) \quad \xrightarrow{\text{FID}} \quad \frac{i}{\sqrt{2}} \left( I_{+1} e^{-i(\phi_1 + \omega \text{fid}_1 t_1)} + I_{-1} e^{i(\phi_1 + \omega \text{fid}_1 t_1)} \right)
\] (2.64)

The 90° pulse is then applied, which gives the result below.

\[
\left\{ \begin{array}{c}
\frac{i}{\sqrt{2}} I_{+1} e^{-i(\phi_1 + \omega \text{fid}_1 t_1)} \\
+ \frac{i}{\sqrt{2}} I_{-1} e^{i(\phi_1 + \omega \text{fid}_1 t_1)}
\end{array} \right\} \xrightarrow{90_{42} \text{w}} \left\{ \begin{array}{c}
\frac{i}{2\sqrt{2}} I_{+1} \left( e^{-i(\phi_1 + \omega \text{fid}_1 t_1)} - e^{i(\phi_1 + \omega \text{fid}_1 t_1 - 2\phi_2)} \right) \\
+ \frac{i}{\sqrt{2}} I_{-1} \left( e^{i(\phi_1 + \omega \text{fid}_1 t_1)} - e^{-i(\phi_1 + \omega \text{fid}_1 t_1 - 2\phi_2)} \right) \\
- \frac{1}{2} I_0 \left( e^{-i(\phi_1 + \omega \text{fid}_1 t_1 - \phi_2)} - e^{i(\phi_1 + \omega \text{fid}_1 t_1 - \phi_2)} \right)
\end{array} \right\}
\] (2.65)

This density matrix will then evolve for a second \( t_1 + t_2 \) period, at which point we can calculate the observable signal in \( t_2 \) (as detection occurs from \( t_2 = 0 \) on). Since evolution under the FID Hamiltonian does not result in any transfer of coherence between different density matrix states (for example \( I_{-1} \) to \( I_{+1} \)), the only coherence we need consider is the \( I_{-1} \) contribution (all others produce a trace of zero with our observable).

\[
\frac{i}{2\sqrt{2}} I_{-1} \left( e^{i(\phi_1 + \omega \text{fid}_1 t_1)} - e^{-i(\phi_1 + \omega \text{fid}_1 t_1 - 2\phi_2)} \right) \quad \xrightarrow{\text{FID}} \quad \frac{i}{2\sqrt{2}} I_{-1} e^{i\omega \text{fid}_2 t_2} \left( e^{i(\phi_1 + 2\omega \text{fid}_1 t_1)} - e^{-i(\phi_1 - 2\phi_2)} \right)
\]

\[
S(t_1, t_2) = \frac{i}{2\sqrt{2}} \left( e^{2i\omega \text{fid}_1 t_1} e^{i(\phi_1 - \phi_2)} - e^{-i(\phi_1 - 2\phi_2 + \phi_r)} \right) e^{i\omega \text{fid}_2 t_2} \text{ tr}[I_{-1} I_{+1}]
\] (2.66)

This signal shows two components. The upper component is the signal coming from direct evolution after the initial 90° pulse (notice that the \( t_1 \) dependence is identical to one where there is no second pulse). The lower component is the echo signal (notice it has no \( t_1 \) dependence) coming from the second pulse. If we try to acquire a spectrum which contains only the echo signal, using only a single set of pulse and receiver phases will not cancel the unwanted component. Suppose now, we add together the signal from four different experiments where the phases of the pulses and receiver \((\phi_1, \phi_2, \phi_r)\) consist of the
following four sets \( \{(0,0,0),(90,0,270),(180,0,180),(270,0,90)\} \) (given in units of degrees). Adding together the four signals will produce the following result.

\[
S(t_1,t_2) = -\frac{i}{4\sqrt{2}} e^{\frac{i\omega}{2} t_1} \left( e^{2i\omega \phi_2} \left( e^0 + e^{-i\pi} + e^0 + e^{i\pi} \right) - \right) \left( e^0 + e^{-2i\pi} + e^{-2i\pi} + e^{-2i\pi} \right) = \frac{i}{\sqrt{2}} e^{i\omega \phi_2} \left( -\sin \omega_{fid} t_2 + i \cos \omega_{fid} t_2 \right)
\]

These phases choose only the coherence pathway that we desire, that is the echo signal. The phase cycle was arrived at by setting the net phase of the evolved signal equal to zero, which for this sequence was \( \phi_1 - 2\phi_2 + \phi_r = 0 \). This equation tells us the mathematical relationship between the phases. However, it does not tell us how many different phases each pulse must be cycled through to remove artifacts. This is actually an old and difficult question which I will not answer completely. The partial answer to this question can be seen in the formula for the signal. The upper signal came from a density matrix element that is proportional to \( I_{+1} \) in both \( t_1 \) periods while the lower signal came from a density matrix that was proportional to \( I_{+1} \) in the first \( t_1 \) period and \( I_{-1} \) in the second. Graphically, this is shown in figure 2.2 where the bold line denotes the coherence pathway of the echo signal and the dashed line represents the coherence pathway of the un-
wanted one pulse signal. This formalism was first put forth by both Bain\textsuperscript{36} and Bodenhausen et al.\textsuperscript{37} and is discussed quite thoroughly in Ernst's book on multidimensional NMR.\textsuperscript{7} In figure 2.2, the density matrix elements are labeled as coherences, in this case +1, 0 and −1; these are often assigned the variable name $p$ and a transfer of coherence between levels is written as $\Delta p$. The coherence pathway for an experiment may be written as a vector $\mathbf{\Delta p} = (\Delta p_1, \Delta p_2, \Delta p_3, \ldots, \Delta p_n)$ of $n$ $\Delta p_i$ elements where $n$ is the number of pulses. The 90°-90° echo experiment may be written (+1, −2). It has been shown in the above references that when a pulse is independently cycled through $m$ phases $\left(0, \frac{2\pi}{m}, \frac{2\pi}{m}, \ldots, \frac{2(m-1)\pi}{m}\right)$, this cycle leads to selection of a specific $\Delta p_i$ and additionally $\Delta p_i \pm (m-1)$, $\Delta p_i \pm 2(m-1)$, etc. In our experiment, the quadrature of our receiver will automatically select only the −1 pathway in $t_2$. Therefore by guaranteeing that the first evolution period is a +1 coherence, we can assure that we observe only the signal we want. It is obvious that using only 2 phases for the first pulse will leave both $\Delta p_1$ of +3, +1, −3 and −1. The +3 and −3 coherence transfers are harmless since the density matrix can only have coherence between +1 and −1 for our system. The −1 coherence transfer is a serious problem and indicates that the unwanted (−1,0) pathway will survive. However, a phase cycle of 3 will result in $\Delta p_1$ of +4, +1, and −2. None of the unwanted (+4 and −2) coherence transfers will produce any observable signal. In the phase cycle for the experiment given earlier, we could have used

$$\{(0,0,0),(120,0,240),(240,0,120)\},$$  \hspace{1cm} (2.68)

however this would necessitate 120° phase shifts which can be difficult on some spectrometers (especially in the receiver phase cycle). This same sort of analysis can be applied to more complex pulse sequences and at the appropriate locations, I will point out the reasoning behind the phase cycles for the experiments used in this thesis. For further information on phase cycling, the previously mentioned references will provide a good starting point as well as additional references contained therein.
Eigenvalues from static samples

The eigenvalues from both the chemical shift and quadrupolar Hamiltonians have already been discussed. However, all of our expressions are in terms of zero and second rank spatial tensors $A_{lm}^{\lambda}$. These spatial tensors are highly dependent on the orientation of the principal axis system (PAS) of a crystallite with respect to the magnetic field (see equations 2.35 and 2.40. Under static (time-independent) conditions, both the quadrupolar and chemical shift energy levels can be calculated explicitly as functions of PAS orientation. Looking first at the chemical shift interaction, we expand $A_{20}^{CS}$ below.

$$A_{20}^{CS} = \sum_{m=-2}^{2} D_{m,0}^{(2)} (\alpha^{CS}, \beta^{CS}, \gamma^{CS}) \rho_{2m}^{CS}$$

$$= \sqrt{\frac{3}{2}} \left[ d_{00}^{(2)} (\beta^{CS}) + \frac{n_{CS}}{J_{c}} e^{-2i\alpha^{CS}} d_{20}^{(2)} (\beta^{CS}) + \right]$$

$$= \sqrt{\frac{3}{2}} \left[ \frac{3\cos^{2} \beta^{CS} - 1}{2} + \frac{n_{CS}}{2} \cos 2\alpha^{CS} \sin^{2} \beta^{CS} \right]$$

This yields energy eigenvalues given below.

$$\Delta E_{m \rightarrow m-1}^{CSA} = \hbar \omega l \left( \delta_{i,\alpha cs} + \delta^{CS} \left[ \frac{3\cos^{2} \beta^{CS} - 1}{2} + \frac{n_{CS}}{2} \cos 2\alpha^{CS} \sin^{2} \beta^{CS} \right] \right)$$

For a quadrupolar nucleus, the first-order quadrupolar eigenvalues are derived in a similar fashion, since they are proportional to $A_{20}^{Q}$. The final result for the first-order quadrupolar contribution to the energy splitting is given below in equation 2.62.

$$\Delta E_{m \rightarrow m-1}^{(1)Q} = \frac{3e^{2} q Q}{4I(I+1)} (2m - 1) \left[ \frac{3\cos^{2} \beta^{Q} - 1}{2} + \frac{n_{Q}}{2} \cos 2\alpha^{Q} \sin^{2} \beta^{Q} \right]$$

$$= \frac{\hbar C_{Q}}{4I(I+1)} (2m - 1) \left[ \frac{3\cos^{2} \beta^{Q} - 1}{2} + \frac{n_{Q}}{2} \cos 2\alpha^{Q} \sin^{2} \beta^{Q} \right]$$

$$C_{Q} = \frac{e^{2} q Q}{\hbar}$$

Figure 2.3 shows the energy level diagram for a spin 3/2 nucleus for a single orientation of the quadrupolar PAS in the absence of chemical shift anisotropy. As was pointed out
earlier, for the central transition (where \( m = 1/2 \) in the above expression) there is no first-order quadrupolar contribution to the energy splitting.

![Diagram of Zeeman and Quadrupolar Energy Splitting for I=3/2 nucleus.](image)

In the case of the central transition, we must also include the second-order quadrupolar correction to the energy splitting as well. This is more difficult to calculate, as the spatial dependence is the sum of two terms. We can first look at the product \( A_{21}^0 A_{2-1}^0 \) by explicitly calculating \( A_{21}^0 \) and \( A_{2-1}^0 \).

\[
A_{21}^0 = \sum_{m=-2}^{2} D_{m,1}^{(2)}(\alpha^Q, \beta^Q, \gamma^Q) \rho_{2,m}^Q
\]

\[
= \sqrt{\frac{3}{2}} \left[ d_{0,1}^{(2)}(\beta^Q)e^{-i\gamma^Q} + \frac{n_0}{\sqrt{6}} d_{2,1}^{(2)}(\beta^Q)e^{-i\gamma^Q - 2i\alpha^Q} \right] \\
= \sqrt{\frac{3}{2}} e^{-i\gamma^Q} \left[ \sqrt{\frac{5}{8}} \sin 2\beta^Q + \frac{n_0}{\sqrt{6}} i\sin 2\alpha^Q \sin \beta^Q \right]
\]

(2.72)
\[ A_{2-1}^Q = -\sqrt{\frac{3}{2}} e^{i\gamma_Q} \begin{bmatrix} \sqrt{\frac{3}{8}} \sin 2\beta_Q - \frac{n_0}{\sqrt{6}} i \sin 2\alpha_Q \sin \beta_Q \\ -\frac{n_0}{\sqrt{6}} \cos 2\alpha_Q \cos \beta_Q \sin \beta_Q \end{bmatrix} \] (2.73)

Multiplying these together gives \( A_{21}^Q A_{2-1}^Q \).

\[ A_{21}^Q A_{2-1}^Q = -\frac{1}{16} \begin{bmatrix} 9 \sin^2 2\beta_Q + n_0^2 \cos^2 2\alpha_Q \sin^2 2\beta_Q - 3 \eta Q \cos 2\alpha_Q \sin^2 2\beta_Q & 4n_0^2 \sin^2 2\alpha_Q \sin^2 \beta_Q \\ 3n_0 \cos 2\alpha_Q \sin^2 2\beta_Q & 4 \eta Q \sin^2 2\alpha_Q \sin^2 \beta_Q \end{bmatrix} \] (2.74)

Likewise, we can calculate the product \( A_{22}^Q A_{2-2}^Q \) from \( A_{22}^Q \) and \( A_{2-2}^Q \).

\[ A_{22}^Q = \sqrt{\frac{3}{2}} e^{-2i\gamma_Q} \begin{bmatrix} \sqrt{\frac{3}{8}} \sin^2 \beta_Q - \frac{n_0}{2\sqrt{6}} i \sin 2\alpha_Q \cos \beta_Q \\ \frac{n_0}{2\sqrt{6}} \cos 2\alpha_Q (1 + \cos^2 \beta_Q) \end{bmatrix} \] (2.75)

\[ A_{2-2}^Q = \sqrt{\frac{3}{2}} e^{i\gamma_Q} \begin{bmatrix} \sqrt{\frac{3}{8}} \sin^2 \beta_Q + \frac{n_0}{2\sqrt{6}} i \sin 2\alpha_Q \cos \beta_Q \\ \frac{n_0}{2\sqrt{6}} \cos 2\alpha_Q (1 + \cos^2 \beta_Q) \end{bmatrix} \] (2.76)

\[ A_{22}^Q A_{2-2}^Q = \frac{3}{16} \begin{bmatrix} \frac{n_0^2}{12} \cos^2 2\alpha_Q (1 + \cos^2 \beta_Q)^2 & + \\ n_0 \cos 2\alpha_Q (1 + \cos^2 \beta_Q) \sin^2 \beta_Q & + \\ \frac{n_0^2}{3} \sin^2 2\alpha_Q \cos^2 \beta_Q + 3 \sin^4 \beta_Q & + \end{bmatrix} \] (2.77)

The sum, \( 2 A_{21}^Q A_{2-1}^Q + A_{22}^Q A_{2-2}^Q \), may be written in terms of products of \( \cos 2i\alpha \) and \( \cos 2j\beta \) where the coefficients \( a_{ij} \) are given in table 2.2.

\[ 2 A_{21}^Q A_{2-1}^Q + A_{22}^Q A_{2-2}^Q = \frac{1}{8} \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} \cos 2i\alpha_Q \cos 2j\beta_Q \] (2.78)

The energy splitting correction from the second-order quadrupolar effect is then given by equation 2.70.

\[ \Delta E_{1/2}^{(2Q)} \rightarrow -\frac{1}{2} = \frac{\epsilon^2 g_Q^2}{32I^2 (2I-1)^2 \lambda_{01}^2} \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} \cos 2i\alpha_Q \cos 2j\beta_Q \] (2.79)

\[ = \frac{\hbar C_Q^2 (I(I+1)-\frac{1}{2})}{32I^2 (2I-1)^2 \lambda_{01}^2} \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} \cos 2i\alpha_Q \cos 2j\beta_Q \]

This energy splitting is shown for a single crystallite orientation in figure 2.3.
Table 2.2 Cosine Expansion Coefficients. The $a_{ij}$ coefficients are used in the expansion of the anisotropic portion of the second-order quadrupolar interaction in equation 2.70.

The total energy splitting, including both chemical shift and quadrupolar contributions, under free precession in a high magnetic field may then be given by equation 2.80.

$$
\Delta E_{m \rightarrow m-1} = h\omega_I + \Delta E_{m \rightarrow m-1}^{\text{CSA}} + \Delta E_{m \rightarrow m-1}^{(1Q)} + \Delta E_{m \rightarrow m-1}^{(2Q)}
$$

It is important to note that in a powder sample, where all orientations of crystallites are present, there exists a continuous distribution of energy splittings corresponding to each individual PAS orientation. This is in contrast to a liquid sample where the rapid motion averages out all orientational dependence of the energy splitting.

Eigenvalues from Rotating Samples

In the previous section, the expression for the free precession energy splitting was derived. This expression has multiple terms which have anisotropic (orientational) dependences. One of the primary goals of solid state NMR is to acquire spectra which look like liquid-state spectra. The goal of high-resolution isotropic spectra has been approached primarily from two direction. The first is the averaging of anisotropic interaction by averaging the spin operator tensors with multiple-pulse schemes. These techniques work quite well for dipolar interactions (see Haeberlen’s book for a more complete review of this subject\textsuperscript{38}). However, for Hamiltonians such as the truncated chemical shift and quadrupolar interactions, multiple-pulse experiments can only average the anisotropic
removing the spatial tensors with time dependent spatial trajectories which approximate isotropic motion. The technique of magic-angle spinning is the most important of these time dependent trajectories. In the magic-angle spinning (MAS) experiment, the sample is rotated rapidly (>4 kHz) about an axis oriented at the angle \( \theta_m = \cos^{-1}(1/\sqrt{3}) \approx 54.74^\circ \) with respect to the magnetic field. This has the effect of introducing a time dependence for a general spinning angle to the spatial tensors \( A_{lm}^\lambda \) given in equation (2.72).

\[
A_{lm}^\lambda = \sum_{n=-l}^{l} \sum_{m'=-l}^{l} D_{nm}^{(l)}(\omega, \mu, \theta, \phi)D_{m'n}^{(l)}(\alpha, \beta, \gamma)\varphi_{lm'}^\lambda
\]  

(2.81)
The $\lambda$ in this expression refers to either the chemical shift, quadrupolar or dipolar interactions. The Euler angles which define the first rotation are $\theta$, the spinning axis angle and $\omega t$, the time dependent rotation angle. These rotations, along with the usual PAS rotations are shown in figure 2.4. When rotation is sufficiently rapid (i.e. $\omega_r > \omega_l \delta^{CSA}$ or $\omega_r > \omega_Q^2 / \omega_l$), the time dependent ($n \neq 0$ in equation 2.81) terms may be ignored (since they will average to zero) and only the time independent terms remain.

$$A_{lm}^\lambda = d_{0m}^{(l)}(\theta) \sum_{m'} (-1)^l D_{m',0}^{(l)}(\alpha^\lambda, \beta^\lambda, \gamma^\lambda) \rho_{lm'}^\lambda$$

(2.82)

For the chemical shift interaction, the important spatial tensor is $A_{20}^{CS}$. In this case, equation 2.82 may be expanded below.

$$A_{20}^{CS} = \sqrt{2} \left( \frac{3 \cos^2 \theta - 1}{2} \right) \left[ \frac{(3 \cos^2 \theta - 1) + \eta_{CS}^2 \cos 2\alpha^{CS} \sin^2 \beta^{CS}}{2} \right]$$

$$\Delta E_{m \rightarrow m-1}^{CSA} = h \omega_l \left[ \delta_{isac} + \delta^{CS} \left( \frac{3 \cos^2 \theta - 1}{2} \right) \left[ \frac{(3 \cos^2 \theta - 1) + \eta_{CS}^2 \cos 2\alpha^{CS} \sin^2 \beta^{CS}}{2} \right] \right]$$

(2.83)

The only difference between this expression and the previous static expression is the second-order Legendre polynomial ($P_2[\cos \theta]$) scaling factor. The choice of the magic-angle is now apparent, since this angle is the one which makes the second-order Legendre polynomial zero and eliminates the anisotropic portion of the chemical shift interaction. Likewise, it can be shown that magic-angle spinning can also remove the effects of both homonuclear and heteronuclear dipolar coupling (both of which have a spatial dependence which can be represented as a single second-order tensor). For the quadrupolar interaction, this same analysis holds for the first-order effect when the spinning rate is larger than the quadrupolar coupling constant.

$$\Delta E_{m \rightarrow m-1}^{(1Q)} = \frac{3 e^2 q Q}{4 I (2I-1)} (2m - 1) \left[ \frac{3 \cos^2 \theta - 1}{2} \right] \left[ \frac{(3 \cos^2 \theta - 1) + \eta_Q^2 \cos 2\alpha^Q \sin^2 \beta^Q}{2} \right]$$

(2.84)
In practice, this may only be observed for nuclei in highly symmetric environment (for example $^{23}\text{Na}$ in NaCl or $^{79}\text{Br}$ and $^{81}\text{Br}$ in KBr) or with a very small nuclear quadrupolar moment (such as the spin 3/2 nuclei $^{7}\text{Li}$ and $^{133}\text{Cs}$). Even for these nuclei, spinning sidebands which arise from the time dependent terms are often observed. For quadrupolar nuclei with a large quadrupolar coupling only the central transition is observable (and excitable as well), which has no first-order quadrupolar contribution to the orientation dependence of the energy splitting. The second-order quadrupolar correction does, in fact, show strong orientational dependence. Under fast spinning conditions, just as before, the time dependent contribution to the $A_{21}^{Q}A_{2}^{Q}-A_{2}^{Q}A_{2}^{Q}$ and $A_{22}^{Q}A_{2}^{Q}-A_{2}^{Q}A_{2}^{Q}$ products may be ignored. As before we may calculate the individual contributions $A_{21}^{Q}A_{2}^{Q}$ and $A_{22}^{Q}A_{2}^{Q}$.

$$A_{2m}^{Q}A_{2-m}^{Q} = \sum_{j=-2}^{2} \sum_{k=-2}^{2} D_{i,m}^{(2)}(\omega, \tau, \theta, 0) D_{k,j}^{(2)}(\alpha^{Q}, \beta^{Q}, \gamma^{Q}) \rho_{2k}^{Q} \times$$

$$\sum_{n=-2}^{2} \sum_{p=-2}^{2} D_{n,m}^{(2)}(\omega, \tau, \theta, 0) D_{p,n}^{(2)}(\alpha^{Q}, \beta^{Q}, \gamma^{Q}) \rho_{2p}^{Q}$$

(2.85)

The removal of the time dependent terms is more difficult, since the product must be expanded completely before dropping the time dependent terms. This eliminates all of the terms except those where $j + n = 0$. As has been shown earlier by Mueller\textsuperscript{15}, the spatial sum may be written as a sum of cosines of the PAS Euler angles $\alpha^{Q}$ and $\beta^{Q}$ in equation 2.77.

$$2A_{21}^{Q}A_{2}^{Q} + A_{22}^{Q}A_{2}^{Q} = \frac{1}{8} \sum_{i=0}^{2} a_{ij}^{'} \cos 2i\alpha^{Q} \cos 2j\beta^{Q}$$

(2.86)

Note that the coefficients $a_{ij}^{'}$ are now defined as

$$a_{ij}^{'} = a_{ij}^{(0)} + a_{ij}^{(2)} P_{2}[\cos \theta] + a_{ij}^{(4)} P_{4}[\cos \theta]$$

(2.87)

where the fourth-order Legendre polynomial $(P_{4}[\cos \theta])$ is given in equation 2.88.
\[ P_4[\cos \theta] = \frac{1}{8} \left( 35 \cos^4 \theta - 30 \cos^2 \theta + 3 \right) \] (2.88)

Each component of \( a'_{ij} \) is defined in table 2.3.

The formulas for the energy eigenvalues under rapid spinning conditions given in equations 2.84 (first-order quadrupolar), 2.86 (second-order quadrupolar) and 2.83 (chemical shift anisotropy) all show both spinning angle and orientational dependence. These dependences manifest themselves in the form of inhomogeneous broadening of the NMR line for powder samples. In the next section, the actual lineshapes resulting from a powder average for the various interactions will be shown. The effect of incomplete averaging due to spinning will be discussed in a later section (see chapter 3).

<table>
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<th>( j )</th>
<th>( a^{(0)}_{ij} )</th>
<th>( a^{(2)}_{ij} )</th>
<th>( a^{(4)}_{ij} )</th>
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<td>(-\frac{12}{7} \left( 1 - \frac{1}{3} \eta_Q^2 \right))</td>
<td>(\frac{81}{1720} \left( 18 + \eta_Q^2 \right))</td>
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<td>0</td>
<td>(-\frac{36}{7} \left( 1 - \frac{1}{3} \eta_Q^2 \right))</td>
<td>(\frac{9}{56} \left( 18 + \eta_Q^2 \right))</td>
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<td>0</td>
<td>0</td>
<td>(\frac{9}{32} \left( 18 + \eta_Q^2 \right))</td>
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<td>0</td>
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<td>(\frac{81}{56} \eta_Q)</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>(\frac{9}{32} \eta_Q^2)</td>
</tr>
</tbody>
</table>

Table 2.3 Coefficients in Anisotropic Cosine Expansion for the 2nd-Order Quadrupolar Correction Under Fast Spinning Conditions.

**Lineshape simulations**

In the absence of spinning, the static eigenvalue equations may be used to obtain the theoretical spectra observed from both spin 1/2 and quadrupolar nuclei. In all cases where a powder sample is simulated the assumptions are the same. First, all orientations
of the crystallite PAS are equally probable (there is no sample alignment or preferential
gometry of the crystallites in the powdered sample). Second, all orientations of the crys-
tallite PAS are present in the sample. Third, the contribution from each crystallite to the
spectrum will be equal. With these three rules, we can construct a powder averaged
spectrum for a static or rotating sample. Mathematically, the process of calculating the
intensity at a given frequency (or energy) is equivalent to doing the following integration
over the sample.

\[ I(\omega) = \int_0^{2\pi} \int_0^\pi \delta(h\omega - \Delta E(\alpha, \beta)) \sin \beta \ d\beta \ d\alpha \]  

(2.89)

In this expression, the \( \sin \beta \) scaling factor is included when converting an integral over a
unit sphere in Cartesian coordinates to spherical coordinates, to maintain a constant
\( d\beta \ d\alpha \) solid angle. Also, the Dirac delta function is defined below.

\[ \delta(a-b) = \begin{cases} 
0 & \rightarrow a \neq b \\
1 & \rightarrow a = b 
\end{cases} \]  

(2.90)

This formula may then be used to create a spectrum by performing the integrals for each
frequency within the sweepwidth of the spectrum. (We will also use equation 2.90 later
in chapter 3 when calculating spinning sideband positions and intensities.) Spectra simu-
lated in this fashion are shown in figure 2.5 for static spin 1/2 nuclei and quadrupolar nu-
clei.

It may be seen that the central transition goes off scale in the first-order
quadrupolar spectrum in figure 2.5. This is because, in the absence of chemical shift
anisotropy or dipolar broadening, the central transition has no first-order broadening. In
the second order quadrupolar spectrum, none of the satellite (outer) transitions are shown,
as they are of negligible intensity in the sweepwidth shown.
This method of simulating spectra works equally well for spinning samples. In figure 2.6, the high speed magic-angle spinning spectra of samples with identical parameters as in figure 2.5 are simulated. The spectrum of the spin 1/2 nucleus is completely averaged into a single narrow line under MAS. This is expected, as all of the anisotropic contribution to the energy splitting is averaged to zero. The second-order quadrupolar MAS spectrum, however, is still quite complex and only about a factor of 3 narrower than the static spectrum. This is expected as well since the second and fourth-order Legendre
polynomials never simultaneously approach zero. In fact, this demonstrates the basic

![Figure 2.6 MAS CSA (a) and 2nd Order (b) Quadrupolar Lineshapes.](image)

Figure 2.6 MAS CSA (a) and 2nd Order (b) Quadrupolar Lineshapes. The simulation parameters are identical to those in figure 2.6. Notice that while the chemical shift anisotropy is completely averaged by MAS, the 2nd order quadrupolar interaction is only slightly reduced (about a factor of 3) from the static simulation.

problem in observing the central transition of quadrupolar nuclei. There is no single spinning axis which completely removes all of the anisotropic broadening to yield a liquid-like spectrum (analogous to MAS for spin 1/2 nuclei). In figure 2.7, variable-angle spinning (VAS) spectra are shown for a variety of spinning angles and quadrupolar asymmetry parameters $\eta_Q$ showing the range of both shoulder and singularity locations.
A problem with the previously mentioned simulation scheme is the speed at which spectra can be simulated. If we wish to use a least squares minimization approach to simulating chemical shift and quadrupolar broadened spectra, the aforementioned method is too slow. A slightly faster method is to divide the overall sweep width into $N$

![Figure 2.7 Quadrupolar VAS Spectra. All spectra are simulated assuming fast spinning limit and constant $C_Q$ and variable angle $\theta$ and $\eta_Q$.](image)

bins. The angles $\alpha$ and $\beta$ are then looped over their integration limits in small step sizes and the frequency at each point is calculated. The scaling factor, $\sin \beta$, intensity is then added to the appropriate frequency bin for this point. In this method, a large number of steps (often over 200 for each angle) must be taken for both $\alpha$ and $\beta$ to obtain spectra.
with correct intensities across the spectrum. Using interpolation to divide the intensity between bins for frequencies which fall between two bin positions fails to give significantly better results (this type of interpolation can reduce the number of steps by perhaps factor of 2).

A second method developed by Alderman et al.\textsuperscript{41} is a much more efficient scheme for calculating powder spectra. In this approach, the surface of a unit sphere (over which integration is performed) is collapsed onto an enclosed octahedron. The advantage of an octahedron is that the face may be divided into a large number of triangles (rather than curved rectangles on a sphere). The first advantage is that it is much easier to interpolate over three points (arising from the division of the surface into triangles) than four (which occurs when the two euler angles $\alpha$ and $\beta$ are stepped in regular steps as in the first method). The second advantage is that the surface may be parameterized into three rational numbers (by dividing each edge of the octahedron into some integer number of segments and counting with integers along each edge) representing the x, y and z coordinates. The formula for these coordinates are linear rather than quadratic in the case of a sphere. The third advantage is that the calculation of sines and cosines is simplified, as it merely ratios of surface coordinates rather than actual calculation of trigonometric functions. Computer programs which utilize these algorithms are discussed and shown in the appendix.