NUCLEAR SPIN RELAXATION OF
POLYCRYSTALLINE 129 XENON

by

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ABSTRACT

Through spin exchange optical pumping, it is possible to achieve upwards of 30% nuclear spin polarization in $^{129}\text{Xe}$ with an NMR signal enhancement of some 5 orders of magnitude over typical thermal signals. Hyperpolarized $^{129}\text{Xe}$ has thus found application in several leading-edge technologies. At 1 T and 4.2 K, the characteristic relaxation time of enriched polycrystalline $^{129}\text{Xe}$ (86% $^{129}\text{Xe}$, 0.1% $^{131}\text{Xe}$) is well over 200 hrs, sufficient for long-term storage and transport.

Longitudinal nuclear spin relaxation of $^{129}\text{Xe}$ at more convenient fields from 1 to 200 G is studied in detail. Significant structure in relaxation times vs. magnetic field is seen; the most prominent new finding being a sharp local long-time $T_1$ maximum of 1000 mins at $\approx 3$ G. Such structure has not been observed in previous measurements of natural Xe. Below temperatures of 10 K, relaxation can be attributed to cross relaxation with $^{131}\text{Xe}$, mediated by spin diffusion. Measurements of $^{129}\text{Xe}$ relaxation as a function of magnetic field, temperature and Xe isotopic content are reported and compared with expected theoretical behaviors.

It is seen that the characteristic nuclear spin relaxation of enriched $^{129}\text{Xe}$ at 4.2 K is nonexponential at these low fields. For fields between 10 G and 200 G, these nonexponential relaxation curves can be fit well with a specific spin diffusion model. Below 10 G no such fit is possible and thus quantum mechanical details of the coupling between $^{129}\text{Xe}$, $^{131}\text{Xe}$ and the bulk lattice are considered. These findings support the hypothesis that cross relaxation with $^{131}\text{Xe}$ is indeed a dominant actor in the nuclear spin relaxation of polycrystalline $^{129}\text{Xe}$ at such low fields and low temperatures.
To Iris, my wife and friend
    and to my children
Gary, Jessica, Daniel, Anita and Nicolas
    who gave me the reason to carry on
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CHAPTER 1

INTRODUCTION

Truth is a careful suitor, she will reveal herself only to those who truly love her. Such has been the case with the research contained in this dissertation. It all began as a quick investigation into nuclear solid-state cross relaxation between the two stable spin-possessing isotopes of frozen Xe, and it has evolved into a three-year study that, to date, has produced many unexpected and interesting results. Hyperpolarized $^{129}\text{Xe}$, with nuclear spins polarized to tens of a percent, has found fruitful application in many areas of physics, biology and medicine [1, 2]. Consequentially, efficiency in producing such polarization as well as the methods to subsequently preserve it [3, 4, 5, 6] have become fields of intense interest.

With an eye toward preserving the polarization, nuclear relaxation of $^{129}\text{Xe}$ at low fields and low temperatures was studied. It is thought that $^{129}\text{Xe}$ cross relaxation with $^{131}\text{Xe}$ is the sole relaxation mechanism in solid $^{129}\text{Xe}$ at very low temperatures (4 K) [7]. The question naturally arises: “What would happen if the $^{131}\text{Xe}$ were removed?” To answer this question, samples of isotopically enriched $^{129}\text{Xe}$ were obtained and studied. It soon became evident, however, that yet another rich layer of solid-state relaxation physics was being revealed. As an example, it was seen that the relaxation curves for both natural Xe and enriched Xe are clearly nonexponential in this regime. The main emphasis of this dissertation will be to report these new findings, to document the experiments and to attempt to base some of these dependencies on established theory. However, some sections will be dedicated to work done in other areas, such as in the production of hyperpolarized $^{129}\text{Xe}$, the construction of a narrowed infrared laser and a small-animal ventilator used for lung imaging. These are all part of ongoing investigations into the
properties and applications of this hyperpolarized noble gas.

Noble gas nuclear magnetic resonance (NMR) has been of interest for many years now. Yen and Norberg, initiating $^{129}\text{Xe}$ NMR studies in the early 1960s, said, "...the simplicity of the rare-gas solids and liquids makes such measurements of particular interest" [8]. As indicated by its name, xenon is truly "strange stuff." It is mostly inert and yet it possesses a large spinless electron cloud that is notably sensitive to its local environment; this leads to large chemical shifts and large van der Waals interactions with neighbors. These qualities make Xe an especially potent NMR probe into molecular chemical environments. Since it rarely forms chemical bonds, it can act as an ideal observer, radiating back information about the local environments to which it adheres. Furthermore, Xe can be found in gas, liquid and solid phases and it also dissolves into many liquids. In the solid phase, Xe forms an fcc Van der Waals crystalline structure where it is possible to use NMR and nuclear relaxation measurements to probe the relatively weak interactions between neighboring nuclei and their surroundings; as well as to make other sensitive measurements, such as atomic self-diffusion and quadrupole ($^{131}\text{Xe}$) spin-lattice relaxation.

The early NMR measurements of $^{129}\text{Xe}$ made by Warren and Norberg corresponded closely to theory [9, 10], yet they were often tedious due to the long relaxation times and limited purity of the samples. Possibly the largest obstacle was the lack of signal strength. Signal intensity is proportional to the $^{129}\text{Xe}$ polarization as induced by an applied magnetic field. Even at the largest obtainable fields, nuclear spin polarizations are only on the order of $10^{-5}$. The advent of nuclear hyperpolarization promised nuclear polarizations some five orders of magnitude larger than polarizations attainable from even the largest available magnetic fields. This was accomplished with help from Kastler who won the Nobel Prize for demonstrating back in the 1940s that circularly polarized light could be used to produce nonequilibrium polarizations in electronic spins [11]. This process was called "optical pumping."

The first hyperpolarized (HP) noble gas, $^3\text{He}$, was produced by Bouchiat, Carver
and Varnum at Princeton [12] in the early 1960s. Following a suggestion by N.A. Naumann, they utilized the “Overhauser nuclear polarization effect” with optically pumped HP Rb atoms in collisional contact with $^3$He nuclei. In the late 1970s, B.C. Grover was the first to successfully produce hyperpolarized $^{129}$Xe [13] through the same process, this time referred to as “spin exchange.” Many significant advances in the study of hyperpolarized noble gases, both experimental and theoretical, were made in the early 1980s by Happer, Cates and co-workers, also at Princeton [14, 15]. They refined an efficient process by which noble gas nuclei could be hyperpolarized. They called this process “spin exchange optical pumping” (SEOP) [16, 17]. It also utilized spin-exchange collisions between the optically polarized electrons of an alkali metal and the noble gas nuclei. It was shown that very high polarizations of the Rb valence electrons are possible by exposure to resonant (794.7 nm) circularly polarized laser light, where nitrogen gas was introduced to reduce radiation trapping and helium gas introduced to broaden the light absorption spectrum in the low-pressure $^{129}$Xe cells. This process (SEOP) is able to produce polarizations of tens of a percent in both the $^3$He and $^{129}$Xe noble gases.

Thus hyperpolarized noble gases can now produce NMR signal strengths that are many orders of magnitude larger than previously possible. This large nonequilibrium polarization of the nuclei is not dependent on the strength of the applied magnetic field. Thus low-field and long-duration relaxation measurements are feasible. The increased signal sensitivity also allows exploration of much smaller sample sizes and concentrations and thus allows discovery of even more obscure phenomena. This has given birth to many new technologies; some of which probe the most fundamental aspects of nature (e.g., testing the standard model [18], quantum mechanical computing [19]) and complex biological processes [1]. The breadth and richness of the work being done with hyperpolarized $^{129}$Xe is ever increasing. This motivates us even more to better understand the relaxation mechanisms that work to reduce this nonequilibrium polarization.

Much of this present work on nuclear relaxation in solid $^{129}$Xe is an extension of the work done by Michael Gatzke in the early 1990s [7]. Gatzke identified several
relaxation mechanisms in solid Xe, including temperature dependent mechanisms such as vacancy diffusion and the Raman scattering of phonons off nuclear spins. He also investigated the field dependent relaxation mechanism mentioned in the first paragraph, namely cross relaxation between $^{129}$Xe and $^{131}$Xe. Gatzke's exhaustive study produced results that were reasonably consistent with these proposed relaxation mechanisms. A notable gap in his research, however, was in the characterization of $^{129}$Xe relaxation at low fields ($< 200$ G), especially in the regime where the temperature dependent mechanisms are negligible ($< 10$ K).

Our research fills in this gap, but still leaves many unanswered questions. As the fundamental relaxation properties of $^{129}$Xe are discovered, the ability to efficiently produce and store hyperpolarized $^{129}$Xe increases. At liquid helium temperatures and at high fields (1 T), for example, it is possible to preserve the polarization of $^{129}$Xe for weeks ($T_1 > 500$ hrs) [3]. As a storage method, however, it requires large, expensive magnets. It is the intent of the research outlined in this thesis to shed light on the low field, low temperature relaxation mechanisms, making it possible to store hyperpolarized $^{129}$Xe at cheaper, smaller fields for longer periods of time.

In Chapter 2, longitudinal nuclear spin relaxation is defined and explored theoretically. This is done developmentally from first principles. First, the spin dynamics of a $^{129}$Xe nucleus in the presence of electromagnetic fields is described. This knowledge is then used to explore the methods used to detect $^{129}$Xe and $^{131}$Xe polarization. Then the dynamics of $^{129}$Xe nuclear spins in the presence of other nuclei is developed. Finally, based on this foundation, nuclear relaxation is addressed directly and hypotheses drawn from the expected theoretical behavior.

Chapter 3 focuses solely on experimental procedures and experimental results. Sections giving detailed accounts of the experimental procedures are interleaved with sections that present the results of the experiment performed. Four major experiments are so presented and some previously unexpected new findings are shown.

In Chapter 4, a detailed analysis of the experimental results is presented and some conclusions drawn. A macroscopic spin-diffusion model is developed that is
shown to fit the data and elucidate the expected behavior of nuclear relaxation on the surface of crystallites in a polycrystalline sample. In Chapter 5 a brief summary and some clear, concise conclusions are presented. This final chapter ties together the theory and results to form a consistent, but still incomplete, picture of the relaxation mechanisms in polycrystalline $^{129}$Xe at low temperatures and at low fields.
CHAPTER 2

NUCLEAR RELAXATION THEORY

2.1 Introduction

In the most general sense, longitudinal nuclear spin relaxation (nuclear relaxation) is a process by which a system of nuclear spins comes to thermal equilibrium with its environment through the exchange of angular momentum and energy. In order to observe such relaxation in a spin system, the system’s magnetization is periodically measured during this process. The magnetization is proportional to the sum of the $n$ individual spin angular momenta of the nuclei in the system, $\tilde{M} \propto \sum_n \langle \hat{I}_n \rangle$. As a matter of convention, it is common to define the direction of the magnetization to be along the $\hat{z}$ axis parallel to an externally applied magnetic field. Therefore, the magnetization projected along this longitudinal direction ($M_z$) is an observable of interest.

The phenomenological Bloch equations [21] distinguish between the longitudinal and transverse components of nuclear relaxation by the use of two single-exponential time constants. The characteristic time at which the longitudinal magnetization approaches equilibrium is defined as “$T_1$” and the characteristic time at which the transverse magnetization approaches equilibrium is defined as “$T_2$”. As discussed in section 2.2.2, the component of the magnetization in the transverse plane is continually precessing around the applied field. It will eventually decay due to the dynamic dephasing of the individual spin precession angles. The precession frequencies are slightly different from nucleus to nucleus due to the variation between local or applied fields throughout the sample. If external or applied field inhomogeneities dominate the inherent local field inhomogeneities, the resulting shortened characteristic transverse decay time is often written as “$T_2^*$”. In this dissertation, however, longitudinal nuclear spin relaxation will be the primary
observable of interest; it will henceforth be called simply nuclear relaxation and the orientation of the applied field will define both the longitudinal direction and the quantization axis. As will be seen, the longitudinal relaxation does not necessarily need to be monoexponential and in general cannot be characterized by a single characteristic constant, $T_1$.

The case where the applied field is brought adiabatically to near zero will be mentioned only briefly at this point, being that at times in the experimental procedure the nuclear systems were exposed to small fields as they were transferred through the laboratory environment. At applied fields comparable to or smaller than the local fields existing in the immediate environment of the nuclei, the universal quantization axis and even the orientation of the longitudinal direction becomes ill-defined. The entropy of the nuclear spin system, however, is preserved in the form of dipolar spin order [20]. Assuming that the total system entropy stays constant while at near-zero field then adiabatic restoration of the larger applied field will also restore the original Zeeman order and thus the net magnetization $M_z$ of the nuclear spin system.

A theoretical framework will be established in order to provide a basis for the physical processes involved in nuclear relaxation. The pertinent theory will be discussed and the relations that govern the expected behavior will be presented. In particular, matrix representations for various quantum operators will be found. Such matrix representations will later be of use both in interpreting theoretical results and in numerically diagonalizing the Hamiltonian where perturbation theory is not applicable.

It is crucial, when considering nuclear spin relaxation, to understand the behavior of a nucleus in the presence of electromagnetic (EM) fields. A nucleus is modeled as a point mass that possesses both charge distribution and spin angular momentum. This nuclear spin, represented by the quantum operator $\hbar \vec{I}$, induces a magnetic moment, $\vec{\mu}$, which is assumed to be parallel to and proportional to the angular momentum:

$$\vec{\mu} = \gamma \hbar \vec{I}$$ (2.1)
where the scalar, $\gamma$, is the gyromagnetic ratio. In xenon, the additional spin-
possessing nuclear characteristics are:

$^{129}$Xe: $I = \frac{1}{2}$; $\gamma = -2\pi \cdot 1177.8$ Hz/G; magnetic dipole

$^{131}$Xe: $I = \frac{3}{2}$; $\gamma = 2\pi \cdot 349.17$ Hz/G; magnetic dipole and electric quadrupole.

When exposed to torque-producing EM fields, the spin angular momentum of a
nucleus can be exchanged with its environment. In the solid Xe lattice, the only two
stable isotopes with nonzero spin are $^{129}$Xe and $^{131}$Xe. The conditions that allow
these two isotopes to exchange angular momentum with each other will be discussed
in section 2.5.3. The $^{131}$Xe nuclei possess an additional quadrupole coupling to
the electric field gradients in the lattice and thus will thermalize more readily
with the lattice, as will be outlined in section 2.4.3. Under certain conditions the
$^{131}$Xe become effective relaxation centers for the $^{129}$Xe nuclei, providing a channel
for angular momentum exchange between the $^{129}$Xe nuclei and the lattice. This
cross-relaxation mechanism is considered to be the primary relaxation mechanism
for solid $^{129}$Xe at temperatures below 10 K [7].

Neighboring $^{129}$Xe nuclei may also interchange angular momentum with each
other via dipole-dipole interactions. The nature of like-nuclei spin interchange
preserves the total spin angular momentum of the $^{129}$Xe nuclear spin system and
thus will not cause relaxation. This process, however, does give rise to spin diffusion
(section 2.4.2), which allows inhomogeneous $^{129}$Xe polarization to be re-distributed
throughout the lattice. Ultimately, spin diffusion provides a channel through which
angular momentum can be transported to the effective relaxation centers.

Above temperatures of about 10 K, the Raman scattering of phonons (whose
vibrations modulate the spin-rotation interaction) causes relaxation. At tempera-
atures exceeding 120 K, vacancy hopping (that modulates the dipolar fields) be-
comes energetic enough to cause relaxation in the nuclei. These thermal relaxation
mechanisms will be briefly discussed in section 2.5.2, and were handled in detail in
Gatzke’s Ph.D. dissertation [7].
Note that at the thermal energies present in this experiment ($< 7 \times 10^{-3} \text{ eV}$), it is a very good assumption that all nuclei and electrons are in the ground state. Therefore no excited atomic or nuclear states need be considered.

### 2.2 Background Theory

A given $^{129}\text{Xe}$ nucleus couples to the magnetic field $\vec{H}$ acting on it by means of its magnetic dipole moment. Such a field may be generated by moving charges and spins in its local environment or by externally applied fields. The Hamiltonian for the so-called Zeeman interaction is

$$\mathcal{H}_Z = -\mu \cdot \vec{H} = -\gamma \hbar \vec{I} \cdot \vec{H}. \quad (2.2)$$

The $^{131}\text{Xe}$ nucleus, in addition to the Zeeman interaction, possesses an electric quadrupole moment that couples to local electric field gradients (EFGs), thus adding to the Hamiltonian a quadrupole interaction term [21]

$$\mathcal{H}_Q = \frac{e^2 Q q}{4I(2I-1)} \left( 2I_z^2 - (I_x^2 + I_y^2) + \eta(I_x^2 - I_y^2) \right) \quad (2.3)$$

where the $\hat{z}$ direction is defined to be along a principal axis of the EFG tensor, $eQ$ is the scalar quadrupole moment of the nucleus. Note that only a single quadrupole moment is needed out of the nine entries in the quadrupole tensor due to tight restrictions on the symmetry of the nuclear charge density in a nucleus of definite angular momentum when considering the dependence of energy differences on nuclear orientation; see Slichter [21] Chapter 10. $eq$ represents the $V_{zz}$ (second derivative) component of the electrical potential at the nucleus and $\eta$ is the asymmetry parameter of the electric field gradient which represents the quantity $(V_{xx} - V_{yy})/V_{zz}$.

If it were indeed possible to map out the EM fields everywhere in the lattice then these two Hamiltonians, in theory, would be sufficient to determine the behavior of the spin lattice system. In solid Xe, however, there are significant time-dependent EM fields, both from neighboring nuclei and electron cloud fluctuations that greatly complicate the picture. This makes the full quantum treatment a somewhat intractable multibody problem. One universal internuclear interaction
is the dipole-dipole interaction between the magnetic moments of nuclear spins in the lattice. The dipole-dipole Hamiltonian can be written as [21, 22]

\[ H_D = \frac{\hbar^2 \gamma_k \gamma_l}{r_{kl}^3} \left( \vec{I}_k \cdot \vec{I}_l - 3(\vec{I}_k \cdot \hat{r}_{kl})(\vec{I}_l \cdot \hat{r}_{kl}) \right) \]  \hspace{1cm} (2.4)

where the \( k \) and \( l \) subscripts index two nuclei separated by the vector \( r_{kl} \). Summations over all of the two-particle dipole-dipole interactions are often utilized in the Hamiltonian. For computational purposes, these sums are normally restricted to nearest neighbors since the dipole-dipole interaction falls off rapidly as \( 1/r_{kl}^3 \). The dipole-dipole interaction does not depend on the applied field.

In solid xenon, the dipole-dipole interaction between \(^{129}\)Xe nuclei is comparable to the Zeeman interaction at applied fields under about 0.3 G (section 2.4.2). Since all of the applied fields in this work greatly exceed 0.3 G, the dipole-dipole Hamiltonian can generally be treated as a small perturbation. The \(^{131}\)Xe quadrupole energies, however, due to electric field gradients (EFGs) in the lattice are comparable to \(^{129}\)Xe Zeeman energies up to applied fields of 10 G in the bulk lattice and may be as high as hundreds of Gauss near lattice defects and surface features [9, 23]. Thus it becomes necessary to use direct diagonalization of the Hamiltonian when considering \(^{129}\)Xe interactions with the \(^{131}\)Xe in the lattice and near the surface or defects. With small systems of particles it is possible to do this numerically; as is done in section 2.5.3 to characterize some of the features of \(^{129}\)Xe-\(^{131}\)Xe cross relaxation.

For a large system of spins, however, statistical methods must be employed to find a solution. The principles of thermal physics dictate that a large interacting system of spins will tend to equilibrate at the point where the total system entropy \((\sigma)\) is maximized. At equilibrium, a “spin temperature” can be characterized in the usual thermodynamic sense:

\[ \frac{1}{k_B T} = \left( \frac{\partial \sigma}{\partial U} \right)_{N,V} \]  \hspace{1cm} (2.5)

where \( k_B, U, N \) and \( V \) are Boltzmann’s constant, the system energy, the number of nuclei and the system volume, respectively. This relationship leads quite beautifully to the Boltzmann distribution of energy-state populations at equilibrium.
When the spin system is at equilibrium and can be characterized by a spin temperature, \( T \), then the fractional population of spins, \( n_j \), in the energy level \( E_j \) is expressed by the Boltzmann distribution:

\[
    n_j = \frac{e^{-E_j/k_BT}}{\sum_i e^{-E_i/k_BT}}. \tag{2.6}
\]

The quantum mechanical operator equivalent to this distribution is the “density functional” operator \( \rho \) which at equilibrium is

\[
    \rho = \frac{e^{-\mathcal{H}/k_BT}}{Tr \{ e^{-\mathcal{H}/k_BT} \}}. \tag{2.7}
\]

The density operator, however, has a more general definition which is valid even in situations where spin temperature is not so well defined. It is defined to measure the density of points in phase space for a quantum ensemble [20]. The total entropy of a system \( \sigma \) thus may be defined in terms of the density operator [24]:

\[
    \sigma = -k_B Tr \{ \rho \ln(\rho) \}. \tag{2.8}
\]

The density operator represents an ensemble average over a system with similar interparticle interactions. The expectation value of any quantum observable \( \langle \mathcal{O} \rangle \) in the system may be given by [21]

\[
    \langle \mathcal{O} \rangle = Tr \{ \rho \mathcal{O} \}. \tag{2.9}
\]

Finally, if the system is placed in a nonequilibrium state represented by an initial density operator, subsequent time evolution of this density operator is governed by

\[
    \frac{\partial \rho}{\partial t} = \frac{i}{\hbar} [\rho, \mathcal{H}]. \tag{2.10}
\]

Once the density operator’s matrix elements are known, then Equation (2.9) may be used to predict the time evolution of any ensemble-averaged observable in the system.

This compact reference list of equations and concepts will now be utilized to help explain the expected nuclear relaxation mechanisms for \(^{129}\text{Xe}\) that exist in solid Xe and also to validate the detection methods used to measure nuclear relaxation in this experiment.
2.2.1 Nuclear Spin Dynamics

Nuclear relaxation of $^{129}\text{Xe}$ in the solid occurs only when the $^{129}\text{Xe}$ nuclei can exchange angular momentum with their environment. For $^{129}\text{Xe}$ nuclei ($I = \frac{1}{2}$), such exchange is mediated by the magnetic field coupling in the Hamiltonian; Equation (2.2). Thus, consider a single $^{129}\text{Xe}$ nucleus exposed to a general, possibly time-dependent, magnetic field, $\vec{H}$. This problem will first be solved in general. Then the particular nature of EM fields that induce changes in the angular momentum of the nucleus will be examined.

For computational purposes, the matrix representation of the Hamiltonian, $\mathcal{H}_z$ in Equation (2.2), will be found in the familiar $I_z$ basis, $\{|m\}; m = -I, \ldots, I\}$. Utilizing the spin raising and lowering operators $(I_+, I_-)$, the projections of the spin operators in this basis can be written [21]:

\begin{align}
I_x|m\rangle &= \frac{1}{2} (I_+ + I_-) |m\rangle \\
&= a_{I,m}^+ |m + 1\rangle + a_{I,m}^- |m - 1\rangle \\
I_y|m\rangle &= \frac{1}{2i} (I_+ - I_-) |m\rangle \\
&= -i (a_{I,m}^+ |m + 1\rangle - a_{I,m}^- |m - 1\rangle) \\
I_z|m\rangle &= m|m\rangle
\end{align}

(2.11) \quad (2.12)

where:

\begin{align}
a_{I,m}^+ &= \frac{1}{2} \sqrt{I(I+1) - m(m+1)} \\
a_{I,m}^- &= \frac{1}{2} \sqrt{I(I+1) - m(m-1)}.
\end{align}

An arbitrary spin state, $|\psi\rangle$, may be written in the $I_z$ basis representation as such:

\begin{equation}
|\psi\rangle = \sum_{m=-I}^{I} C_m|m\rangle \quad \Rightarrow \quad \vec{\psi} = \begin{pmatrix} C_{-I} \\
C_{-I+1} \\
\vdots \\
C_{I-1} \\
C_{I} \end{pmatrix}
\end{equation}

(2.14)

where $\vec{\psi}$ is the vector representation of the wave function in this basis. Now for $I = \frac{1}{2}$, it can be directly shown from Equations (2.11, 2.12, 2.13) that the matrix
representations for the spin operators $I_x$, $I_y$, and $I_z$ ([I]_{kl} = \langle m_k | I_j | m_l \rangle$) are the well known Pauli matrices,

$$I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad I_y = \frac{1}{2} \begin{bmatrix} 0 & i & 0 \\ -i & 0 & 0 \end{bmatrix}, \quad I_z = \frac{1}{2} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (2.15)$$

Note that Equations (2.11, 2.12, 2.13) may be also be used to construct such matrix representations for any value of the angular momentum quantum number, $J$. Substituting the operators in Equation (2.15) into the Zeeman Hamiltonian of Equation (2.2), results in the matrix representation of this Hamiltonian (in the $I_z$ basis),

$$\mathcal{H}_Z = -\frac{\hbar}{2} \begin{bmatrix} -\omega_z & \omega_x + i\omega_y \\ \omega_x - i\omega_y & \omega_z \end{bmatrix}. \quad (2.16)$$

where

$$\bar{\omega} = \gamma \bar{H}. \quad (2.17)$$

The time evolution of the wave function ($\bar{\psi}$) in this arbitrary field ($\bar{H} = \bar{\omega} / \gamma$) is then found, as usual, by solving:

$$i\hbar \frac{\partial \bar{\psi}}{\partial t} = \mathcal{H}_Z \bar{\psi}. \quad (2.18)$$

The Hamiltonian, $\mathcal{H}_Z$, can be diagonalized by applying a similarity (unitary) transformation,

$$S_Z = \frac{1}{\sqrt{2\omega(\omega + \omega_z)}} \begin{bmatrix} -(\omega + \omega_z) & \omega_x + i\omega_y \\ \omega_x - i\omega_y & \omega + \omega_z \end{bmatrix} \quad (2.19)$$

where

$$\omega = \sqrt{\omega_x^2 + \omega_y^2 + \omega_z^2}. \quad (2.20)$$

The resulting diagonalization is

$$S_Z \mathcal{H}_Z S_Z^\dagger = -\frac{\hbar}{2} \begin{bmatrix} -\omega & 0 \\ 0 & \omega \end{bmatrix}. \quad (2.21)$$

In general, a similarity transform that changes the basis of a wave function will also transform the Schrödinger Equation (2.18) as such

$$\psi' = S \psi \quad \rightarrow \quad i\hbar \frac{\partial \psi'}{\partial t} = \left\{ S \mathcal{H} S^\dagger - i\hbar S \frac{\partial S^\dagger}{\partial t} \right\} \psi' \quad (2.22)$$

where the quantity in the curly brackets, $\left\{ \ldots \right\} \equiv \mathcal{H}'$, can be thought of as the effective Hamiltonian in the new primed reference frame.
All the pieces are now in place to solve for the behavior of the $^{129}\text{Xe}$ nucleus in an arbitrary magnetic field. Before any specific cases are considered, however, it is helpful to become familiar with the rotation operators in the $I_z$ basis as these will be key to interpreting the physical meaning of quantum operators. Right hand oriented rotations of an angle, $\theta_j$, around the $j \in \{x,y,z\}$ axis, respectively are applied by utilizing the following quantum operators (for $I = \frac{1}{2}$):

$$R_j(\theta_j) = e^{i\theta_j I_j} = \cos(\theta_j/2) + 2i \sin(\theta_j/2)I_j,$$  \hspace{1cm} (2.23)

Specifically, rotations around the $\hat{z}$ axis are achieved by applying the following operator:

$$R_z(\theta_z) = \begin{bmatrix} e^{-i\theta_z/2} & 0 \\ 0 & e^{i\theta_z/2} \end{bmatrix}.$$  \hspace{1cm} (2.24)

This operator may also be applied to rotate the coordinate axis or to express wave functions in terms of rotating reference frames.

Expanding this to a nucleus of any spin, $I = \{0, \frac{1}{2}, 1, \frac{3}{2}, \ldots\}$, the general matrix representation for an arbitrary rotation can best be expressed in terms of Euler angles, $\alpha, \beta, \gamma$, which represent the application of three three successive rotation operators $[25]$

$$R_\gamma R_\beta R_\alpha = e^{i\gamma I_z} e^{i\beta I_y} e^{i\alpha I_z}.$$  \hspace{1cm} (2.25)

The first and last rotation operators, $R_\alpha$ and $R_\gamma$, are diagonal in the $I_z$ basis. The matrix elements, $[\cdots]_{lm}$, are of the form:

$$[R_\alpha]_{lm} = [e^{i\alpha I_z}]_{lm} = \delta_{lm} e^{im} \text{ where } l, m = -I, -I + 1, \ldots, I - 1, I.$$  \hspace{1cm} (2.26)

The matrix elements for the $R_\beta$ rotation operator around the $y$ axis is listed in most text books on Group Theory $[25]$

$$[R_\beta]_{lm} = (-1)^{m-l} \sqrt{\frac{(I + m)!}{(I - m)! (I + l)! (I - l)!}} \times \xi^{-(m-l)/2} (1 - \xi)^{(m+l)/2} \left( \frac{d}{d\xi} \right)^{I-m} \xi^{I-l} (1 - \xi)^{I+l}.$$  \hspace{1cm} (2.27)

where

$$\xi = \sin^2 \frac{\beta}{2}.$$
Of course, rotation of the axis is accomplished by applying the inverse operators in reverse order:

\[
(R_\gamma R_\beta R_\alpha)^\dagger = R_\alpha^\dagger R_\beta^\dagger R_\gamma^\dagger.
\]  

(2.28)

These rotation operators are useful to rotate the quadrupole Hamiltonian in Equation (2.3) when it refers to a principal axis that is not oriented in the same direction as the applied field.

2.2.2 Spin Dynamics in Constant Magnetic Fields

In the case of a constant magnetic field, \( H_0 \) in the \( \hat{z} \) direction, the Hamiltonian matrix is represented by substituting \( \omega_x = 0, \omega_y = 0, \) and \( \omega_z = \omega_0 = \gamma H_0 \) into Equation (2.16). In this case, the solution to Equation (2.18) is simple:

\[
\begin{bmatrix}
    e^{-i\omega_0 t/2} & 0 \\
    0 & e^{i\omega_0 t/2}
\end{bmatrix}
\begin{bmatrix}
    \psi_0 \end{bmatrix}
\]

(2.29)

where \( \psi_0 \) is the spin state at \( t = 0 \). Comparing this solution to the rotation operator \( R_z(\omega_0 t) \) of Equation (2.24), it is obvious that the motion is described by taking a constant wave function representing constant angular momentum (\( \psi_0 \)), and rotating it around the \( \hat{z} \) axis in the positive sense with angular frequency \( \omega_0 \). This is the familiar precession of a spin around a constant magnetic field. Such motion does not change \( \langle I_z \rangle \), the expectation value of the angular momentum of the nucleus in the \( \hat{z} \) direction, and thus has no effect on the average nuclear magnetization of a sample. In essence, a constant magnetic field does not cause nuclear relaxation.

2.2.3 Relaxation-producing Magnetic Fields

As mentioned in the last section, the nuclear spins in a system will all precess around a constant magnetic field. Such rotations around the \( \hat{z} \) axis with angular frequency \( \omega_0 = \gamma H_0 \) do not change the expectation value of the angular momentum \( \langle I_z \rangle \) and hence do not change the magnetization, \( M_z \). Relaxation-producing fields, therefore, must be time-dependent. Suppose, that the longitudinal field is time-dependent: \( \omega_0(t) = \gamma H_0(t) \). The dynamical solution is similar to that of the time-independent case except that the rate of angular precession of the spin around the \( \hat{z} \) axis changes in time. The quantity in the exponent of Equation (2.29), \( \omega_0 t \),
will be replaced by $\int_0^t \omega_0(t') \, dt'$. Thus field modulations in the longitudinal direction do not cause nuclear relaxation. As before, rotations about the $\hat{z}$ axis leave $\langle I_z \rangle$ invariant.

Now consider the behavior of the $^{129}$Xe nucleus in the presence of modulating fields in the transverse direction with a single angular frequency $\omega_r$ and amplitude $\omega_1 = \gamma H_1$:

$$\begin{align*}
\omega_x &= \omega_1 \cos(\omega_r t), \\
\omega_y &= -\omega_1 \sin(\omega_r t), \\
\omega_z &= \omega_0.
\end{align*}$$

Thus the Hamiltonian, from Equation (2.16), in the lab frame is

$$\mathcal{H}_r = -\frac{\hbar}{2} \begin{bmatrix}
-\omega_0 & \omega_1 e^{-i\omega_r t} \\
\omega_1 e^{i\omega_r t} & \omega_0
\end{bmatrix}$$

where Euler’s equation ($e^{i\theta} = \cos(\theta) + i \sin(\theta)$) has been utilized. It is convenient to solve this in a reference frame that is rotating at the same angular frequency ($\omega_r$) as the rotating transverse magnetic field. Utilizing a rotating similarity transformation:

$$S_r = \begin{bmatrix}
e^{i\omega_r t/2} & 0 \\
0 & e^{-i\omega_r t/2}
\end{bmatrix}$$

the Hamiltonian in the rotating frame ($\mathcal{H}'_r$), as found from Equation (2.22), is

$$\mathcal{H}'_r = -\frac{\hbar}{2} \begin{bmatrix}
-(\omega_0 - \omega_r) & \omega_1 \\
\omega_1 & \omega_0 - \omega_r
\end{bmatrix},$$

which is time-independent and can be solved by observing that this Hamiltonian corresponds to that of a spin in a static effective magnetic field where $\omega'_x = \omega_1$, $\omega'_y = 0$ and $\omega'_z = \omega_0 - \omega_r$. Dividing these field components by $\gamma$ and writing them in vector notation reveals the effective static field in the rotating frame,

$$\vec{H}_{\text{eff}} = H_1 \vec{x}' + (H_0 - \frac{\omega_r}{\gamma}) \vec{z}'. $$

The behavior of a nuclear spin in a static field has already been described; the spin will precess around the effective static field in the rotating frame with angular frequency

$$\omega_{\text{eff}} = \sqrt{\omega_1^2 + (\omega_0 - \omega_r)^2}. $$
Finally, a field that produces relaxation has been found. Since the effective field (\(\tilde{H}_{\text{eff}}\)) is at a non-zero angle with respect to the \(\hat{z}\) axis, rotation of the spin around the effective field will periodically modulate \(\langle I_z \rangle\) with angular frequency \(\omega_{\text{eff}}\). The direction of the effective field can be modified by changing \(\omega_r\), \(H_0\) or \(H_1\). Thus nuclear spins can be caused to rotate about any axis conceivable.

One critical observation can now be made. When \(H_1 \ll H_0\) the effective field will lie near the \(\pm \hat{z}\) axis unless \(\omega_r \approx \omega_0\); only then are large variations of \(\langle I_z \rangle\) possible. Therefore, nuclear relaxation can only be mediated by EM fields that have a transverse component close to the Larmor frequency \((\omega_0)\). Such field modulations may come from a variety of sources: spin-rotation, dipole-dipole interactions, modulations in magnetic shielding or anti-shielding, etc. A nuclear spin may in like manner couple to lattice phonons and extract a small portion of their energy and angular momentum in a Raman scattering process. Likewise, rapid motion through field gradients caused by such mechanisms as collisions, surface hopping, vacancy diffusion, etc. may also provide the field modulations necessary for spin angular momentum exchange. Finally, field oscillations from paramagnetic atoms are also possible. All of these are known sources of nuclear spin relaxation \([10]\).

### 2.3 NMR Detection Methods

#### 2.3.1 Pulsed NMR

In the case of pulsed NMR, the nuclear spins are suddenly exposed to transverse magnetic radiation of amplitude \(H_1\) and of frequency \(\omega_r \approx \omega_0\). Thus the nuclear spins will start precessing around the effective field in the rotating frame (see last section), \(\tilde{H}_{\text{eff}} \approx H_1 \hat{x}'\), with an angular frequency of \(\omega_1\) \([\text{Equation (2.36)}]\). This behavior will persist until the pulse ends, at which point the spin will have moved through a “tip” angle of

\[
\theta_{\text{tip}} = \omega_1 t_p
\]

where \(t_p\) is the duration of the pulse. Therefore, the excess of spins (producing \(\vec{M}\)) that are initially oriented along the applied field will effectively be rotated to an angle \(\theta_{\text{tip}}\) off the \(\hat{z}\) axis. Such rotation will tip some or all of the sample mag-
netization into the transverse plane \[|\vec{M}| \sin(\theta_{||})\]. This magnetization, as with the nuclear spins, will now continue to precess around the applied field \((H_0)\) at the Larmor frequency \((\omega_0)\) in the lab frame. The EM radio-frequency signal produced by this precessing magnetization can be “picked up” by a coil placed around the sample. The signal strength will be shown in the next section to be directly proportional to \(|\vec{M}|\), the magnitude of the magnetization that was originally in the \(\hat{z}\) direction. This signal will eventually decay due to \(T_1\) or \(T_2\) processes as already discussed; recall that variations in local fields and thus precession frequencies throughout the sample cause a dephasing of the transverse magnetization over time. Thus the signal will decay with a characteristic time \(T_2\) due to inherent local dipolar field inhomogeneities. If external field inhomogeneities dominate, the transverse magnetization can decay even faster, with a characteristic time defined as \(T_2^*\). In a solid, such transverse decay is generally much shorter than \(T_1\). The signal thus obtained is called the free induction decay (FID).

2.3.2 Pulsed NMR Signal Detection

Observation of the precessing transverse magnetization of a sample is normally done by coupling the alternating magnetic fields produced by the magnetization precession to a copper coil whose axis is parallel to this alternating field and is wrapped around the sample. The alternating field from the sample thus induces an electromotive force (voltage) across the coil. Electronics are then employed to filter and amplify this signal. This is often accomplished by the use of a resonant “tank circuit” which is simply a high-quality capacitor \(C_T\) placed in parallel with the coil. Ohm’s Law will be used to model the expected behavior of the circuit:

\[ V = Z_T I, \]  

(2.39)

where \(V\) is the voltage across the coil, \(Z_T\) is the impedance of the coil and the circuitry placed in parallel with it and \(I\) is the net current running through the tank circuit. In general, the steady-state alternating voltage across the circuit can be expressed as a complex exponential: \(V = V_0 e^{i\omega t}\) where \(V_0\) is the real amplitude and \(\omega\) the angular frequency of the sinusoidal oscillation. It is assumed, as usual,
that only the real part of this complex number is the physically relevant quantity. The impedance \( Z_T \) may also be expressed in this form: \( Z_T = Z_0 e^{i\theta_T} \). Thus the current can be found through the circuit from Equation (2.39),

\[
I = \frac{V_0}{Z_0} e^{i(\omega t - \theta_T)}. 
\]  

(2.40)

Notice that there is a possible phase difference between the voltage across the circuit and current through the circuit caused by the impedance.

Consider the signal created by the sample’s magnetization \( \vec{M} \) precessing around the \( \hat{z} \) axis at an angle \( \theta \) from the \( \hat{z} \) axis. The magnetic flux generated by the sample through the coil is proportional to the magnitude of the resulting alternating field. Therefore, \( \Phi \) can be expressed as:

\[
\Phi = C_\phi |\vec{M}| \sin(\theta) e^{i\omega_0 t} 
\]  

(2.41)

where \( C_\phi \) is a real proportionality constant containing some fundamental constants and information about the geometry of the coil. The induced voltage across the coil, by Faraday’s Law, is

\[
V = -\frac{\partial \Phi}{\partial t} = -i\omega_0 C_\phi |\vec{M}| \sin(\theta) e^{i\omega_0 t} 
\]  

(2.42)

and thus it can immediately be seen that the signal amplitude is directly proportional to the magnitude of the magnetization, \( |\vec{M}| \).

The impedance of a parallel capacitor \( C_T \) and coil, with inductance \( L \) and a small resistance \( r \), can be formulated from elementary electronics [26],

\[
Z_T = i\omega_0 \frac{L^2 + (r/\omega_0)^2}{L(1 - \omega_0^2 LC_T) - r^2 C_T + ir/\omega_0}. 
\]  

(2.43)

Thus, from Equation (2.40), the net current is

\[
I = -\frac{\sqrt{[L(1 - \omega_0^2 LC_T) - r^2 C_T]^2 + (r/\omega_0)^2 C_\phi |\vec{M}| \sin(\theta)}}{L^2 + (r/\omega_0)^2} e^{i(\omega_0 t - \theta_T)}. 
\]  

(2.44)

At resonance, where \( L(1 - \omega_0^2 LC_T) = r^2 C_T \), it follows that minimal net current will flow through the tank circuit. Thus the maximum amount of power will be available to do work on any connected circuitry. Far from resonance, however, most
of the current will be shunted through the tank circuit. This resonance phenomena effectively filters out unwanted frequencies. If one is careful to always adjust the applied field so as to acquire the signal at the same consistent frequency, $\omega_0$, then the response of the electronics, will be consistent and the signal strength measured will be proportional to the magnetization, $|\vec{M}|$, of the sample. This arrangement, therefore, is sufficient to measure nuclear relaxation. Due to the extraordinarily large signals from the hyperpolarized solids, it is not necessary to have a large quality factor $Q$ for the coil. ($Q$ is the ratio of total energy in the oscillator to energy lost every cycle.) A coupling capacitor $C_C$ is often placed in series with the tank circuit and external circuitry to eliminate DC coupling and aid in matching impedance. See section 3.3 for an example of a typical detection circuit.

### 2.3.3 Adiabatic Fast Passage NMR

Another method to measure the magnetization of a sample is achieved by adiabatic fast passage of the nuclear spins through resonance. Specifically, the signal from the precessing magnetization is detected as the precessing magnetization is adiabatically tipped into the transverse plane. Such control of the magnetization is possible due to the tendency of the nuclear spins to follow a slowly moving effective magnetic field. As discussed in section 2.2.3, the effective magnetic field in the rotating frame, $H_{\text{eff}} = H_1 \hat{x}' + (H_0 - \omega_r/\gamma) \hat{z}'$, can be controlled by varying the magnitude of the applied field $H_0$ in the presence of a modulating transverse field $H_1$ rotating with angular frequency $\omega_r$ in the lab frame. When $H_0$ is brought slowly through resonance (where $H_0 = \omega_r/\gamma$) the effective field will pass through the transverse plane (where $\tilde{H}_{\text{eff}} = H_1 \hat{x}'$). Adiabatic inversion of the nuclear spins is thus achieved by starting $H_0$ far above resonance and then adiabatically lowering it through resonance to a point far below resonance. It is easily seen that the effective field $\tilde{H}_{\text{eff}}$ starting near the $\hat{z}$ axis, will move through the transverse plane and end up near the $-\hat{z}$ axis. It will now be shown that the nuclear spins indeed will closely track the effective field under the adiabatic condition.

In order to demonstrate that a spin will follow a slowly rotating magnetic field,
consider, for a moment, a spin, initially in the \( \hat{x} \) direction, in a magnetic field \( \vec{H} \) that also starts in the \( \hat{x} \) direction yet is slowly rotating around the \( \hat{z} \) axis with angular frequency \( \omega_s \). Consider a rotating frame that is also rotating around the \( \hat{z} \) axis at the same frequency. In this rotating frame, therefore, the magnetic field is stationary, pointing along the \( \hat{x}' \) axis. The spin dynamics for stationary fields in a rotating frame were discussed in section 2.2.2. From Equation (2.36), in this rotating frame, there exists an effective field \( \vec{H}_{\text{eff}} = H\hat{x}' - \frac{\omega_s}{\gamma} \hat{z}' \). The spin will precess around the effective field at a constant angle \( \theta_p = \tan^{-1}\left(\frac{\omega_s}{\gamma} / H\right) \). Thus if

\[
\frac{\omega_s}{\gamma} \ll H,
\]

then the spin will always be nearly aligned with the field \( \vec{H} \). This is known as the adiabatic condition.

Returning back to the case where the nuclear spin and the applied field \( \vec{H}_0 \) are in the \( \hat{z} \) direction and a smaller transverse field \( \vec{H}_1 \) is rotating with angular frequency \( \omega_r \) in the \( x\)-\( y \) plane, the effective field of Equation (2.36) is at an angle \( \theta \) off the \( \hat{z} \) axis such that

\[
\sin(\theta) = \frac{H_1}{\sqrt{H_1^2 + (H_0 - \omega_r/\gamma)^2}}.
\]

Therefore, if the field \( H_0 \) is changing with time, it can be shown that

\[
\omega_s = \frac{\partial \theta}{\partial t} = \frac{H_1}{H_1^2 + (H_0 - \omega_r/\gamma)^2} \frac{\partial H_0}{\partial t}.
\]

Since \( \omega_s \) goes through a maximum at resonance, where \( H_0 = \omega_r/\gamma \), the adiabatic condition from Equation (2.45), \( \omega_s/\gamma \ll H_{\text{eff}} \), can be written:

\[
\frac{1}{\gamma H_1} \frac{\partial H_0}{\partial t} \ll H_1.
\]

This defines the upper limit to the rate at which \( H_0 \) can be changed. For us, the adiabatic condition is easily satisfied at field-sweep rates of 20-100 Gauss per second with a total sweep time of less than 10 sec. The lower limit, hence the “fast passage” constraint, simply requires that the spins are adiabatically inverted on a time scale much faster than relaxation in the rotating frame, \( T_{1p} \). For solid \( ^{129}\text{Xe} \),
$T_{1p}$ is on the order of many minutes and thus there is no stiff constraint on fast passage.

In practice, the small modulating transverse field with amplitude $H_1$ can be produced by a coil placed around the sample, perpendicular to the applied field. This modulating field is made strong enough to entirely dominate any local fields in the lattice. This resulting “RF broadening” assures that the spin interactions with the externally generated fields will dominate; the broadening refers to the phenomenon expected from examining Equation (2.46); as $H_1$ grows, the width of the resonance increases.

In $^{129}$Xe, the local fields are on the order of 150 mG, estimated by using a computer to average over the fields of several hundred randomly oriented dipole fields in a “Monte Carlo” fcc lattice. In the experiment, with $H_1 \approx 500$ mG, the adiabatic condition required that $H_0$ change much slower than about 1000 G/s. Thus field ramp rates, also limited by the inductance of the Helmholtz coils providing the applied field, should be in the range of 10-100 G/s.

### 2.3.4 Detecting the AFP signal

A single coil can be used for both generating the $\tilde{H}_1$ field and simultaneously detecting the signal from the precessing magnetic moment of the sample. The coupling of the coil, with inductance $L$ and impedance $Z_T = i\omega_r L$, to the sample in such circumstances can be modeled by using Equation (2.39) with two driving voltages; one from the RF generator, and the other much smaller voltage from the induced EMF due to the modulating magnetization of the sample ($-\partial\Phi/\partial t$):

$$V_{RF} - \frac{\partial\Phi}{\partial t} = i\omega_r LI.$$  \hspace{1cm} (2.49)

The flux generated by the sample through the coil can be found by combining Equation (2.41) and Equation (2.46):

$$\Phi = C_\phi |\vec{M}| \frac{H_1}{\sqrt{H_1^2 + (H_0 - \omega_\tau /\gamma)^2}} e^{i\omega_r t}. \hspace{1cm} (2.50)$$

Since the current running through the coil generates $\tilde{H}_1$, and both $\tilde{H}_1$ and $\tilde{H}_{eff}$ are rotating with the same phase in the transverse plane (so locked by the spin
dynamics) it follows that the current through the coil must be in phase with the flux modulations produced by the sample. Thus the current can be written as: 

\[ I = I_0 e^{i\omega_r t} \]

where \( I_0 \) is real and constant in time. Substituting these values for \( \Phi \) and \( I \) into Equation (2.49) with some algebraic manipulations results in:

\[
V_{RF} = i\omega_r \left[ L + \frac{C_\phi}{I_0} |\vec{M}| \frac{H_1}{\sqrt{H_1^2 + (H_0 - \omega_r/\gamma)^2}} \right] I_0 e^{i\omega_r t}. \quad (2.51)
\]

The quantity in the square brackets \([\ldots]\) of Equation (2.51) can be considered to be the effective inductance, \( L' \), of the coil-sample coupling; compare \( V_{RF}(L) = i\omega_r LI \) to Equation (2.51), \( V_{RF}(L') = i\omega_r L'I \). The inductive coupling of the coil to the rotating transverse magnetization, therefore, serves to shift the inductance of the coil, \( L \), by an amount that is directly proportional to the magnetization of the sample, \( L - L' \).

In order to detect this slight inductance shift by the phase shift it produces in the signal voltage, \( V_{RF}(L') \), a second sample-free “dummy” coil is driven by the same source then the signal from the “dummy” coil, \( V_{RF}(L) \), can be subtracted from the signal from the sample coil, as such:

\[
V_{RF}(L') - V_{RF}(L) = i\omega_r C_\phi |\vec{M}| \frac{H_1}{\sqrt{H_1^2 + (H_0 - \omega_r/\gamma)^2}} e^{i\omega_r t}. \quad (2.52)
\]

The voltage of the difference signal is therefore directly proportional to the magnetization of the sample, \( |\vec{M}| \). From Equation (2.52), it is also obvious that the shape of the expected difference signal with respect to \( H_0 \) is the square root of a Lorentzian.

The experimental realization of such a detection scheme is accomplished by constructing a bridge circuit; two parallel equivalent circuits connected to a differential amplifier. When both circuits are balanced, they produce identical signals in response to a driving voltage and the output from the differential amplifier is zero. The sample coil is connected to one circuit and the “dummy” coil to the other. As \( H_0 \) is brought from above resonance to below (or the other way around), the inductance of the sample coil shifts and the magnitude of the difference signal from the differential amplifier traces out the square root of a Lorentzian whose height is
proportional to the sample magnetization and whose width is related to the strength of the RF field \((H_1)\), see Equation (2.52). A phase sensitive lock-in amplifier can also be effectively used to filter out noise and isolate the signal. The actual bridge circuit and apparatus used in the experiment are described in Chapter 3, section 3.5.

The impedance of the other circuit elements connected to the coil does have an effect on the output signal. Due to tedious nature and size of the full calculation, it was not included. However, the end result is that the magnitude of the difference signal is still proportional to the sample magnetization as long as \( |L - L'| \ll L \). Such was always the case in this experiment.

### 2.4 Nuclear Spin Interactions

Up to this point the dynamics of single \(^{129}\text{Xe}\) nuclei in a prescribed EM field have been discussed. The dynamics of nuclei in the presence of other nuclei, however, are much more complex. The quantum mechanical state of a system of two interacting nuclear spins, for example, must include all the possible energy states of both nuclei and their interactions. This is incorporated nicely into the Hamiltonian formalism. Arbitrary spin states of nucleus (1) and nucleus (2) can each be individually expanded in the \( I_z \) basis:

\[
|\psi_1\rangle = \sum_k C_k |m_k\rangle \\
|\psi_2\rangle = \sum_l C_l |m_l\rangle
\]  

where \( k \) is exclusively used to label the spin (1) state and \( l \) to label the spin (2) state. It is possible to form a single basis (product space) for both nuclear spins by taking a direct product of the two individual bases, \(|m_km_l\rangle = |m_k\rangle \otimes |m_l\rangle\). The product-basis is orthonormal because each of the constituent bases are. That is,

\[
\langle m_km_l' | m_km_l \rangle = \delta_{k'k} \delta_{l'l} \quad \text{where} \quad \delta_{k'k} = \begin{cases} 1 & \text{if } k = k' \text{ and } l = l' \\ 0 & \text{otherwise} \end{cases} \]  

The total number of product-basis functions, therefore, is the product of number of bases in each subspace. That is, if spin (1) has \(2I_1 + 1\) bases and spin (2) has
2I_2 + 1, the (1)-(2) basis contains (2I_1 +1) \cdot (2I_2 +1). In this new basis, an arbitrary state can be expanded as thus:

\[ |\psi_1\psi_2\rangle = \sum_{k,l} C_k C_l |m_k m_l\rangle \]  \hspace{1cm} (2.56)

where the \( C_k \) and \( C_l \) are exactly the same coefficients as the individual expansions in Equations (2.53) and (2.54). The individual spin states can be extracted, up to a phase factor, from this product-space state by use of the orthonormality of the states. Given an arbitrary state, represented by \( C_k C_l \), it follows that

\[ \sum_l (C_k C_l)^* C_k C_l = C_k^2 \sum_l C_l^2 = C_k^2. \]  \hspace{1cm} (2.57)

which provides the magnitudes (yet loses the phase information) for state (1). An arbitrary observable, \( \mathcal{O}_1 \), that acts only on spin state (1) in such a fashion:

\[ \mathcal{O}_1 |\psi_1\rangle = \sum_k C_k |m_k\rangle \]  \hspace{1cm} (2.58)

but leaves spin state (2) unaffected can be constructed in the product-basis as such:

\[ \mathcal{O}_1 |\psi_1\psi_2\rangle = \sum_{k,l} C_k C_l |m_k m_l\rangle. \]  \hspace{1cm} (2.59)

Thus the matrix elements for the representation of \( \mathcal{O}_1 \) in the product basis (i.e. \( \langle m_l m_k | \mathcal{O}_1 | m_k m_l \rangle \)) can be found only by knowledge of the effect of \( \mathcal{O}_1 \) on the basis set \( |m_k\rangle \) for spin (1). It is easy to show that, for operators so constructed,

\[ \langle \psi_2 \psi_1 | \mathcal{O}_1 | \psi_1 \psi_2 \rangle = \langle \psi_1 | \mathcal{O}_1 | \psi_1 \rangle. \]  \hspace{1cm} (2.60)

That is to say, expectation values of observables on any of the constituent nuclear spins can be extracted from a state in the product basis.

In particular, the spin operators, \( \vec{I}_1 \) and \( \vec{I}_2 \), can be constructed from Equations (2.11, 2.12, 2.13). For example:

\[ I_{z1} |m_k m_l\rangle = m_k |m_k m_l\rangle \]  \hspace{1cm} (2.61)

\[ I_{z2} |m_k m_l\rangle = m_l |m_k m_l\rangle \]  \hspace{1cm} (2.62)

have the product basis as eigenvectors. In the next section this basis will be used to solve for the complete dynamics of a two-spin system.
2.4.1 Dynamics of Two Interacting $^{129}\text{Xe}$ Nuclei

In order to characterize the dynamics of interacting $^{129}\text{Xe}$ nuclei ($I_1 = I_2 = \frac{1}{2}$) in a lattice, consider the spin dynamics of two neighboring $^{129}\text{Xe}$ nuclei that are presumed isolated from any other interactions in the lattice. This two-spin system interacts only by way of the dipole-dipole interaction and is exactly solvable. To be definite, suppose that the applied field $H_0$ is in the $\hat{z}$ direction and the nuclei lie along the $\hat{z}$ axis, then the Hamiltonian can be written [Equations (2.2) and (2.4)]:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_D = -\hbar \gamma (I_{z1} + I_{z2}) H_0 + \frac{\hbar^2 \gamma^2}{r^3} (I_{x1} I_{x2} + I_{y1} I_{y2} - 2 I_{z1} I_{z2})$$

(2.63)

where $\gamma$ is the gyromagnetic ratio of $^{129}\text{Xe}$ ($-2\pi \cdot 1177.8$ Hz/G). In the following ordered product basis, $[[\frac{1}{2} - \frac{1}{2}], [\frac{1}{2} + \frac{1}{2}], [\frac{1}{2} - \frac{1}{2}], [\frac{1}{2} + \frac{1}{2}]]$, the matrix representation of the Hamiltonian can be written explicitly by finding the matrix elements (in this product basis) of the $\tilde{I}_1$ and $\tilde{I}_2$ operators based on Equations (2.11, 2.12, 2.13) and patterned after what was done in Equations (2.61) and (2.62) and then by substituting the matrix representations of these operators into Equation (2.63):

$$\mathcal{H} = -\hbar \gamma H_0 \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} + \frac{\hbar^2 \gamma^2}{r^3} \begin{pmatrix} -\frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}.$$  

(2.64)

This Hamiltonian is diagonalized by the following similarity (unitary) transformation:

$$S = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$  

(2.65)

The resulting diagonalization is

$$S \mathcal{H} S^\dagger = \hbar \gamma \begin{pmatrix} H_0 - \frac{\hbar \gamma}{2r^3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & \frac{\hbar \gamma}{r^3} & 0 & 0 \\ 0 & 0 & 0 & -H_0 - \frac{\hbar \gamma}{2r^3} \end{pmatrix}.$$  

(2.66)

The energy eigenvalues on the diagonal of Equation (2.66) are plotted vs. increasing field in Figure 2.1. In this case $|+\frac{1}{2} + \frac{1}{2}|$ is an energy eigenstate, as is $|-\frac{1}{2} - \frac{1}{2}|$. 
Figure 2.1. Energy eigenvalues for a system of two interacting $^{129}$Xe nuclei (placed parallel to the field and 6.15 Å apart) vs. field (Gauss) [on left] and time evolution of $\langle I_z \rangle$ for the first nuclei from the initial state $| + \frac{1}{2}, - \frac{1}{2} \rangle$ at 5 G [on right].

The other two energy eigenstates are admixtures, as seen from Equation (2.65); they are $\frac{1}{\sqrt{2}}(| + \frac{1}{2} - \frac{1}{2} \rangle + | - \frac{1}{2} + \frac{1}{2} \rangle)$ and $\frac{1}{\sqrt{2}}(| + \frac{1}{2} - \frac{1}{2} \rangle - | - \frac{1}{2} + \frac{1}{2} \rangle)$.

In addition to diagonalizing the Hamiltonian, the similarity transform $S$ also transforms wave functions written in the angular momentum basis, $\psi_{kl} = C_k C_l$ (as outlined above) to the eigenbasis of the Hamiltonian, $\psi_E$. That is,

$$\psi_E = S \psi_{kl}. \quad (2.67)$$

In the eigenbasis of the Hamiltonian, the solution to the Shrödinger equation, yielding the time evolution of the wave function, is particularly simple:

$$\psi_E(t) = D_t \psi_E(0) \quad \text{where} \quad D_t = \begin{pmatrix} e^{-iE_{11}t} & 0 & 0 & 0 \\ 0 & e^{-iE_{21}t} & 0 & 0 \\ 0 & 0 & e^{-iE_{31}t} & 0 \\ 0 & 0 & 0 & e^{-iE_{41}t} \end{pmatrix}. \quad (2.68)$$

and where the $\{E_j\}$ are the diagonals of Equation (2.66). Essentially, the full dynamics of the two-spin system are now solved in the eigenbasis. Equation (2.67) may now be used to convert the wave function in Equation (2.68) back into the familiar $kl$ product basis:

$$\psi_{kl}(t) = S^t \psi_E(t) = S^t D_t S \psi_{kl}(0) = P(t) \psi_{kl}(0). \quad (2.69)$$
where $P(t) = S^1 D_t S$ is known as the propagator. It will act on any initial state, $\tilde{\psi}_{kl}(0)$, and propagate it forward in time. For completeness, the propagator is explicitly

$$
P(t) = \begin{pmatrix} e^{-i\omega_1 t} & 0 & 0 \\
0 & \frac{1}{2} (e^{-i\omega_2 t} + e^{-i\omega_3 t}) & -\frac{i}{2} (e^{-i\omega_2 t} - e^{-i\omega_3 t}) \\
0 & -\frac{1}{2} (e^{-i\omega_2 t} - e^{-i\omega_3 t}) & \frac{1}{2} (e^{-i\omega_2 t} + e^{-i\omega_3 t}) \end{pmatrix}
$$

(2.70)

where $\omega_j = E_j/\hbar$.

With the propagator in hand, the full dynamics of the system are known starting from any initial state, $\tilde{\psi}_{kl}(0)$. The dynamics can be read out by examining the expectation values of the angular momentum operators, $\vec{l}_1$ and $\vec{l}_2$. Referring to Equation (2.60), the expectation values were computed as usual; $\langle \vec{l}_j \rangle = \langle \tilde{\psi}_{kl}^\dagger(t) \vec{l}_j \tilde{\psi}_{kl}(t) \rangle$, where $j \in \{1, 2\}$. The results for a few initial states are shown in Table 2.1.

In this particular example, the $^{129}\text{Xe}$ atoms are located along the $\hat{z}$ axis. To solve a more general case where the second $^{129}\text{Xe}$ atom is at an angle $\theta$ off the $\hat{z}$ axis (relative to the magnetic field) from the first atom, the same procedure may be followed, though the results are somewhat messy. For simplicity, first-order degenerate perturbation theory may be employed [27] assuming the dipole-dipole interaction, Equation (2.4), is small compared to the Zeeman interaction ($\hbar \gamma H_0 \gg \hbar^2 \gamma^2 / r^3$), which is true in solid $^{129}\text{Xe}$ for fields above approximately 300 mG. Such perturbation theory is well known and can be found in any quantum physics text and thus only the results will be presented here:

<table>
<thead>
<tr>
<th>Initial State</th>
<th>$\langle I_{y1} \rangle$</th>
<th>$\langle I_{z1} \rangle$</th>
<th>$\langle I_{y2} \rangle$</th>
<th>$\langle I_{z2} \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\frac{1}{2}, -\frac{1}{2}$</td>
<td>0</td>
<td>$-\frac{1}{2}$</td>
<td>0</td>
<td>$-\frac{1}{2}$</td>
</tr>
<tr>
<td>$-\frac{1}{2}, +\frac{1}{2}$</td>
<td>$+\frac{1}{2} \sin(\omega_3 t)$</td>
<td>$-\frac{1}{2} \cos(\omega_3 t)$</td>
<td>$-\frac{1}{2} \sin(\omega_3 t)$</td>
<td>$+\frac{1}{2} \cos(\omega_3 t)$</td>
</tr>
<tr>
<td>$+\frac{1}{2}, -\frac{1}{2}$</td>
<td>$-\frac{1}{2} \sin(\omega_3 t)$</td>
<td>$+\frac{1}{2} \cos(\omega_3 t)$</td>
<td>$+\frac{1}{2} \sin(\omega_3 t)$</td>
<td>$-\frac{1}{2} \cos(\omega_3 t)$</td>
</tr>
<tr>
<td>$+\frac{1}{2}, +\frac{1}{2}$</td>
<td>0</td>
<td>$+\frac{1}{2}$</td>
<td>0</td>
<td>$+\frac{1}{2}$</td>
</tr>
</tbody>
</table>
\begin{align*}
E_1 &= \hbar \gamma H_0 - \frac{\hbar^2 \gamma^2}{4r^3} \left(3 \cos^2(\theta) - 1\right) \\
E_2 &= 0 \\
E_3 &= \frac{\hbar^2 \gamma^2}{2r^3} \left(3 \cos^2(\theta) - 1\right) \\
E_4 &= -\hbar \gamma H_0 - \frac{\hbar^2 \gamma^2}{4r^3} \left(3 \cos^2(\theta) - 1\right).
\end{align*} \tag{2.71}

To first order, the eigenstates of the Hamiltonian do not change with \( \theta \) since such angular dependence is found only in the small perturbation term. Therefore the expectation values, calculated using the same basis, will not change form, to first order, and the results in Table 2.1 still apply. Thus substituting into them the perturbed energies from Equation (2.71), the general angular frequency of the dipole-dipole induced spin oscillations may be found. To first order,

\[ \omega_3 = \frac{E_3}{\hbar} = \frac{\hbar \gamma^2}{2r^3} \left(3 \cos^2(\theta) - 1\right). \] \tag{2.72}

For \(^{129}\text{Xe}, \frac{\hbar \gamma^2}{(2r^3)} \approx 2\pi \cdot 56 \text{ Hz}\). Since each cycle involves two spin "flip-flops", the spin-flip rate between neighboring \(^{129}\text{Xe}\) is \( W_s \approx 112 \left(3 \cos^2(\theta) - 1\right) \) per second. These results will be used in the next section to help characterize spin diffusion.

In conclusion, the complete dynamics of a two-spin \(^{129}\text{Xe}-^{129}\text{Xe}\) interacting system have been found by direct diagonalization of the full Hamiltonian. The energy spectrum so derived was used to map out the quantized energy levels of the two-spin system. If the system were not allowed to exchange energy with any external sources, then transitions between nondegenerate energy states would be forbidden. In the case of two \(^{129}\text{Xe}\) nuclei, however, there can be a degeneracy in the Zeeman energies between the two states with nuclei of opposite spins: \(| + \frac{1}{2} - \frac{1}{2} \rangle \) and \(| - \frac{1}{2} + \frac{1}{2} \rangle \). There also exists a dipole-dipole interaction potential that, when placed in the Hamiltonian, lifts this degeneracy to produce two nondegenerate eigenstates consisting of admixtures of these two opposite-spin states. The time evolution of any initial state was then found by solving the time-dependent Schrödinger equation to find the propagator. With the propagator, the complete time evolution the wave function is known when given any initial state.
It was seen that if the nuclei are prepared in the specific initial state \( | + \frac{1}{2} - \frac{1}{2} \rangle \), this being a linear combination of the two parallel energy eigenstates, then due to the phase evolution of the wave function over time, the expectation values for the angular momentum of the two individual nuclei oscillate cyclicly in time, indicating that there is a dynamic transfer of angular momentum back and forth between the nuclei. The expected transition rate between the spin-up and spin-down state for the first nucleus was then found to be exactly proportional to the dipole-dipole interaction energy. Thus it can be seen that the first nucleus, if placed in a spin-up state (adjacent to the second nucleus in a spin-down state), has a finite probability of being flipped to a spin-down state over time due to its interaction with the second nucleus. The total angular momentum and energy of the two-spin system, however, is always conserved.

In the case of two interacting \(^{129}\text{Xe}\) nuclei, the dynamics of the expectation values paint a classical picture. The interacting spins will each precess around their average total angular momentum vector in such a way as to preserve the component of the total angular momentum in the \( \hat{z} \) direction at all times and they do this at a frequency that is directly proportional to the dipole-dipole interaction energy.

### 2.4.2 Spin Diffusion

Interchange of spin angular momentum between adjacent \(^{129}\text{Xe}\) nuclei in the solid allows transport of spin angular momentum from nucleus to nucleus among the \(^{129}\text{Xe}\) in the lattice. As seen in the last section, the exchange rates between nuclei are entirely independent of the field, \( H_0 \). This process is referred to as spin diffusion, aptly named because it is a random walk diffusion process that may be modeled by the diffusion equation.

To see this, consider a one-dimensional (1-D) chain of \(^{129}\text{Xe}\) nuclei placed at an atomic distance \( r \) from each other. The probability that a given nuclear spin, at point \( x \), will “flip” from \(-\frac{1}{2}\) to \(+\frac{1}{2}\) by exchange of angular momentum with its neighboring spins at \( x + r \) is \( P_- (x) P_+ (x + r) \), where \( P_- (x) \) is the probability that the spin at point \( x \) is \(-\frac{1}{2}\) and \( P_+ (x + r) \) is the probability that the neighboring spin at \( x + r \) is \(+\frac{1}{2}\). As shown in the preceding section, the exchange rate between these
The neighbors of opposite spin is

\[ W_s \approx \frac{\hbar \gamma^2}{2\pi r^3} \left( 3\cos^2(\theta) - 1 \right) \]  

(2.73)

per second, where \( \theta \) is the direction of the applied magnetic field off the \( +\hat{x} \) axis. Therefore, \( W_s P_-(x)P_+(x + r) \) indicates the rate at which a \( +\frac{1}{2} \) spin at \( x + r \) is exchanging its spin with a \( -\frac{1}{2} \) spin at \( x \). In like fashion it is possible to find the transition rates due to all possible configurations of neighboring states.

The polarization density of this 1-D chain of spins \( n(x, t) \) can also be defined in terms of these probabilities:

\[ r \cdot n(x, t) = P_+(x) - P_-(x) = 2P_+(x) - 1, \]  

(2.74)

the right hand side follows because \( P_+(x) + P_-(x) = 1 \). It is now possible to determine the rate at which the polarization is changing due to interactions between nearest neighbors. It is the difference between the rate at which the spin is flipped up and the rate which it is flipped down:

\[
 r \frac{\partial n(x, t)}{\partial t} = 2 \frac{\partial P_+(x)}{\partial t} \\
 = 2W_s \left[ P_-(x)P_+(x - r) + P_-(x)P_+(x + r) - (P_+(x)P_-(x - r) + P_+(x)P_-(x + r)) \right] \\
 = 2W_s \left[ P_+(x - r) + P_+(x + r) - 2P_+(x) \right]. 
\]  

(2.75)

This can immediately be compared to the well-known difference equations for the second derivative:

\[
 r \cdot \frac{\partial^2 n(x, t)}{\partial x^2} = 2 \frac{\partial^2 P_+(x)}{\partial x^2} \\
 = 2 \frac{P_+(x + r) - P_+(x) - (P_+(x) - P_+(x - r))}{r^2} \\
 = \frac{2}{r^2} [P_+(x + r) + P_+(x - r) - 2P_+(x)].
\]  

(2.76)

Combining Equation (2.75) and Equation (2.76) results in the diffusion equation,

\[
 \frac{\partial n(x, t)}{\partial t} = W_s r^2 \frac{\partial^2 n(x, t)}{\partial x^2}. 
\]  

(2.77)

The coefficient of diffusion \( D \) can now be identified as the constant multiplier in Equation (2.77). That is, \( D = W_s r^2 \). It then follows from Equation (2.73) and by
recognizing that the transition rates scale with the occupancy fraction $f$ of $^{129}$Xe in the lattice [7],

$$D \approx \frac{\hbar \gamma^2 f}{r} \left(3 \cos^2(\theta) - 1\right).$$  \hfill (2.78)

A number of simplifying assumptions have been made in this illustration, only two-body spin-transfer rates have been considered with a 1-D chain of nuclei, yet the range of numerical values obtained for the diffusion coefficient in Equation (2.78) is comparable to both theoretical and experimental results. In section 4.3, the experimental data at fields above 140 G was fit with a diffusion coefficient of $D = 26 \times 10^{-14}$ cm$^2$/s. The three-dimensional (3-D) theory developed in Gatzke’s doctoral dissertation [7], yields an approximate value of $D = 24 \times 10^{-14}$ cm$^2$/s for enriched $^{129}$Xe. Compare this, for example, to the diffusion coefficient obtained from Equation (2.78) when the applied magnetic field is taken to be along one of the lattice vectors, $\theta = 0^\circ$, and $r = 6.15$ Å (the lattice constant) with $f = 0.86$ (isotopically enriched $^{129}$Xe). Equation (2.78) yields a value of $D = 25.7 \times 10^{-14}$ cm$^2$/s. For other orientations, slightly different results are obtained. If $\theta = 90^\circ$ and $r = 6.15/\sqrt{2}$ Å, for example, $D = 18.2 \times 10^{-14}$ cm$^2$/s. The maximum diffusion rate is obtained when $\theta = 0^\circ$ and $r = 6.15/\sqrt{2}$ Å: $D = 36.4 \times 10^{-14}$ cm$^2$/s. As can be seen, these values compare favorably to the diffusion coefficients obtained from data fits in section 4.3 and Gatzke’s theoretical value, each having error margins of about 20%.

In both the experimental data fit and Gatzke’s theoretical treatment, the net spin diffusion is assumed isotropic. This was done for computational simplicity and is accomplished by averaging the various spin-interchange rates, $W_{s,j}$, over the crystal lattice. One should keep in mind, however, that diffusion depends on the strength of the dipole-dipole coupling which itself has angular dependence. In particular, with a chain of spins at the magic angle of $54.7^\circ$ (where $3 \cos^2(\theta) - 1 = 0$) from the applied field, the dipole-dipole coupling disappears and thus spin diffusion in that direction is null. The polycrystalline structure of the sample as a whole, however, guarantees that crystallite orientations with respect to the applied field are random variables. Also the crystal lattice is only 86% $^{129}$Xe in the enriched samples.
and 26% $^{129}\text{Xe}$ in the natural samples. In order to “diffuse around” obstacles such as spinless nuclei, spins must “flow” at a distribution of many different angles around the obstacles. This also may serve to average out the angular dependence of spin diffusion.

In conclusion, spin diffusion takes place due to dipole-dipole induced spin interchange between the $^{129}\text{Xe}$ nuclei in the lattice. It is expected to exist in the xenon lattice with an averaged isotropic diffusion coefficient near $D \approx 25 \times 10^{-14}$ cm$^2$/s for enriched Xe. Spin diffusion strictly preserves the total angular momentum (polarization), of the $^{129}\text{Xe}$ spin system and therefore causes no direct nuclear relaxation. Spin diffusion, however, does provide a channel through which the angular momentum of the $^{129}\text{Xe}$ spin system may be transported to relaxation centers and thus must be considered an accomplice to the ultimate nuclear spin relaxation mechanism.

2.4.3 Dynamics of a $^{131}\text{Xe}$ Nucleus

The dynamics of the $I_z = \frac{3}{2}$ quadrupole $^{131}\text{Xe}$ nucleus will now be examined in the presence of an electric field gradient (EFG) and an applied magnetic field. This treatment is somewhat complicated by the tensoral characteristic of the quadrupole potential. The principal axis of the quadrupole field tensor can be made to point in any direction. Thus the Hamiltonian $\mathcal{H}_{ZQ} = \mathcal{H}_Z + \mathcal{H}'_Q$ when expanded using Equations (2.2) and (2.3),

$$\mathcal{H}_{ZQ} = -\hbar \gamma_2 I_{z2} H_0 + \frac{e^2 Q q}{4I(2I - 1)} \left(2I_{z2}^2 - (I_{x2}^2 + I_{y2}^2) + \eta(I_{z2}^2 - I_{y2}^2)\right)$$

is written in a mixed reference frame where $I_{z2}$ is along the magnetic field axis and $I'_{z2}$ is along the principal axis of the quadrupole tensor. This can be remedied by rotating the $\tilde{I}'$ operators so that both coordinates coincide. By symmetry, coordinates may be chosen so that it is only necessary to rotate the primed operators around the $\hat{y}$ axis [Equation (2.27)] such that

$$\tilde{I}'_2 = R_\beta \tilde{P}_2 R^\dagger_\beta.$$
The pure quadrupole splitting at zero applied field ($\mathcal{H}_Z = 0$) can be determined by the following:

$$\langle m|\mathcal{H}_Q|m\rangle = \frac{e^2 Q q}{4} \left[ m^2 - \frac{5}{4} \right]. \quad (2.81)$$

It is easy to see that the energy difference between the $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$ states is $e^2 Q q/2$.

For consistency between the sections in this chapter, this quadrupole splitting will be expressed in units of the Zeeman energy of the $^{129}$Xe nucleus in a magnetic field $H_Q$ chosen such that

$$e^2 Q q/2 = \hbar \gamma_1 H_Q \quad (2.82)$$

where $\gamma_1$ is the gyromagnetic ratio of $^{129}$Xe. In these units, the quadrupole splitting in the bulk xenon lattice, as was found by Warren and Norberg, is $H_Q = 4$ G [10]. All energies in this section will thus be expressed likewise in terms of the Zeeman energy of the $^{129}$Xe nucleus.

The $\mathcal{H}_{ZQ}$ Hamiltonian, combining Equation (2.79) and (2.80), can now be diagonalized. Figure 2.2 shows the energy states vs. applied field for various values of $\beta$ when $\eta = 0$ (zero asymmetry). At applied fields around 7 G and 13 G, the energy levels “cross.” Notice that the splitting that lifts the degeneracy at these crossing points depends strongly on the orientation of the principal axis of the EFGs (at the angle $\beta$) with respect to the applied field.

The energy level crossing points are significant. If energy is not externally injected or removed from the spin-EFG system, then transitions between energy eigenstates are prohibited except at degeneracies, seen as energy level crossings on the map. At fields much larger than the last level crossing on the right side of the graphs in Figure 2.2 (at 100 G for example) the Zeeman separation between angular momentum states is large enough so that the $m$ quantum numbers are considered “good.” Thus at 100 G, transitions between the angular momentum states are energetically prohibited. It is only near these level crossings, where admixtures of the angular momentum states exist with similar energies, that cyclic energy-free exchange of angular momentum can be experienced between the $^{131}$Xe nucleus and the lattice EFGs. This can be seen by examining the time evolution of the $\langle I_z \rangle$
Figure 2.2. Energy eigenvalues of the $^{131}\text{Xe}$ nucleus vs. field at various angles of the EFG principal axis ($\beta$), $H_Q = 4$ G. For energy scale see Equation (2.82).

expectation values directly (as was done in section 2.4.1) or by studying the angular momentum “transition probabilities” that will be presented shortly.

The magnitude of the EFG encompassing a $^{131}\text{Xe}$ nucleus also carries a significant effect. As the EFG strengthens, the quadrupole splitting increases and the locations of the level crossings move upfield and broaden. At a quadrupole splitting of $\hbar\gamma_1 \cdot 20$ G, for example, the first crossing is at 34 G and the second crossing is broad ($\pm 30$ G) and is centered at about 70 G. This is a significant result because it indicates that energy-free exchange of angular momentum with the lattice can
exist up to fields of 100 G. At quadrupole splittings equivalent to $H_Q = 30$ G, for example, angular momentum exchange with the lattice is enhanced in the $^{131}$Xe nuclei up to applied fields of $H_0 = 200$ G. Thus the EFG strengths can cause a far-reaching effect when considering lattice interactions with $^{131}$Xe nuclei.

The EFGs found in the xenon lattice are due to mutually induced electric dipole moments (EDMs) between the xenon atoms. Since xenon atoms polarize readily in an electric field, even small fluctuations in neighboring atoms induce coherent EDM fluctuations. This produces van der Waals binding energies in solid xenon of about 0.1 eV. In the bulk lattice, the coherent EDMs nearly cancel, yet small fluctuations still exist. This gives rise to the $H_Q = 4$ G quadrupole splitting in bulk xenon [10]. At the surface of the crystallite or near dislocations and vacancies, the fluctuating EDMs cannot cancel and thus much stronger EFGs are produced.

The total angular momentum along the $\hat{z}$ axis is not generally preserved. Classically this can be understood by reasoning that since the electric field gradient (EFG) produces a torque on the nucleus, an opposite torque is applied to the objects generating the EFG. Thus angular momentum can be passed to and from the lattice cyclically. If the principal axis of the EFG is parallel to the applied field, $\beta = 0^\circ$, then $\langle I_{2z} \rangle$ is preserved; the EFG then acts much like an additional applied magnetic field.

In the lattice, the EFGs are randomly oriented. The applied fields at which the energy levels cross, however, do not vary appreciably with EFG orientation. The transition frequencies between angular momentum states, $W_\tau$, which are proportional to these splittings, however, do vary significantly with orientation. To prevent clutter, only a few graphs were presented and only written descriptions offered about a few observations concerning the behavior of the $^{131}$Xe nucleus at different EFG angles. At $\beta = 0^\circ$, for example, the transition frequencies are zero everywhere, that is to say that $\langle I_{2z} \rangle$ is preserved. As $\beta$ is increased, the transition frequencies between angular momentum states increase as the degeneracy is lifted at the crossing points. At the magic angle, 54.7°, the nondegeneracy at the level crossing is at a maximum and the spin dynamics at the transition points seem
almost chaotic as seen in the $\langle I_{z2} \rangle$ expectation value (this is a written description). Past the magic angle, at $\beta = 90^\circ$, cyclic transitions between the angular $m = \pm \frac{1}{2}$ and $m = \pm \frac{3}{2}$ angular momentum states become completely dominant. This is illustrated by the transition probabilities that will now be presented.

The angular momentum transition probabilities are very informative. Transition probabilities between two angular momentum states, $|m_k\rangle$ and $|m_l\rangle$, depend on the nature of the time evolution of the initial state, $P(t)|m_l\rangle$. Since the propagator $P(t)$ can be found by diagonalizing the Hamiltonian, see Equation (2.69), the time-dependent angular momentum transition probabilities can be expressed by

$$T_{kl}(t) = |\langle m_k | P(t) | m_l \rangle|^2.$$  \hspace{1cm} (2.83)

Such probabilities are time-dependent and cyclical; as the wave equation evolves in time, the probability that the nuclear spin will end up in the $|m_k\rangle$ state, for example, changes. Given a well-defined initial spin state, the probability that the nucleus will be found in any given final state can be calculated over time. Such probability oscillates around a “mean probability” that does not change with time. The time-averaged probability of starting in a state $m_l$ and ending up in state $m_k$

$$\bar{T}_{kl} = \lim_{t \to \infty} \frac{1}{t} \int_0^t T_{kl}(t') \, dt'$$ \hspace{1cm} (2.84)

will be called the time-independent angular momentum transition probability or simply the transition probability. It is convenient to write these probabilities in matrix form. This will be done for various examples including those featured in Figure 2.2.

It may seem strange, at first, that angular momentum transition probabilities are mentioned without including a time-dependent perturbation into the Hamiltonian to drive such transitions. Note, however, that transitions between energy eigenstates are not being considered here; indeed the time-independent Hamiltonian guarantees that total system energy is conserved over time. However, energy-free exchange of angular momentum between the individual spins and fields in the system are allowed under certain circumstances. The system, for example, must
initially be in a certain mixture of energy eigenstates such that quanta of energy can be exchanged between objects in the system and an interaction potential must exist between these objects that drives the exchange [21]. Under such special circumstances, the time evolution of the total-system wave function, as governed by the time-dependent Schrödinger equation, will allow the states of individual spins in the system to evolve cyclicly in time such that there is a finite probability that a spin in a definite initial spin-state undergoes a transition to another spin-state when measured. This is what is meant by transition probability in this context.

Starting with $\beta = 0^o$, a quadrupole splitting equivalent to $H_Q = 4 \text{ G}$ and an applied field of $H_0 = 7.25 \text{ G}$, the transition probability matrix obtained from Equation (2.83) and (2.84) is:

$$\tilde{T}(0^o) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$  \hfill (2.85)

This matrix can be read as follows: Reading across the first row, if the spin is initially in a $m = -\frac{3}{2}$ state then there is 100% probability that it will stay in this state and 0% probability of a transition to any other angular momentum state. Reading across the second row, if a spin is initially in a $m = -\frac{1}{2}$ state, there is a 0% probability of transition to a $m = -\frac{3}{2}$ state, 100% probability of staying in an $m = -\frac{1}{2}$ state, 0% transition probability to the $m = +1/2$ state, and so on; the rows being labeled by $[\frac{-3}{2}, \frac{-1}{2}, \frac{1}{2}, \frac{3}{2}]$ and the columns likewise.

For $\beta = 20^o$ and $H_Q = 4 \text{ G}$ with $H_0 = 7.25 \text{ G}$ and $H_0 = 13 \text{ G}$, respectively:

$$\tilde{T}(20^o) : \begin{pmatrix} 0.93 & 0.05 & 0.01 & 0.01 \\ 0.05 & 0.50 & 0.12 & 0.33 \\ 0.01 & 0.12 & 0.57 & 0.30 \\ 0.01 & 0.33 & 0.30 & 0.36 \end{pmatrix}.$$  \hfill (2.86)

For $\beta = 54.7^o$ and $H_Q = 4 \text{ G}$ with $H_0 = 7.25 \text{ G}$ and $H_0 = 13 \text{ G}$, respectively:
For $\beta = 90^\circ$ and $H_Q = 4 \, \text{G}$ with $H_0 = 7.25 \, \text{G}$ and $H_0 = 13 \, \text{G}$ respectively:

\[
\begin{align*}
\mathcal{T}(90^\circ) : & \quad [7.25 \, \text{G}] \\
& \begin{pmatrix}
0.65 & 0.0 & 0.35 & 0.0 \\
0.0 & 0.88 & 0.0 & 0.12 \\
0.35 & 0.0 & 0.65 & 0.0 \\
0.0 & 0.12 & 0.0 & 0.88 \\
\end{pmatrix} \\
& \begin{pmatrix}
0.86 & 0.0 & 0.14 & 0.0 \\
0.0 & 0.94 & 0.0 & 0.06 \\
0.14 & 0.0 & 0.86 & 0.0 \\
0.0 & 0.06 & 0.0 & 0.94 \\
\end{pmatrix}.
\end{align*}
\]
the small perturbation. In essence, at low enough fields, spontaneous angular momentum exchange between the quadrupole nucleus and the lattice via the EFG coupling is somewhat reduced. As an example, the transition probability matrix, $\tilde{T}(1\,G)$, when $\beta = 20^\circ$ and $H_Q = 4\,G$ is

$$
\tilde{T}(20^\circ) : [1\,G] \begin{pmatrix}
0.86 & 0.14 & 0.0 & 0.0 \\
0.14 & 0.85 & 0.0 & 0.01 \\
0.0 & 0.0 & 0.82 & 0.18 \\
0.0 & 0.01 & 0.18 & 0.81
\end{pmatrix}.
$$

(2.91)

These matrix elements do not change more than a few percent from $H_0 = 0.01$ to $H_0 = 4$; thus illustrating the phenomenon that significant transition probabilities only occur near the more closely degenerate level crossings.

In summary, the dynamics of a $^{131}$Xe nucleus subject to an applied magnetic field and a lattice generated EFG have been solved and examined. The map of the energy levels vs. applied field reveals places where these energy levels “cross”. Only at the so called avoided (nearly degenerate) crossings is significant spontaneous angular momentum exchange seen between the $^{131}$Xe nuclei and the lattice EFGs. Within reasonable limits on the quadrupole energy, $4\,G < H_Q < 30\,G$, the coupling to the lattice is seen to be significant when $5\,G < H_0 < 200\,G$. Within this region, diagonalization of the full Hamiltonian must be used to study the dynamic behavior of the $^{131}$Xe nucleus and the spontaneous transition probabilities.

By themselves, these spontaneous and cyclic spin transitions caused by the coupling between $^{131}$Xe and the lattice EFGs do not cause spin relaxation in the $^{131}$Xe nuclei. For this there must be an exterior thermal reservoir that can exchange energy with the nuclei. Assuming that such a reservoir exists, however, strong coupling between the $^{131}$Xe and the lattice EFGs greatly facilitates this exchange. The purpose of this section has been to explore this coupling. In the next section, relaxation mechanisms will be addressed directly and the role that $^{131}$Xe plays in the transfer of spin angular momentum from the $^{129}$Xe nuclei to the lattice will be explored in more depth.
2.5 $^{129}\text{Xe}$ Relaxation Mechanisms

2.5.1 Introduction

In the solid xenon lattice, the nuclear spin relaxation mechanisms of interest are those processes that allow the $^{129}\text{Xe}$ nuclei to exchange angular momentum with their surroundings; that is exchange with $^{131}\text{Xe}$ nuclei (cross-relaxation), or with thermal lattice modulations such as phonons (spin-rotation) and vacancy hopping, or with the electrons of paramagnetic impurities. Thermal mechanisms such as phonon scattering and vacancy hopping, however, are prevalent only at higher temperatures and thus can be eliminated by lowering the temperature of the lattice. Relaxation due to paramagnetic impurities will be assumed negligible in this treatise; an assumption supported by the very long relaxation times observed at high field. This shifts the focus to only the $^{129}\text{Xe}$-$^{131}\text{Xe}$ cross-relaxation mechanism which is primarily field dependent, relying on the quantum mechanical details of the interactions between the two isotopes. In this section the focus will be primarily on $^{129}\text{Xe}$-$^{131}\text{Xe}$ cross relaxation, aside from a brief mention of the thermal relaxation mechanisms mentioned above.

Perturbation theory cannot be employed when solving for angular momentum exchange probabilities between neighboring $^{129}\text{Xe}$ and $^{131}\text{Xe}$ nuclei because the Zeeman energies at low fields [Equation (2.2)] are not larger than all of the other interaction energies in the lattice. In bulk xenon, the $^{131}\text{Xe}$ quadrupole-lattice energies are estimated to be of the same order of the $^{129}\text{Xe}$ Zeeman energies at fields of around 7 G [7] and dipole-dipole interactions in $^{129}\text{Xe}$ are on the order of 150 mG. Since many of the measurements in these experiments were at fields below 10 G and interesting features in the data occur between 1-5 G, it becomes necessary to use another method, the direct diagonalization of the Hamiltonian, in order to obtain reliable energy spectra and $^{129}\text{Xe}$ spin dynamics.

After a brief discussion of thermal relaxation mechanisms, a two-body Hamiltonian for the $^{129}\text{Xe}$-$^{131}\text{Xe}$ system will be presented and diagonalized. The full dynamics of this system will be discussed as focus is placed on one or two points in the parameter space. Some generalizations will then be attempted and expected
behavior discussed. Finally, an appeal to thermal physics will be made to further cement some of the physical concepts.

### 2.5.2 Temperature Dependent Relaxation Mechanisms

This section is intended to be brief and is included only for completeness. As will be shown, our main experiment was designed to eliminate any known temperature dependent relaxation mechanisms and to focus on the mechanisms which depend solely on magnetic field strength and $^{131}$Xe isotopic concentration. It is helpful, however, to include some reference to possible temperature dependent mechanisms; at least in an effort to convince ourselves that they have indeed been frozen out at our operating temperature: liquid Helium at 4.2 K.

Spin-rotation coupling exists between the $^{129}$Xe nuclei and the spinless electron clouds or other nuclei in the lattice. Even in diamagnetic solid xenon, phonons may cause relative angular motion of electrons or other nuclei around any given $^{129}$Xe nucleus. The Hamiltonian, $\mathcal{H}_{SR}$, for this spin-rotation interaction is

$$\mathcal{H}_{SR} = -\hbar \gamma H_r (\vec{I} \cdot \vec{J})$$  \hspace{1cm} (2.92)

where $H_r$ is the strength of the field coupling and $\vec{J}$ is the relative angular momentum caused by phonons.

As discussed in detail in Gatzke’s dissertation [7], there are two major types of temperature dependent mechanisms in the lattice. The first is due to the Raman scattering of phonons and the second due to vacancy hopping in the lattice. Gatzke [7] found that the activation energy of $E_d/k_B = 1650$ K for thermally activated vacancy hopping in natural xenon fit his data well at temperatures from 145 K to the melting point (161 K) where vacancy diffusion dominates. Earlier efforts by Yen and Norberg [8] and Eisenstadt and Redfield [28] both measured vacancy diffusion activation energies in xenon with $E_d/k_B > 1000$ K. Since the nuclear relaxation due to vacancy diffusion, $T_{1d}$, is given by [7]

$$\frac{1}{T_{1d}} = A e^{E_d/k_B T}$$  \hspace{1cm} (2.93)

where $A$ is a constant. It follows that the ratio of $T_{1d}(4.2 \text{ K})$ to $T_{1d}(145 \text{ K})$ is $e^{0.24E_d/k_B}$, which is greater than $e^{200}$. From this alone, it is obvious that nuclear
relaxation due to atomic diffusion at 4.2 K is entirely negligible. The vacancy diffusion relaxation mechanism only begins to dominate at temperatures above 120 K.

The first temperature dependent relaxation mechanism mentioned was the Raman scattering of phonons. Again all arguments are taken from Gatzke's dissertation. The Debye temperature of solid xenon is $\theta_D \approx 55$ K. Relaxation by the "direct" absorption of phonons, at frequencies rivaling the Larmor frequencies (from 1 kHz to 20 MHz), has been shown to be negligible [29]. The Raman scattering cross section for high-energy phonons (with wavelengths on the order of atomic distances), however, is significant. Through a Raman scattering process, high-energy phonons can still impart a small amount of energy and angular momentum to a nuclei. However, according to the Plank distribution, these high-energy phonon states deplete quickly at temperatures less than about 10 K for solid xenon [30, 23]. The calculations are quite involved and are all documented in Gatzke's dissertation.

The real evidence that all temperature dependent relaxation processes have been frozen out, however, is in the extraordinarily long relaxation times encountered at high field and 4.2 K. Both Gatzke's experimental results [3] and the results reported in section 3.3.3 show $T_1$ on the order of many hundreds of hours at 1 T and 4.2 K. Such a phenomenon would not be possible if these relaxation processes were still significant at such low temperatures. This is not the case at liquid nitrogen temperature (77 K), however. At 77 K, the nuclear relaxation mechanisms at 1 T can be attributed mainly to phonon scattering; as significant high-energy phonon occupations do occur at this temperature.

2.5.3 $^{129}$Xe–$^{131}$Xe Cross Relaxation

Having eliminated thermal relaxation mechanisms for the $^{129}$Xe nuclei at liquid helium temperatures (4.2 K), the only remaining relaxation mechanisms are due to the interaction of the $^{129}$Xe nuclei with their own local environments. The $^{131}$Xe nuclei, however, still have a strong electrical coupling to EFGs in the lattice through their electric quadrupole moment, as discussed in section 2.2. As such, the whole focus shifts to cross relaxation between $^{129}$Xe and $^{131}$Xe in the lattice.
There are two processes involved in this relaxation mechanism. First, exchange of angular momentum between the $^{129}$Xe and $^{131}$Xe nuclei and, second, the subsequent coupling of the $^{131}$Xe to the lattice; mainly due to its quadrupole interaction with the lattice EFGs. Ultimately this linkage allows thermal contact between the lattice and the $^{129}$Xe nuclei and is the mechanism for cross relaxation. $^{131}$Xe plays a dominant role in this relaxation mechanism by allowing the $^{129}$Xe nuclei to transfer angular momentum to the lattice.

In order to more closely examine the quantum mechanical nature of the $^{129}$Xe-$^{131}$Xe-EFG interaction, the full two-body Hamiltonian was diagonalized (as outlined in section 2.4). The energy levels vs. applied field were closely examined in order to determine at what fields they cross (where Zeeman splittings between $^{129}$Xe and $^{131}$Xe nuclei energetically coincide) and if so whether an angular momentum exchange probability exists at these specific fields. The full dynamics were solved at the more prominent level crossings, expectation values calculated and the transition rates determined. In order to illustrate the general results of this investigation, one nuclear orientation with respect to the magnetic field and lattice EFGs will be presented in detail and generalizations will be drawn about what would be expected if an average over all nuclear and EFG orientations were made.

The full two-body Hamiltonian for the interacting $^{129}$Xe-$^{131}$Xe nuclei is

$$\mathcal{H} = \mathcal{H}_{Z1} + \mathcal{H}_{Z2} + \mathcal{H}_D + \mathcal{H}_Q$$  \hspace{1cm} (2.94)$$

as given by Equations (2.2, 2.3, 2.4) in section 2.2 and where the subscript (1) refers to the $^{129}$Xe nucleus and (2) the $^{131}$Xe nucleus. Using the methods described in section 2.4, this Hamiltonian was diagonalized and the spin dynamics completely solved for any given set of initial parameters. The parameter space for this problem, however, was large. The variable \( r \) represents the internuclear distance, \( \theta \) represents the angle of the internuclear vector relative to the \( \hat{z} \) axis. The Euler angles \( \alpha, \beta \) and \( \gamma \) (not to be confused with the gyromagnetic ratio) are used to indicate the relative orientation of the principal axis of the EFG quadrupole tensor. \( \mathcal{H}_Q \) represents the strength of the inherent quadrupole energy due to the EFGs from the lattice and
\( \eta \) is the asymmetry parameter for the quadrupole tensor. Thus it was impractical to pursue complete exploration of this large parameter space. A few examples of spin dynamics at specific points in this parameter space will be examined and some general conclusions and observations offered.

In Figure 2.3 the energy levels vs. applied field are shown for this system with the following parameters: \( r = 4.34 \text{ Å}, \theta = 0^\circ, \beta = 54.7^\circ, H_Q = 4 \text{ G}, \) the rest are zero. Many energy level crossings can be seen; some of these crossings represent fields where the Zeeman energy of the \(^{129}\text{Xe}\) nucleus matches the difference between two of the energy levels of the \(^{131}\text{Xe}\) nucleus. At these degeneracies in this two-spin system, energy-free exchange of angular momentum between the nuclei, mediated by the dipole-dipole interaction, is dramatically enhanced. Particular focus is placed on the \( H_0 = 13.23 \text{ G} \) level crossing. The dynamics of the \(^{129}\text{Xe}\) nucleus, shown by the expectation value \( \langle I_{z1} \rangle \) at this field, are shown on the right of Figure 2.3. Here \( \langle I_{z1} \rangle \) oscillates in time indicating that the \(^{129}\text{Xe}\) nucleus has an increased probability of flipping at the transition rate of about twice every second. This probability is time dependent and oscillates with a period of about one second as seen in Figure 2.3.

The time-independent transition probability from spin up to down as computed

![Figure 2.3. Energy eigenvalues of two interacting \(^{129}\text{Xe}-^{131}\text{Xe}\) nuclei vs. field [on left]. Time evolution of \( \langle I_{z1} \rangle \) from the initial state \( | -\frac{1}{2}, -\frac{3}{2} \rangle \) at the 13.23 G level crossing [on right].](image-url)
from Equation (2.84) gives the average probability of a transition happening over half a period; this is computed to be about 6% in this example. Thus the average transition rate would be about once every 8 seconds. Keep in mind that this represents only one of the level crossings at only one specific point in parameter space. In order to calculate an experimentally measurable quantity, averages over all possible nuclear orientations, distances and EFGs in the lattice would need to be taken. Even if this were done, the result would be approximate at best and would necessarily depend on assumptions about the strength and orientations of the EFGs in the lattice.

The strength and orientation of the EFGs in the lattice that interact with the $^{131}$Xe nuclei are related to the strength of the $^{131}$Xe relaxation centers. Qualitatively, the energy level crossings that mark the much enhanced probability of angular momentum interchange between the $^{129}$Xe and $^{131}$Xe nuclei depend on the quadrupole energy. With $H_Q = 20$ G, for example, there are level crossings well into the 60-80 G range, see Figure 2.4, indicating increased probability of cross relaxation in this range of fields. See the discussion in section 2.5.3. Such large EFGs, however, are a factor of five larger than those expected in the bulk

![Figure 2.4](image)

**Figure 2.4.** Energy eigenvalues vs. field when $H_Q = 20$ G for two interacting $^{129}$Xe-$^{131}$Xe nuclei; showing that the degeneracies (crossings) move to higher fields as $H_Q$ increases.
lattice and thus would be experienced only at lattice defects and on the surface of the crystallites. Only at fields smaller than 15 G, again referring to Figure 2.3, would there be significant probability of cross relaxation in the bulk lattice, where $H_Q \approx 4$ G. At this specific point in parameter space and at fields above 15 G, angular momentum interchange between neighboring $^{129}$Xe and $^{131}$Xe nuclei in the bulk is negligible. Therefore, the predominant relaxation centers at fields above 15 G would be located only at lattice defects and on crystallite surfaces.

It is particularly interesting to note that for $H_Q = 4$ G, as expected in the bulk Xe lattice (Figure 2.3), and at fields less than 3 G, there are no level crossings. At this range of fields, the quadrupole energy dominates the Zeeman energies. This indicates that the probability of angular momentum interchange is diminished at low fields, below 3 G, prior to the first level crossing. Despite ambiguities about the EFG distribution in the bulk lattice, if the EFG strength were not to go below $H_Q = 4$ G, it could be argued that for all possible nuclear orientations, relaxation would be curtailed in this range of fields where the spin dynamics are determined more by the local EFGs and less by the effects of the applied or local fields. The natural result of this diminished coupling at fields below 3 G would be that $^{129}$Xe relaxation slows down at these fields. In section 3.5.1, the experimental data exhibits slower relaxation in precisely this range of fields.

In summary, nuclear relaxation due to spin interchange with $^{131}$Xe in the bulk, where $H_Q = 4$ G and at fields between 0-3 G is expected to be slow, this due to lack of energy level crossings at these fields. Between 3 G and 15 G, there are level crossings and relaxation in the bulk can be active, but weak. Above 15 G, bulk relaxation due to $^{131}$Xe is very unlikely. However, due to the relatively high EFGs possible near lattice defects and on the surface, $H_Q$ could be many times larger than the bulk value at these specific locations; level crossings (and thus cross relaxation) would occur at much higher fields near these locations. The $^{131}$Xe at the surface or at lattice defects can become effective relaxation centers for fields extending even into hundreds of Gauss.

At this point another important observation should be made. The total angular
momentum lost over time due to this time-independent Hamiltonian is zero. It has been shown, however, that at certain level crossings and conditions, angular momentum may be exchanged between the lattice and the two nuclei cyclically. Another mechanism must also be considered to determine how the lattice can carry away this energy and angular momentum, say by induced time-dependent fluctuations in the EFGs. Such mechanisms are thermal, involving an exchange of energy quanta, and cannot be treated directly by this method. However, this very mechanism is central to the discussion of nuclear relaxation.

Appealing to the concept of spin temperature and heat transfer, it may be postulated that the states of the $^{131}$Xe nuclei, as an ensemble average, are maintained at a certain temperature. As such, the equilibrium populations of energy levels for the $^{131}$Xe nuclei can be described by the Boltzmann distribution in Equation (2.6). If there is a channel to distribute energy from the $^{131}$Xe nuclei to the $^{129}$Xe nuclei, as has been shown in this section, then “heat” transfer is possible from the lattice, which is maintained at some higher temperature, through the $^{131}$Xe, at some intermediate temperature (by means of the quadrupole coupling), and ultimately to the $^{129}$Xe nuclei. The nature of the EM fields, however, that allow heat transfer to and from the lattice are not at our disposal, and thus relaxation times must be experimentally determined.

The density functional formalism provides a powerful method to solve for the time evolution of a system towards thermal equilibrium. However, without information about the time-dependent parts of the Hamiltonian which cause nuclear relaxation in the $^{131}$Xe, this formalism is entirely equivalent to the diagonalization technique that has already been employed and yields no new results. Since the propagator, $P(t)$, can be found by the diagonalization technique, the time evolution of any initial state, $|\psi_0\rangle$ (even when this initial state represents an ensemble average over many individual initial states) is $|\psi\rangle = P(t)|\psi_0\rangle$. Having solved for the state of the system $|\psi\rangle$ over all time, no other information can be derived. For completeness, though, an argument will be made to show this equivalence.

Given a time-independent Hamiltonian, $\mathcal{H}$, a convenient representation of the
The propagator can be written by direct solution of the Schrödinger equation (2.18):

\[ P(t) = e^{-i\mathcal{H}t/\hbar}. \]  

(2.95)

The density functional, therefore, can be written as

\[ \varrho = |\psi\rangle \langle \psi| = P(t)|\psi_0\rangle \langle \psi_0|P^\dagger(t). \]  

(2.96)

Performing standard time differentiation on the density functional yields

\[ \frac{\partial \varrho}{\partial t} = P(t)|\psi_0\rangle \langle \psi_0|P^\dagger(t) \left( \frac{i}{\hbar} \mathcal{H} \right) + \left( -\frac{i}{\hbar} \mathcal{H} \right) P(t)|\psi_0\rangle \langle \psi_0|P^\dagger(t) \]  

(2.97)

\[ = \frac{i}{\hbar} [\varrho \mathcal{H} - \mathcal{H} \varrho] \]

\[ = \frac{i}{\hbar} [\varrho, \mathcal{H}] \]

which is the time evolution of the density functional as shown in equation (2.7). Therefore if the propagator is known, then the time evolution of the density functional is also known and no further information is possible.

### 2.5.4 Summary

In this section, at least a conceptual view of the expected behavior of nuclear relaxation due to $^{131}$Xe relaxation centers has been presented. To recapitulate, spin diffusion allows angular momentum to be transferred among the $^{129}$Xe nuclei via dipole-dipole couplings between nuclei (section 2.4.2). This angular momentum can then be transferred to the $^{131}$Xe nuclei in the lattice. Such transfer is allowed only at specific magnetic fields determined by the relative placement of the two nuclei and the nature of the EFGs present at the location of the $^{131}$Xe nuclei. Then by thermal processes, angular momentum is transferred to the lattice [via the quadrupole $^{131}$Xe-EFG coupling (section 2.4.3)] and lost from the $^{129}$Xe spin system. This cross relaxation process is henceforth assumed to be the dominant mechanism in xenon solid by which nuclear relaxation takes place at liquid helium temperatures.
CHAPTER 3
THE NUCLEAR RELAXATION EXPERIMENTS

3.1 Introduction

In this chapter, longitudinal nuclear relaxation experiments on solid polycrystalline Xe will be outlined. These experiments were specifically designed to investigate and document nuclear relaxation in the previously unexplored regime of low fields (less than 200 G) and low temperatures (77 K and 4.2 K). It is of particular interest to investigate the role that $^{131}$Xe plays in the nuclear relaxation of polycrystalline $^{129}$Xe in this regime. The experimental procedures and apparatus employed in these experiments will be documented with a level of detail necessary to reproduce them if desired. Below is a brief introductory synopsis of the four major experiments performed:

Nuclear relaxation of $^{129}$Xe at 77 K: Nuclear relaxation data were acquired at various fields between 1 G and 500 G for both natural (26.4% $^{129}$Xe and 21.2% $^{131}$Xe) and enriched (86% $^{129}$Xe and 0.1% $^{131}$Xe) xenon. Several methods of freezing the samples were explored. Data acquisition was done by field cycling; quickly ramping the field to the nuclear magnetic resonance (NMR) field, using pulsed NMR to collect the data, and then quickly ramping the field back to the field of interest. Detailed experimental procedures are outlined in section 3.3.1 and experimental results presented in section 3.3.2.

Nuclear relaxation of $^{129}$Xe at 4.2 K: The same range of fields and methods were used to collect data as in the first experiment. In addition, samples with varying isotopic concentrations were studied. Due to unexpected results, some efforts were made to insure that systematic errors were not significant.
Detailed procedures are outlined in section 3.3.3 and results presented in section 3.3.4.

**Cross polarization and relaxation of $^{131}\text{Xe}$:** This experiment specifically focused on measuring the $^{131}\text{Xe}$ NMR signal at high field after having lowered the field sufficiently to allow cross polarization with hyperpolarized $^{129}\text{Xe}$ over a range of mixing times. The subsequent $^{131}\text{Xe}$ nuclear relaxation at high field was also studied. Samples of natural Xe (21.2% $^{131}\text{Xe}$) were exclusively used. Detailed procedures and results are in section 3.4.

**Nuclear relaxation of $^{129}\text{Xe}$ using AFP at 4.2 K:** A distinct NMR detection method, Adiabatic Fast Passage (AFP), was used to measure nuclear relaxation in this final experiment. Data sets were taken in order to help reinforce the results of the second experiment and eliminate possibilities of systematic error. Data collection for this method was rapid and automated. Detailed explanations and procedures are in section 3.5 and the results presented in section 3.5.1.

Longitudinal nuclear spin relaxation (as defined in section 2.1) was measured by monitoring the NMR signal strength as it decayed over time. Conventionally such are referred to as $T_1$ measurements. The author hesitates to use this terminology due to the distinctly nonexponential character of the decays seen. No single time constant, $T_1$, can be used to describe some of these decay curves; the observed decay rates are clearly time-dependent. However, the terminology $T_1$ "long" ($T_{1L}$) is used to describe the time constant of the nearly exponential long-time tail (typically after about 6 hours of relaxation) and $T_1$ "short" ($T_{1S}$) refers to the approximate time constant minutes after the field was first lowered to the field of interest. The following sections will focus on experimental procedures and experimental results.
3.2 Sample Preparation

3.2.1 Cell Preparation

Careful preparation of the closed test-tube-shaped (4 cc) pyrex cells used to polarize and freeze the $^{129}$Xe was critical to the success of the experiment. The 5 cm long cell body, made of 1 mm thick 12 mm diameter pyrex tubing, had a rounded end, which served as a laser window during optical pumping. A 5 mm diameter pyrex tube was attached to the other end of the cell and connected to a pyrex manifold used for cell preparation. The pyrex manifold, with four cells connected, was then attached to a clean stainless-steel gas distribution manifold that included an oil-free high-vacuum turbomolecular pump. See Figure 3.1.

A high-purity rubidium ampule was opened and dropped inside a glass retort inside the pyrex manifold under nitrogen gas. The glass retort was then quickly sealed off with a torch and the entire manifold was evacuated and leak tested. An oven was placed around the cells on the pyrex manifold and they were baked at approximately 400°C at high vacuum for a few days to bake off the cell-wall impurities.

![Diagram of the gas manifold used in cell preparation.](image)
At the end of the bakeout, the rubidium was distilled twice through built-in retorts and then the original rubidium retort was torched off and removed. A small amount of the distilled Rb metal was chased into the first cell (A) with a torch. This cell was then submerged in liquid nitrogen and the desired pressures of xenon gas mixture (enriched and natural xenon) were introduced (typically 4 atm-cc of gas) into the volume-calibrated stainless steel manifold. When the Xe gas was released into the pyrex manifold it quickly condensed inside the cold cell; the freezing point of Xe is around 160 K, well above the temperature of liquid nitrogen at 77 K. Approximately 70 mBar of nitrogen gas and 600-1000 mBar of helium gas, for use during optical pumping (as covered in the next section), were then introduced into the manifold. This first cell (A) was then torched off and detached from the pyrex manifold and the entire manifold re-evacuated. This procedure was repeated for the next three cells. The four cells were given names (consisting of a catalog number with A, B, C or D appended to determine the order of the cells on the manifold, for example: 18A, 18B, 18C and 18D). See Table 3.1 for the list of cells used in these experiments and the room-temperature partial pressures of the gases contained in the cells.

These cells were then placed inside an oven and baked at 100°C for several more days to cure them. This curing process helped stabilize the wall relaxation

<table>
<thead>
<tr>
<th>Cell</th>
<th>Xe (mBar)</th>
<th>He (mBar)</th>
<th>$T_1$ (min)</th>
<th>$^{35}\text{Xe}$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>18A</td>
<td>260</td>
<td>1000</td>
<td>42</td>
<td>0.1</td>
</tr>
<tr>
<td>18B</td>
<td>1150</td>
<td>1000</td>
<td>38</td>
<td>0.1</td>
</tr>
<tr>
<td>26D</td>
<td>1230</td>
<td>900</td>
<td>8</td>
<td>21</td>
</tr>
<tr>
<td>38A</td>
<td>1200</td>
<td>620</td>
<td>4</td>
<td>0.2</td>
</tr>
<tr>
<td>38B</td>
<td>1200</td>
<td>640</td>
<td>4</td>
<td>0.44</td>
</tr>
<tr>
<td>38C</td>
<td>1200</td>
<td>640</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>39A</td>
<td>1230</td>
<td>660</td>
<td>12</td>
<td>0.1</td>
</tr>
<tr>
<td>39B</td>
<td>1100</td>
<td>670</td>
<td>12</td>
<td>0.2</td>
</tr>
<tr>
<td>39C</td>
<td>1200</td>
<td>670</td>
<td>10</td>
<td>0.4</td>
</tr>
<tr>
<td>39D</td>
<td>1550</td>
<td>660</td>
<td>38</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 3.1. Xenon cell data at room temperature and 30 G. 70 mBar of nitrogen gas is also in each cell.
properties of the cell. Minimizing wall relaxation in the gas phase is critical to optimizing both the maximum polarization and the holding time of the hyperpolarized $^{129}\text{Xe}$ in the cell. The gas-phase relaxation time $T_1$ listed in Table 3.1 indicates this holding time at 30 G. Since wall relaxation rates limit the maximum polarization achievable during optical pumping, only cells with a $T_1$ better than 30 min could achieve polarizations above 30% in the polarizer (as described in the next section).

### 3.2.2 $^{129}\text{Xe}$ Gas Polarizer and Polarimetry

A polarizer was constructed to polarize $^{129}\text{Xe}$ gas through spin exchange optical pumping (SEOP) [5]. Specifically, a $^{129}\text{Xe}$ cell was placed in a sample holder and covered with a fiberboard-encased aluminum windowed oven and heated to a temperature anywhere from 95°C to 105°C. The resulting Rb vapor in the cell was then exposed to circularly polarized (794.7 nm) laser light from a frequency-narrowed 3 W diode laser. See Figure 3.2. Such photons, possessing definite energy and angular momentum, can be absorbed only by Rb “spin-down” valence electrons moving them into the spin-up $D_1$ excited state. Nitrogen quenching gas serves to nonradiatively de-excite the $D_1$ electrons to the ground state, with high efficiency, to either a spin-up or spin-down state with equal probability. Those electrons in a spin-up state are transparent to subsequent photons, those in the spin-down state are able to absorb a photon and be flipped up. With enough photons, the spin-down state will quickly (in microseconds) be depopulated and the thus Rb electrons can normally be polarized to near unity.

Collisions of the Rb atoms with the xenon atoms, however, tend to destroy the Rb polarization [14], therefore lower xenon partial pressures aid pumping efficiency [15]. However, during some of these collisions, spin exchange via Fermi contact between the Rb electron and the $^{129}\text{Xe}$ nucleus occurs. This spin exchange rate $\gamma_{se}$ is generally slow (one or two per hour) and thus the longitudinal relaxation rate $\Gamma = 1/T_1$ in the $^{129}\text{Xe}$ gas, typically dominated by relaxation on the cell wall, must be slow ($T_1 > 30$ min) in order for the $^{129}\text{Xe}$ nuclei to accumulate substantial polarization. The polarization transient $P_N(t)$ during optical pumping is given by:
Figure 3.2. Diagram of the $^{129}$Xe polarizer.

$$P_N(t) = \langle P_A \rangle \frac{\gamma_{se}}{\gamma_{se} + \Gamma} \left[ 1 - e^{-(\gamma_{se} + \Gamma)t} \right],$$  \hspace{1cm} (3.1)

where $\langle P_A \rangle$ is the time- and volume-averaged rubidium vapor electron polarization. The cells used in these experiments were optimally pumped at temperatures ranging from 95°C to 105°C. One atmosphere of helium gas was added to pressure broaden the $D_1$ absorption line of the Rb in an attempt to better match the broad spectral width of the pumping diode laser. There is much interest in the efficiency of $^{129}$Xe optical pumping and several articles have been published on this topic, both
A frequency narrowed tunable 3 Watt diode laser operating near 794.7 nm was constructed for this experiment [33, 34]. A Coherent S-79-3000C-200-H diode laser package with an integrated thermistor, for measuring laser temperature, and thermo-electric cooler (TEC) was thermally mounted on an air-cooled heat sink. An Omega CNi16D54 temperature controller, used bridge linearized feedback from the thermistor to regulate the base voltage of a Darlington power transistor that in turn controlled the current through the TEC. Stable temperature regulation of the laser within ±0.01°C was achieved with this arrangement. At 15°C, the free-running line width of the laser was about 1.4 nm and the beam profile had a 30° divergence perpendicular to the diode junction and 9° parallel to it.

A 3.5 mm focal length, 0.85 N/A aspheric lens in conjunction with two 50 mm focal length (I/R coated) cylindrical lenses were mounted on a rigid cage connected to the laser and used to carefully collimate the beam resulting in a parallel beam with a constant 5x7 mm rectangular Gaussian profile. Frequency narrowing was achieved by means of optical feedback from a 1800 l/mm UV (low efficiency) holographic diffraction grating placed in Littrow configuration with the beam [33] (at an angle such that the first-order diffraction was sent directly back toward the incident beam). A 1/2 waveplate was also placed in the optical path to adjust the intensity of the optical feedback. With this feedback, the laser line width was narrowed to a FWHM of 0.2 nm with an intensity of 2 W at full power as taken from the zeroth order of the grating. The laser temperature, the grating angle and feedback were varied to optimize the spectral power of the laser at the Rb $D_1$ resonance frequency of 794.7 nm. The completed laser was tunable over a range of about ±1 nm by rotation of the optical cage around the grating via the use of a micrometer actuator. After a warm-up period of about 30 min, frequency stability was excellent (as measured by the Rb fluorescence and by a 0.27 m monochrometer).

A forced-hot-air oven was also constructed that could be temperature regulated to 0.1°C by use of another Omega controller, driving a filament heater which warmed the injected air. A set of Helmholtz coils were wound to produce the small
(≈30 G) uniform magnetic field needed for NMR detection of $^{129}$Xe gas polarization. A low-field pulsed NMR spectrometer, designed by Conradi et al. [35], was also constructed to monitor the net magnetization of the $^{129}$Xe gas both during and after pumping. Lastly, a filtered infrared camera was utilized to detect the Rb $D_2$ fluorescence (780 nm light emitted when the laser is correctly tuned). See Figure 3.2. Uniform, field-aligned laser distribution throughout the cell during pumping was found to be one of the most critical factors to consider while optimizing pumping efficiency. Using this polarizer, $^{129}$Xe polarizations better than 30% were obtained for cells in which gas $T_1$ relaxation times were better than 30 min. Each cell exhibited a different optimal pumping temperature (for cell 18B this was 96°C).

The absolute polarization of the $^{129}$Xe gas was obtained by comparison of the $^{129}$Xe gas NMR signal intensity to that of protons in a liquid water sample of equal shape and volume. The Pulsed NMR Signal intensity $S$ is proportional to the number of excess longitudinal spins in the sample ($nVP$, where $n$ is the spin density, $V$ is volume and $P$ is the polarization) multiplied by the strength of the magnetization that is tipped into the transverse plane by an RF pulse $[\frac{\hbar}{2}\sin(\frac{\gamma H_1 t_p}{2})]$, where $\gamma$ is the gyromagnetic ratio, $H_1$ is the magnitude of the RF pulse and $t_p$ is the duration of the RF pulse (see section 2.3.1). Recall that $\gamma H_1 t_p = \theta_{tip}$ is the “tip” angle of the magnetization off the applied-field axis, see Equation (2.38). Therefore, with small tip angles ($\sin(\theta_{tip}) \approx \theta_{tip}$) and samples of $^{129}$Xe gas and water having roughly the same volume at equal RF frequencies and pulse magnitudes, the signal ratio between a $^{129}$Xe sample and protons in water is:

$$\frac{S_{^{129}}}{S_p} = \left( \frac{n_{^{129}}}{n_p} \right) \left( \frac{P_{^{129}}}{P_p} \right) \left( \frac{\gamma_{^{129}}}{\gamma_p} \right)^2. \quad (3.2)$$

Using the proton density of $6.69 \times 10^{22}$ spins/cm³ in water at room temperature and the fact that the polarization of the protons follows the Boltzmann distribution ($P_p \approx hf/2k_B T$ at high temperatures), the absolute polarization of enriched (86%) $^{129}$Xe at room temperature is calculated to be:

$$P_{^{129}} = \frac{(0.332\%) \text{ (frequency in MHz)} \ S_{^{129}}}{Xe \text{ pressure in atm} \ S_p}. \quad (3.3)$$
The NMR signals of $^{129}\text{Xe}$ and water ($S_{129}$ and $S_p$) were measured by using a fixed tuned NMR probe at a frequency of approximately 11.8 MHz in a 1 T electromagnet. A cell with hyperpolarized $^{129}\text{Xe}$ gas was placed in the probe. The field was set to $^{129}\text{Xe}$ resonance. A low-flip-angle pulse was then transmitted and a free induction decay (FID) collected by the high-field spectrometer. The Xe cell was replaced by a water sample of equal shape and volume. The field was adjusted to be the proton resonance (at the same frequency) and an identical pulse was sent and FID collected. The magnitude of these two FID signals were then substituted into Equation (3.3). It should be mentioned that immediately before and after collecting the high-field FID for the hyperpolarized $^{129}\text{Xe}$ sample, a FID was also taken by the low-field NMR spectrometer inside the polarizer. This served to calibrate the low-field spectrometer and also to estimate the percentage of polarization lost in transferring the cell out of the polarizer, into high field and back into the polarizer. Typically this loss was very small (less than 3%).

### 3.2.3 Freezing the Hyperpolarized $^{129}\text{Xe}$ Sample

It has become apparent throughout all of these experiments that the low-field nuclear relaxation properties of solid enriched $^{129}\text{Xe}$ depend significantly on the method of freezing the sample. This was first manifest when repeated experiments on the same cell with identical preparation (large area vapor deposition) and experimental parameters produced relaxation curves, though qualitatively similar in shape, that would vary as much as 20% from the mean when it came to the long-time relaxation times ($T_{1L}$). Later, samples were intentionally prepared using two significantly different solidification processes, frozen liquid opposed to vapor deposition. The differences in the characteristic nuclear relaxation between such samples were entirely inconsistent. In particular, no two samples of frozen liquid $^{129}\text{Xe}$, even with the same cell and identical experimental conditions, exhibited similar relaxation characteristics. In one case, the characteristic relaxation of frozen liquid was closely monoexponential (see section 3.3.2). In other cases, nuclear relaxation in frozen liquid samples exhibited nonexponential behavior, but both
the qualitative and quantitative behavior between trials was entirely inconsistent. Due to the varying results in frozen liquid samples, no consistent results can be reported other than the general observation that nuclear relaxation in enriched $^{129}$Xe samples at low-field depends strongly on the solidification process.

Cell to cell variations were also seen (50% differences in $T_{1L}$ from cell to cell) to the extent that it was decided to use only one cell (18B) in the majority of the experiments for self-consistency and in order to eliminate the influence of possible unknown variations between cells. Thus it is important to carefully document the procedure used to freeze the Xe samples used in the experiments.

The freezing procedure involves placing the 1 cm long, 5 mm diameter pull-off of the cell into liquid nitrogen while inside the large (1 T) uniform magnetic field found in the center of the pole faces of an electromagnet. This procedure preserves close to 100% of the $^{129}$Xe nuclear polarization, as confirmed by revolatilizing the frozen sample in the same high field and transferring it back to the polarizer to re-acquire the low-field NMR signal. The polarization, however, is not so preserved if the sample is frozen or thawed in a smaller field using the same procedure. Even fields as high as 1000 G outside the pole faces of the electromagnet or in the field of a permanent magnet (1600 G) yielded poor returns. This is an experimental observation made over many trials. In fact, the polarization was completely destroyed in most attempts to freeze the sample outside the poles of the electromagnet.

Samples were frozen consistently by the following procedure: When the sample was fully polarized, the oven was turned off. After the oven temperature fell below 85°C, the laser was blocked and the cell was removed from the polarizer sample holder and cooled (still inside the 30 G field) by placing it in a stream of compressed air until the Rb solidified. Freezing was accomplished by smoothly removing the cell from the oven and inserting one-half of the pull-off into a cup of liquid nitrogen situated between the pole faces of the electromagnet at 1 T for exactly 2 min. See Figure 3.3. A snowy, white, dendritic condensate was seen to form on the cold walls of the pull-off. This technique is termed the “large area deposition” method and
was used most often. Other methods (as shown in Figure 3.3) were also employed.
The “small area deposition” method involved dipping just the tip of the pull-off into the liquid nitrogen and waiting several minutes for a small white “snowball” to form near the tip. “Frozen liquid” was formed by repeatedly melting the solid into a liquid with the slight touch of a warm finger then quickly submerging the pull-off under the surface of the liquid nitrogen until a small “ice cube” had completely formed. The ice cube often appeared fractured and had a milky white appearance.

Samples thus prepared were momentarily taken out of the high field and as quickly as possible inserted into an NMR probe and lowered into a dewar filled with liquid cryogens that was also situated in a high field. Transfers of 10-15 seconds were common. Polarization losses due to this transfer were variable (up to 50% loss of signal estimated due to transferring enriched samples and up to 90% loss in natural samples, relative to the best signal). The relaxation time for solid natural samples is estimated to be only of the order of several seconds when in the fields encountered during these transfers. Curiously, in about 50% of the transfers for natural Xe and 10% of the transfers for the enriched samples, all detectable polarization was destroyed in the transfer; transfers were normally either successful or complete failures.
3.3 The Pulsed NMR Experiment

In order to study relaxation at low fields, stable fields ranging from 1 G to 200 G (±3%) were sustained between the pole faces of a Varian electromagnet during the many minutes (or even hours) between data acquisitions. A set of secondary coils, designed to fit over the soft iron pole faces on the electromagnet, was utilized for this purpose. These secondary coils were connected to a current-regulated benchtop power supply. For fields less than 30 G, it was necessary to turn off the power supply to the large Varian electromagnet and adjust the remanent field with these secondary coils. Large hysteresis effects in the iron cores required that the current in the small coils be adjusted several times before a sample could be loaded; the secondary coils were so adjusted such that the field consistently returned to the same desired value every time the electromagnet was ramped down and/or turned off. Fields larger than 30 G required that the electromagnet remain on and fine tuning was done with the secondary coils after every field cycle. The field was measured with a Hall probe accurate to about 1/2 G.

Once the sample was frozen and loaded, the field was kept at 1 T while the initial NMR set-up was done. The enriched samples at 4.2 K were often held at high field for several hours without any measurable loss of signal. For the samples at 77 K, however, only 30-60 min of high field relaxation measurements were taken before the initial ramp-down. After ramping the field down to the desired low-field value, relaxation data were collected by cycling the field back up to resonance (1 T) to acquire a FID and then back down. One such field cycle took approximately 45+ seconds. Field cycling was exclusively used to acquire the data for the pulsed NMR method. Spacing between acquisitions was normally about 1/6 of the expected instantaneous \( T_1 \), but not less than 10 min. Resolution was thus limited by the time uncertainty of this field cycling method (estimated to be about 1 min per acquisition).

A versatile and flexible heterodyned NMR spectrometer, designed by Conradi [36], was used to acquire the pulsed NMR signals from the solid samples. See Figure 3.4.
Figure 3.4. Diagram of pulsed NMR apparatus.

Fixed-tuned probes, to be submerged in the cryogens with the sample, were also constructed. The Q of these probes was generally in the 50-100 range. The RF coil was made with 20-30 turns of 28 gauge magnet wire wrapped around a Teflon form and sealed with a moderate coat of “5 minute epoxy” (50-50 mix). These probes were generally tuned to around 11.8 MHz (for a 1T field) at cryogenic temperatures. The standard probes consisted of a coupling capacitor $C_C$ in series with the parallel RF coil $L$ and tuning capacitor $C_T$ combination. The coil has a small resistance, $r$. See Figure 3.5.
Figure 3.5. Diagram of a standard NMR probe.

It was necessary to keep the probe circuitry completely submerged in the liquid cryogens during data acquisition in order to consistently maintain precise tuning. The resonant frequency of the probe \( f_0 \) is [26]

\[
    f_0 = \frac{1}{2\pi} \sqrt{\frac{1}{L(C_T + C_C)}}. \tag{3.4}
\]

Good approximate values for the capacitors \( C_C \) and \( C_T \) can be obtained in the following manner [26]: the value of \( r \) and \( L \) is first obtained by placing a known test capacitance, \( C \), in parallel with the bare coil. While this circuit is connected across a frequency synthesizer, the frequency, \( f \), is varied until the maximum signal amplitude is obtained, as measured on an oscilloscope. At this point \( L = \frac{1}{(2\pi f)^2 C} \).

The \( Q \) of the coil is obtained by adjusting the frequency by \( \Delta f \) until the magnitude of the signal has dropped to about 71% of the maximum. At this point \( Q = \frac{f}{2\Delta f} \) and \( r = \frac{1}{Q} \sqrt{L/C} \). If the desired impedance of the probe is 50 ohms, then the ratio \( \frac{C_T}{C_C} = \sqrt{50/r} - 1 \) can be calculated. Since \( C_T + C_C = \frac{1}{(2\pi f_0)^2 L} \) [from Equation (3.4)], where \( f_0 \) is the desired NMR frequency, simple algebra can be used to solve for \( C_C \) and \( C_T \).

Due to the relative enormity of the signals obtained from the hyperpolarized samples, a calibrated attenuator was placed between the preamplifier and the
intermediate frequency (IF) amplifier (see Figure 3.4) in order to avoid saturation of subsequent amplification stages. It was often necessary to initially attenuate the signal by 20-50 dB.

The signal to noise ratio was estimated at be on the order of 2000 initially for enriched samples (cell 18B). Mac NMR software, linked to a Tecmag Apollo system, was utilized to generate the pulse sequences and acquire the FID data. A single pulse of 1 μs was generally used followed by 3 ms of data acquisition. A calibrated transmit attenuator was also placed just before the RF amplifier to adjust the amplitude of the RF pulse.

It is important to note that, with a hyperpolarized sample, the longitudinal magnetization lost due to an RF pulse is never regained. Thus care must be taken not to destroy too large a portion of the sample magnetization when a pulse is transmitted. For this reason, the pulse amplitude is adjusted via the transmit attenuator until less than 0.6% of the signal is lost after each pulse. This corresponds to a spin “tip angle” ($\theta_{\text{tip}}$) of less than 5°. Before most of the relaxation experiments, the tip angle was calculated by pulsing the sample 20 times in rapid succession and measuring the signal before ($S_b$) and after ($S_a$) the series of pulses and then by using:

$$\theta_{\text{tip}} = \frac{180}{\pi} \cos^{-1} \left( \frac{S_a}{S_b} \right)^{1/20}.$$  \hspace{1cm} (3.5)

Since some of the sample's polarization is lost at each pulse, excessive acquisitions should be avoided. Yet, when field cycling, it is necessary to come to a precise resonant field in order to acquire consistent FID data. Often many acquisitions were required to fine-tune the field before a good acquisition was possible. The random number of pulses required to take a point introduced loss and uncertainty.

In order to gain more precise control over the field, a separate proton NMR field-lock was built (with the help of colleagues). This field lock consisted of a simple NMR spectrometer set for proton frequencies at 1 T ($\gamma_p = 2\pi \cdot 4258$ Hz/Gauss) and a tunable probe with a water sample placed inside the pole faces of the Varian electromagnet. Refer to Figure 3.4. When set at exactly the desired field, the zeros of the proton FID were centered at some point on the oscilloscope. It was then
a simple matter return to this field later on. The field-lock was also designed to
generate automatic feedback to the magnet power supply in order to compensate
for field drift. Using the field lock, it was possible to find precisely the correct field
before each data acquisition, thus only one pulse per data point was required.

3.3.1 Procedures at Liquid Nitrogen Temperature

Over 50 relaxation measurements were taken at liquid nitrogen temperatures
(77 K); involving 6 different cells with both natural and enriched Xe, frozen using
different methods and at fields between 4 G and 1 T. Sample preparation and
loading procedures were refined during this period to the point where signal to
noise ratios initially were in the thousands. This allowed precise relaxation data to
be acquired over three orders of magnitude in signal intensity.

The loading procedure was as follows: a large glass vacuum-insulated dewar
(see Figure 3.4) was suspended from a frame above the Varian electromagnet. The
last 6 inches at the bottom of the dewar were centered between the pole faces of
the Varian electromagnet and filled with liquid nitrogen. After the sample was
prepared and frozen, it was placed inside a pre-cooled probe surrounded by an
aluminum cylindrical RF shield especially designed to quickly snap shut and fit
snuggly into the bottom of the dewar. The probe, sample and case were then
swiftly lowered into the dewar and the dewar filled to the top with liquid nitrogen.
The pulsed NMR field cycling procedure outlined in the last section was then used
to collect the data.

Most of the effort at liquid nitrogen temperatures was concentrated in taking
relaxation measurements in the 5-70 G range. Relaxation in fields between 150 and
2500 G for natural xenon has already been studied [7]. The high field measurements
were all taken near 1 T, where cross relaxation between the $^{129}$Xe and $^{131}$Xe is
negligible (see section 2.5.3). Such measurements can thus be used to estimate the
background thermal relaxation processes (and possibly other relaxation processes)
that persist regardless of the magnetic field strength. Several measurements were
taken at high field for each cell. In most cases, tip angle measurements were also
made before any relaxation data were taken. Such high-field data were used as
a rough estimate of the background relaxation rate of the sample. In all cases, uncertainties are reflected in the error margins.

As summarized in the next section, relaxation measurements were taken for natural Xe, enriched $^{129}$Xe, using both the large area deposition and frozen liquid method of freezing. In addition, one specialized experiment was done to determine if the nonexponential part of the relaxation could be reinitialized by rotating the sample some $10^0$ relative to the magnetic field well after the long-time exponential behavior was established (after 10 hours). Such rotation would necessarily change the local distribution of $^{131}$Xe nuclei that are in resonant contact with the $^{129}$Xe nuclei (see section 2.5.3) and possibly would reinstate the rapid relaxation that is characteristic when the sample is first brought to low field. Such rotation, however, had a null effect and therefore no results will be presented. For a discussion on these results, see section 4.2.1.

3.3.2 Results at Liquid Nitrogen Temperatures

As expected [7], relaxation of $^{129}$Xe at high field, for enriched xenon, was exponential with a $T_1$ of $150\pm16$ min. However, at low fields the relaxation curves were distinctly nonexponential (with only the possible exception of one trial of the frozen liquid, Figure 3.6). In an effort to characterize the nonexponential nature of these relaxation curves, it was found that all of the curves at 77 K can be closely fit with a biexponential function \(Ae^{-t/T_{1L}} + Be^{-t/T_{1S}}\). A possible physical basis for a multiexponential fit is presented in section 4.2.2. Thus two relaxation times were used to characterize these relaxation curves. $T_{1L}$ described the long-time relaxation of the tail, which is closely exponential, and $T_{1S}$ described the short-time rate. In order to extract $T_{1L}$ and $T_{1S}$, least squares fitting to a biexponential was used. Numerically, this is entirely equivalent to the semi-log graphical method of extrapolating the long-time tail, with slope $T_{1L}$, back to $t = 0$ with a ruler in order to find the intercept, $A$, and then subtracting $Ae^{-t/T_{1L}}$, so obtained, from all points to reveal the short-time relaxation curve, $B e^{-t/T_{1S}}$. The least squares fitting method, however, was preferable to the graphical method.

Typical normalized relaxation curves for enriched $^{129}$Xe at field values between 4
Comparison of Frozen Liquid vs. Large Area Deposition for Enriched 129Xe at 10 Gauss and 77 K

**Figure 3.6.** Relaxation of frozen liquid vs. deposition methods at 77 K, showing the *only* near exponential decay seen in frozen liquid.
and 75 G are presented in Figure 3.7. From this graph it can be seen that when the field is increased, both the long-term relaxation times $T_{1L}$ and short-term relaxation times $T_{1S}$ increase. Qualitatively, this behavior is as generally expected due to the decreased coupling between $^{129}$Xe and $^{131}$Xe at increased fields (see section 2.5.3).

Recall that the strength and orientation of the local EFGs in the lattice determine whether or not a $^{131}$Xe nucleus can be a relaxation center. As the field is raised, a decreasing subset of the $^{131}$Xe near the stronger EFGs on crystallite surfaces and near lattice defects are able to become active relaxation centers. The experimental results reflect this trend and are summarized in Figure 3.8. Note that there is a strong correlation between the long-term and short-term relaxation times in this regime.

The large error margins for $T_{1L}$ and $T_{1S}$ reflect the trial to trial variations and do not represent the precision of the data fitting. Uncertainties due to data fitting for any given relaxation curve were generally less than 1%. However, variations in the relaxation times from freezing to freezing were often more than 10% and sometimes closer to 20%. Such errors were determined by making two or more identical measurements on the the same cell in close succession. Trial to trial variations were thus seen to dominate all other uncertainties. Several possible explanations for this phenomenon are presented in Chapter 4. In theory such variations may be attributed to the fact that $^{131}$Xe relaxation centers can be stronger or more numerous near lattice defects, grain boundaries and surfaces. Thus the distribution of relaxation centers and overall $^{129}$Xe nuclear relaxation can be sensitive to subtle differences in the microstructure of the condensate during freezing; all other parameters were held constant between trials. Similar deviant behavior was common during the entire duration of these experiments, even at liquid helium temperatures. Cell to cell variations are also a concern and will become more important in the low temperature experiments presented in the following sections. The uncertainties in $T_{1S}$ also reflect the inability to resolve the quick initial decays. As mentioned in section 3.4, the pulsed NMR method has an associated temporal uncertainty due to field cycling the large electromagnet. To keep this uncertainty under 10%, it is
Figure 3.7. Typical relaxation curves for $^{129}\text{Xe}$ at 77 K for fields ranging from 4 to 70 G.
Figure 3.8. Short- and long-time characteristic relaxation times $vs.$ field for $^{129}$Xe at 77 K.
necessary to acquire data points no less than 10 min apart. Therefore the rapid relaxation characteristics in the first few tens of minutes cannot be adequately resolved by the pulsed NMR method. The AFP method (section 3.5), in contrast, provides a 2 min point to point resolution of this early decay.

Considering the differences in nuclear relaxation between samples that where solidified by the condensation methods and that of the frozen liquid method, it is clear that drastically changing the solidification process results in significant differences in the relaxation characteristics. When “frozen liquid” was formed by liquefying then freezing the sample, these differences could be easily distinguished (see Figure 3.6).

Differences between the “large area deposition” (LAD) method and the “small area deposition” (SAD) method, in contrast, could not be so resolved. Interestingly enough, there were also significant differences at high field (1 T) in relaxation times between frozen liquid and the deposition methods for cell 18B. The relaxation time $T_{1FL} = 123 \pm 15$ min for the frozen liquid was smaller compared to $T_{1LAD} = 150 \pm 16$ min of the deposition method. Yet for cell 18A, the relaxation times for the two methods were roughly the same at $\approx 170$ min. Due to the length of these experiments, high field measurements for cell 18A were not repeated, and thus statistical analysis of trial to trial or cell to cell variation was not possible.

### 3.3.3 Procedures at Liquid Helium Temperature

At liquid helium temperature (4.2 K), $^{129}$Xe relaxation times (at high field) were found to be well over 200 hours. Thus there was no urgency to start immediate data acquisition after loading a sample, yet the handling of the liquid helium was problematical. A stainless-steel Super Varitemp Janis Dewar with a tail (Figure 3.9) was used to hold the liquid helium. To prepare this dewar, the sample chamber and liquid helium tank were thoroughly purged with helium gas and kept at positive helium pressure via an external compressed helium cylinder and regulator. Care was taken to run helium gas through the small tube and needle valve connecting the liquid helium tank to the sample chamber. Purging the needle valve stem was also helpful by removing the o-ring seal off the valve stem on the top of
Figure 3.9. Janis Super Varitemp liquid helium dewar with probe inserted.
the dewar and allowing helium to leak out for a while. The vacuum jacket was pumped down to high vacuum using a diffusion pump and liquid nitrogen was placed in the liquid nitrogen tank overnight, which by slow conduction precooled the dewar. A North Shore temperature controller was hooked up to a platinum thermistor to monitor the temperature of the sample chamber during cooling. Sample chamber temperatures down to 100 K were obtained by this precooling procedure. A manifold was built to monitor liquid helium tank pressure and exhaust flow, sample chamber pressure and exhaust flow, as well as the vacuum jacket pressure via a thermocouple.

After the dewar was precooled, the needle valve was closed completely then opened 1/4 turn. The helium gas was disconnected and liquid helium was transferred into the liquid helium tank after which the LHe tank was corked off. Then the needle valve was opened several turns and the cap of the sample chamber released until helium gas burped out. This allowed liquid helium to move into the sample chamber. The sample chamber temperature reading would quickly drop to temperatures near 4.2 K indicating that liquid helium had been introduced into the chamber. With liquid helium in the sample chamber, the probe and sample holder can be introduced and cooled. The probe is equipped with a 100 kΩ carbon resistor whose resistance is very sensitive to temperatures below 10 K. At 77 K this resistance is 150 kΩ, and at 4.2 K it is near 12 MΩ. This carbon resistor is placed above the sample, probe and electronics and is used to indicate whether such are submerged during data acquisition. After the sample holder is inserted, the level of the liquid helium in the sample chamber must be carefully monitored. Depending on the level and pressure of the liquid helium tank, the needle valve should be opened between 1/2 and 7/8 of a turn to maintain a constant flow of liquid helium in the sample chamber. If not correctly adjusted, the level in the sample chamber may drop or rise undesirably. The resistance of the carbon resistor will give some indication of the level, though it is not linear with temperature and not calibrated.

Finally, after the dewar is prepared, the frozen hyperpolarized \(^{129}\)Xe samples can be loaded by having an assistant raise the probe and sample holder to the top
of the dewar, by quickly transferring the frozen sample into the holder, and then by swiftly and carefully lowering the sample and holder back into the dewar. Liquid helium will be burned off in the process and thus the needle valve may have to be opened to allow the sample chamber to be quickly flooded again. In most cases, the samples were left at 4.2 K in high field for several hours before the low-field data were acquired.

Low field measurements were acquired using the field cycling procedure already discussed in section 3.3. Nuclear relaxation at fields between 1 and 500 G was studied and experiments similar to those performed at liquid nitrogen temperatures were done to study the dependence of relaxation times on freezing techniques.

Two additional experiments were done. In the first, the field was changed abruptly after some 600 min at the initial field. A distinct “kink” was seen in the data graph (see next section). This method is referred to as the “kink” method and was used extensively to gather information about relative relaxation rates between lower fields (2-5 G) and higher fields (100-500 G). Most of the data collected above 100 G was done with this kink method. It allowed measurements to be made quicker, being that as many as three $T_{1L}$ long-time relaxation times could be measured on one sample without the necessity of waiting 10 or more hours for the nonexponential part to die out after a new sample is loaded. Following the kink, the relaxation was demonstratively exponential. It was found later, however, that when using the kink method, the relaxation times depended partially on the order (history) of the field exposures. Returning back to a prior field did not necessarily result in the same relaxation time (see next section). Thus larger errors must be assumed for the points taken using the kink method.

Samples were prepared with different concentrations of $^{131}$Xe (0.1%, 0.2%, 0.4%, 0.6% and 0.8%). Relaxation measurements were taken on these samples to study the dependence of $^{131}$Xe concentration on nuclear relaxation. Two sets of cells (38A-C and 39A-D) were thus prepared by utilizing various mixtures of natural and enriched xenon. The second set of cells (39A-D) was coated with a commercial siliconizing agent SufraSil (Pierce Scientific) that has been shown to improve cell
wall times [37] and therefore pumping efficiencies. No such enhancement was seen in wall times, however (see Table 3.2.1). The experimental results for the various $^{131}\text{Xe}$ concentrations are included in the next section and in section 3.5.1.

### 3.3.4 Results at Liquid Helium Temperatures

At liquid Helium temperature (4.2 K), thermal relaxation mechanisms are expected to be negligible (see section 2.5.2). This is directly evidenced by the exceedingly long relaxation times experienced for both enriched and natural $^{129}\text{Xe}$ at high field (1 T). Samples from at least seven cells were held at 4.2 K and high field (1 T) for many hours (some up to days). Signal losses were only slightly discernible and it was determined that the relaxation time ($T_1$) at high field was at least 200 hours or greater. There was one exception. Curiously, cell 38C (0.8% $^{131}\text{Xe}$) repeatedly exhibited monoexponential relaxation times of $T_1 \approx 600 \text{ min}$ at high field. This result may also cast doubts on the accuracy of the low-field relaxation measurements made with cell 38C (displayed below in this section and in section 3.5.1). [Cell 38C is the only cell with 0.8% $^{131}\text{Xe}$ concentration.] No explanation was found for this anomaly, yet it suggests the possible inclusion of relaxive paramagnetic impurities in the xenon lattice. Recall that at 4.2 K, the only known relaxation mechanism available, neglecting impurities, is cross relaxation between the $^{129}\text{Xe}$ and $^{131}\text{Xe}$, which again is theoretically negligible at high fields (1 T). For a discussion on this topic, see section 2.5.3.

In Figure 3.10, relaxation curves between natural xenon (21% $^{131}\text{Xe}$) and enriched xenon (0.1% $^{131}\text{Xe}$) are compared at 4.2 K and 30 G. This comparison offers firm experimental evidence that $^{131}\text{Xe}$ is indeed a dominant actor in the $^{129}\text{Xe}$ nuclear relaxation process at these fields. The nonexponential nature of $^{129}\text{Xe}$ nuclear relaxation in the enriched sample, however, is especially obvious. This is particularly true during the first few minutes at 30 G where the relaxation time of the enriched sample is still rapid, near 30 min.

As with the samples at liquid nitrogen temperatures, the relaxation curves at low field are nonexponential and the short-time relaxation characteristics $T_{1S}$ are still not able to be adequately determined (see section 3.3.2). There are significant
Figure 3.10. Comparison of relaxation in natural vs. enriched $^{129}$Xe at 4.2 K.
differences, however, between the nonexponential character at 77 K and at 4.2 K.
First, the low-temperature relaxation curves are no longer able to be fit well with a
biexponential. A triexponential \( (Ae^{-t/T_{1s}} + Be^{-t/T_{1m}} + Ce^{-t/T_{1L}}) \) fit was employed
merely as a numerical method to extract \( T_{1L} \) and its uncertainty from the relaxation
curves. In fact, even the triexponential fit was not adequate for some of the longer
relaxation curves. In Chapter 4, however, a model is proposed with physically
significant parameters that does fit many of the relaxation curves with specific
multiexponential expansions from a diffusion model.

The most striking feature discovered in the relaxation of enriched \(^{129}\)Xe at liquid
helium temperatures is a local \( T_{1L} \) maximum at 3 G. See Figure 3.11, Figure 3.12
and Figure 3.13. Examination of the relaxation curve at 3 G reveals the following
characteristic behavior: when the field is first lowered, relaxation rates initiate
relatively fast \( (T_{1S} \approx 5 \text{ min}) \) compared to higher fields. Yet then, after just a
few minutes a quickly changing intermediate rate occurs \( (T_{1m} \approx 100 \text{ min}) \). After
a few hundred minutes, relaxation has slowed dramatically to a very slow rate
\( (T_{1L} \approx 800 \text{ min}) \) compared to the relaxation at nearby higher fields. When the
experiment is repeated at higher fields, from 10 to 100 G (see Figure 3.13), the
long-time relaxation times \( (T_{1L}) \) become much shorter up to a broad minimum at
150 to 250 G after which relaxation times begin to increase with field. Section 4.4
of Chapter 4 is dedicated to the analysis of this behavior. Incidentally, efficient
storage of hyperpolarized \(^{129}\)Xe at 3 G would occur only after approximately 95%
of the polarization had relaxed due to the rapid initial decay.

Because of this \( T_1 \) maximum, a few experiments were done to determine if
environmental EM noise (with power in the 1 kHz to 330 kHz range) may be causing
relaxation. The sample was shielded with a grounded fine copper screen inside the
dewar and the magnet was moved to a slightly different location. No significant
differences were detected either at 75 G or 3 G. Furthermore, the Adiabatic Fast
Passage experiment in section 3.5 was implemented primarily to verify these results
by comparison to data obtained from a different environment and NMR detection
method. Ultimately, this behavior was seen by both methods and in several different
Figure 3.11. Typical Normalized $^{129}$Xe relaxation curves at 4.2 K.
Figure 3.12. Early nonexponential behavior of the $^{129}\text{Xe}$ relaxation curves at 4.2 K; showing only the first 100 min of relaxation.
Figure 3.13. Summary of Long-time relaxation ($T_{1L}$) vs. field at 4.2 K.
cells (38A, B, C and later with AFP in 39A, B, C and D). Yet no such $T_1$ maximum was seen in any of the cells containing natural Xe.

The isotopic dependence of $T_{1L}$ at 3 G and 4.2 K was studied using cells 38A (0.2% $^{131}$Xe), 38B (0.44% $^{131}$Xe) and C (0.8% $^{131}$Xe). Cells 38A (0.2% $^{131}$Xe) and 38B (0.44% $^{131}$Xe) both yielded a $T_{1L} \approx 450$ min and cell 38C had a $T_{1L} \approx 200$ min. Unfortunately, the purity of the sample in 38C was in question (see first paragraph) and observed variations upwards of 50% in the $T_{1L}$ between cells containing identical enriched $^{129}$Xe samples have been seen. These observations preclude any definite conclusion from the data just presented. A new set of cells (39A, B, C and D) with varying $^{131}$Xe concentrations were made for use with the AFP method. Those results will be presented in section 3.5.1.

The results of the “kink” experiment were revealing. As an example (see Figure 3.14), when the applied field was changed abruptly from 5 G to 150 G (after the initial nonexponential decay), the relaxation time ($T_{1L}$) also changed abruptly from 620 min to 82 min. Following the kink, the characteristic relaxation was observably exponential. At this point the field could be abruptly changed every 1 to 3 hours with similar results. The rapid nonexponential decay was never reinitiated.

The kink method was efficiently used to collect $T_{1L}$ data at several higher fields (> 150 G) during a single decay. Unfortunately, it was later seen that the $T_{1L}$ so obtained had a dependence on the history of the field changes. In Figure 3.14, for example, returning the field to 5 G does not result in the same $T_{1L}$. With the aid of the AFP method, it was seen that slow nonexponential behavior, acting over several hours, is still in effect even after 20 hours. Relaxation times tend to gradually elongate over a period of several hours. An experiment was done, switching abruptly from an “exponential” ($T_{1L} \approx 800$ min) 3 G tail to 150 G where $T_{1L}$ was measured at 100 min over a few hours and then back to 3 G where $T_{1L}$ was about 500 min. The last four data points (taken over a 3-hour period) in this example were fit best with an exponential where $T_{1L} \approx 600 \pm 100$ min. This, of itself, is not conclusive but suggestive. For reference: in an extended AFP experiment at
Figure 3.14. Kink method; showing response of $T_{1L}$ to rapid changes in field after the initial nonexponential decay at 4.2 K.
3 G, the relaxation time for this same cell (18B) after 1000 min, was $T_{1L} \approx 800$ min as expected; however, after 2000 min this relaxation time had gradually increased to $T_{1L} \approx 1000$ min. (errors are under 5%). This gradual upward tendency in $T_{1L}$ was typical when characterizing relaxation at fields less than 10 G over very long periods of time.

The relaxation curve of a frozen liquid sample (cell 18B) at 4.2 K and 3 G was visibly very different than the standard deposition samples under the same conditions (see Figure 3.15). Specifically the short-time relaxation times were longer, the relaxation slow-down more gradual and the long-time, $T_{1L}$, relaxation time for this Frozen Liquid sample was also larger ($T_{1L} = 1240 \pm 30$ min) than that of the standard deposition methods ($T_{1L} \approx 900$ min). From this it is clear that the method of freezing the sample impacts both qualitatively and quantitatively on the characteristic relaxation properties of the sample, suggesting that differences in crystallite structure may be an important factor when considering trial to trial variations. Due to difficulties in maintaining the polarization in a natural xenon sample while freezing, frozen liquid samples of natural xenon were not able to be investigated.

### 3.4 The $^{131}$Xe Cross Polarization and Relaxation Experiment

In Chapter 2, the three major internuclear interactions that exist in solid $^{129}$Xe at liquid helium temperatures were discussed in detail. The first interaction is the interchange of spin angular momentum between the nuclei of neighboring $^{129}$Xe atoms the lattice. This first interaction drives spin diffusion (section 2.4.2). The second interaction is the exchange of spin angular momentum between neighboring $^{129}$Xe and $^{131}$Xe nuclei in the lattice. This second interaction drives cross polarization between the two nuclear systems. The third interaction is the thermal coupling between the $^{131}$Xe nuclei and the lattice. This third interaction causes nuclear relaxation in the $^{131}$Xe nuclei. The second combined with the third results in cross relaxation between the $^{129}$Xe nuclei and the effective $^{131}$Xe relaxation centers in the lattice (see section 2.5.3). Furthermore, it was argued that at fields above 10 G only
$^{129}$Xe Relaxation for Different Freezing Methods
at 4 K and 3 Gauss

Figure 3.15. Comparison of relaxation curves for the frozen liquid vs. the deposition method at 3 G and 4.2 K.
the $^{131}$Xe nuclei located in special places on the surface of crystallites or near lattice defects could become effective relaxation centers. At fields below 10 G, however, it was argued that $^{131}$Xe nuclei in the bulk of the crystallites could also become effective relaxation centers (section 2.5.1).

The following experiment was designed to verify the second and third internuclear interactions. It is modeled after a similar experiment done by Gatzke in 1992 [7]. Gatzke showed experimentally that if a hyperpolarized natural Xe sample is held at a field somewhere below 7 G (the mixing field) for a few seconds (the mixing time) and ramped back up to high field, then cross polarization between hyperpolarized $^{129}$Xe and $^{131}$Xe in the solid had occurred (due to the second interaction); the NMR signal of $^{131}$Xe was greatly enhanced and simultaneously the NMR signal of the $^{129}$Xe significantly diminished. In this work, Gatzke’s experiment was carried a step further; cross polarization at various mixing times and mixing fields was examined. The relaxation time ($T_1$) of $^{131}$Xe at high field (1 T) was also examined (the third interaction).

Pulsed NMR was used to measure the $^{131}$Xe signal after the field was cycled down to various mixing fields (both above and below 7 G) and held for various mixing times. To do this, a probe was tuned to $^{131}$Xe resonance at $\approx 1$ T. A sample of natural xenon was then loaded and the $^{131}$Xe FID (if any) was acquired. A series of pulses were sent to destroy all the initial $^{131}$Xe magnetization. The $^{129}$Xe signal was obtained by ramping the Varian electromagnet to $^{129}$Xe resonance. Tip angle measurements for $^{129}$Xe were made. The field was then as quickly as possible ramped down to the desired mixing field (0-30 G), it was held there for a given mixing time (10-180 seconds) and then the field was ramped back up to the $^{131}$Xe resonance (1 T) and data acquired. After each cross polarization cycle, the $^{131}$Xe signal was monitored over time in order to determine the $T_1$ of the $^{131}$Xe at high field. See section 2.4.3.
3.4.1 Results of the $^{131}$Xe Cross Polarization and Relaxation Experiment

Cross polarization between $^{129}$Xe and $^{131}$Xe was seen most strongly after a 10 second exposure to a field of $0 \pm 0.5$ G. In this case, the signal to noise ratio of $^{131}$Xe (directly after cycling the field) was close to 30; this compared to the null $^{131}$Xe signal before mixing. On the other hand, the signal for the $^{129}$Xe decreased by 10-20% after a cycle. Recall that at high field, the relaxation time of $^{129}$Xe is practically infinite in comparison. The $T_1$ of $^{131}$Xe at 1 T averaged over all measurements was $11.5 \pm 2$ min. This measured $T_1$ is surprisingly much faster than those reported by Norberg ($T_1 > 60$ min) [9].

Table 3.2 summarizes the results at other mixing fields (accurate to $\pm 0.5$ G) and mixing times (accurate to $\pm 7$ seconds). The ratio between the initial $^{131}$Xe signal and $^{129}$Xe signal ($S_{131}/S_{129}$) is normalized to the largest obtained ratio (2.2%). The percentage of $^{129}$Xe signal lost during the mixing cycle is also shown in the last column. All percentages listed are accurate to within $\pm 10\%$.

As indicated, cross polarization (mixing) was not discernible until the field dropped well below 10 G. At lower fields (0-4 G), the cross polarization was rapid (on the order of seconds). Notice that after just 3 min at 0 G, both the $^{131}$Xe and the $^{129}$Xe had, for the most part, relaxed completely. This suggests that not only is there strong coupling between the nuclei of neighboring $^{129}$Xe and $^{131}$Xe in

<table>
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<th>Mix Field (G)</th>
<th>Mix Time (s)</th>
<th>$N(S_{131}/S_{129})$</th>
<th>$S_{129}$ Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>100%</td>
<td>10%</td>
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<tr>
<td>0</td>
<td>20</td>
<td>100%</td>
<td>60%</td>
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<td>180</td>
<td>2%</td>
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<td>10</td>
<td>70%</td>
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<td>30</td>
<td>20</td>
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Table 3.2. Normalized cross polarization signal ratio at various mixing fields and times (100% being the largest signal obtained after cross polarization) and associated loss in $^{129}$Xe signal.
natural xenon at very low fields (second interaction), but that the $^{131}\text{Xe}$ coupling to the lattice is strong also (third interaction). The percentage of $^{129}\text{Xe}$ signal lost during mixing is only included to indicate that significant loss had occurred. No conclusions can be drawn from these figures, it is not certain to what extent cross polarization had already taken place in the sample freezing and transfer process or to what extent $^{129}\text{Xe}$ polarization had already been locally depleted around the $^{131}\text{Xe}$ sites before the controlled mixing took place.

Note that even assuming very small crystallites (1000 Å), the percentage of atoms on the surface of the crystallites would be less than 0.1% of those in the bulk. The signal for $^{131}\text{Xe}$ atoms solely on the surface, even polarized to 100%, would constitute a signal on the order of 1000 times less than the $^{129}\text{Xe}$ signal. Such a signal would be completely undetectable with this apparatus. These results clearly indicate that cross polarization at very low fields takes place in the bulk solid of the crystallites.

### 3.5 The Adiabatic Fast Passage (AFP) Experiment

An entirely separate experimental set up (see Figure 3.16) and signal detection strategy was required in order to implement the AFP detection of the magnetization of the frozen $^{129}\text{Xe}$ samples. Firstly, the Janis Super Varitemp dewar, necessary to maintain liquid helium temperatures, was moved out of the electromagnet and placed between a pair of air-cooled Helmholtz coils.

These coils were connected to a computer-controlled power supply and were capable of being quickly ramped between fields anywhere between 0 to 300 G. Due to the transverse components of the stray fields in the environment, however, it was impossible to bring the magnetic field to exactly zero with this set up. Note that unlike the electromagnet, where stray flux tends to be gathered and redirected by the large soft iron poles, the Helmholtz coils have no means of redirecting the stray fields. The transverse field due to stray fields, however, had a strength of less than 1 G; possibly as low as 0.2 G as measured by the Hall probe. Field calibration was done by entering two parameters into the computer software, the longitudinal
stray field and the Gauss per Amp character of the Helmholtz coils. With these parameters, the field was able to be automatically calibrated within 2% over the entire range (0-300 G), thus verified by the Hall probe.

As discussed in section 2.3.3, AFP signals were acquired when the $^{129}$Xe nuclear spins were in the process of adiabatic inversion. This requires the presence of a continuous transverse RF excitation whose strength was made to be larger than any local fields or field inhomogeneities present in the sample. Such RF broadening required RF field strengths ($H_1$) of better than 300 mG. Values for $H_1$ were found

**Figure 3.16.** Diagram of experimental apparatus for the AFP experiment.
by measuring the induced voltages through a small coil of known area inserted into the probe. The Q of the probe, however, does change considerably when brought to liquid helium temperatures, and thus such a measurement of $H_1$ was only approximate; yet it was shown that values of 300 mG were easily obtained even with room temperature coils.

An RF coil was constructed to detect the AFP NMR signal at a low field of about 80 G. The resonant frequency at this field is approximately 94 kHz. These low frequencies allowed the tuning electronics to be placed outside the Janis dewar without much loss. The tuning box was thus separated by up to 2 meters of coaxial cable from the RF coil in the sample chamber. The RF coil was made from a Teflon form wrapped with as much as 200 turns of Lietz wire and sealed with epoxy. A single coil was used for both the RF excitation and NMR detection. An SRS DS340 15 MHz function synthesizer provided the RF signal. A lower quality BK Precision 4040A function synthesizer was first tried unsuccessfully. A high quality frequency synthesizer was a strict requirement. The RF was running continuously while the field was ramped through resonance, any satellite harmonics served to artificially accelerate the nuclear relaxation.

The probe fabricated for this experiment had an optimal resonance at 97.1 kHz (82.4 G) when at 4.2 K and a Q of about 110. The small phase shift caused by the slight change in inductance that the coil experiences when the sample magnetization rotates must be detected over the large background RF excitation signal (see section 2.3.3). Thus inside the tuning box, there was a separate dummy circuit which could be carefully adjusted to be exactly equivalent to the RF coil and tuning electronics (both the impedance and frequency response). See section 2.3.4. This dummy circuit was an almost exact mirror of the coil circuitry. See Figure 3.17. The dummy coil in the tuning box was a replica of the RF coil in the sample chamber; except that a small variable inductor was added in series for fine adjustment.

All other components were the same except that voltage dividers were added in order to match the amplitudes of the coil and the dummy circuits. The expected result was that when the same RF excitation is fed into both circuits, their response
will be exactly equivalent, both in amplitude and in phase. These two signals were then sent into a differential preamplifier and the output of the differential preamplifier into a sensitive analog lock-in amplifier (see Figure 3.16). This bridge circuit, so constructed, was very sensitive to slight differences between the two equivalent circuits. When the sample passed through resonance inside the RF coil, the difference in the inductance between the two circuits was detected as a proportional DC offset from the lock-in amplifier.

It was necessary to balance the bridge before data could be taken and it was re-balanced periodically throughout the experiment. Initially, an oscilloscope was useful to directly monitor the output of the two circuits. The phase was adjusted with the variable inductor and amplitudes adjusted with the voltage dividers until the traces on the scope from both coincided. The next step involved monitoring the output of the differential preamplifier and making adjustments to zero the output signal. The final step was to zero the lock-in amplifier and then adjust the phase detection of the lock-in amplifier such that a small inductive detuning resulted in maximum deflection of the meter. At this point, only the variable inductor in the tuning box (which controls the phase difference) would be used to re-balance the

**Figure 3.17.** Diagram of the bridge circuit used in AFP detection.
bridge circuit periodically. For reference, the differential preamplifier was set on an amplification of 10X. The input sensitivity on the lock-in set to 50 mV, the filter set to 30 ms and the phase set to -45°. Noise was typically on the order of 10 mV at these settings and signal strengths on the order of 20 V, thus signal to noise ratios (as in the pulsed NMR apparatus) were on the order of 2000 initially and the dynamic range was such that the lock-in amplifier gain did not have to be adjusted during the experiment as the signal declined.

Software was written in Labview (AFP.VI) and installed on a PC (Polariz02) in the C:/AFP directory. This worked in conjunction with a National Instruments DAQ card which acted as the nerve center for this experiment. One of the digital to analog (D/A) outputs on the DAQ card was configured to control the power supply current which drove the Helmholtz coils. An analog to digital (A/D) input channel collected the AFP signal from the lock-in amplifier, and a TTL data channel was used to turn the RF on and off. The software was configured by inputing a page of global parameters, such as ramp rates, RF frequencies and acquisition rates. Once configured, data acquisition was done automatically at specified time delays. Once an acquisition cycle has begun, the RF was automatically turned on, a countdown ensued allowing time to re-balance the bridge if necessary, then the field was ramped rapidly to a field just above (or below) resonance. Data were acquired while the field was ramped adiabatically (section 2.3.3) through resonance and back. The field was then ramped back to the desired field and the RF was turned off. This experiment would run unassisted for many hours, even overnight, given that the liquid helium level in the sample chamber did not require adjustment.

As shown in section 2.3.3, two square root of Lorentzian peaks were expected to be produced, one for the forward ramp through resonance and one for the reverse ramp. The amplitude was expected to be proportional to the sample magnetization, and the width proportional to the RF field strength ($H_1$). These two peaks can be compared to find the magnetization lost due to a single acquisition cycle. The customized software can find the best Lorentzian fit using a hybrid Levenberg-Marquardt nonlinear fitting algorithm which adjusts for the baseline offset and
The fit was extraordinarily good for all data collected. The RF excitation strength was adjusted to minimize the losses due to acquisition. For our apparatus, at 2 V peak to peak from the synthesizer \((H_1 \approx 800 \text{ mG})\), signal losses were less than 1% per acquisition and the width of the Lorentzian curves were consistent to well under 1% throughout. The data acquisitions were displayed on a graph and automatically saved. Relaxation curves were also automatically plotted over time on a semi-log graph and saved.

Using the AFP setup, full relaxation curves at 4.2 K were obtained for cell 18B (enriched \(^{129}\text{Xe}\)) over several fields and data were also collected for other cells of varying isotopic content. The main research objective for this experiment was to verify the data obtained earlier by the pulsed NMR method and to thus eliminate the possibility that some subtle systematic effects were influencing the results. Several relaxation curves were obtained at very low fields (between 1 and 10 G) in order to verify and characterize the \(T_{1L}\) maximum discovered earlier. In addition, due to the quick response time of the Helmholtz coils, it was also possible to cycle the field faster. Time uncertainties for each signal acquired were estimated to be about 15 seconds, making it possible to take points every 2 min (as opposed to 10 min required for the pulsed NMR setup). This increases resolution of the short-time relaxation \((T_{1S})\) and allows more detailed study of the characteristic relaxation when the field is first dropped where relaxation times are typically on the order of 5 min.

The sample loading procedure for this method was slightly different than that of the pulsed method. It was not possible to maintain fields larger than 300 G with the Helmholtz coils. Thus to preserve the magnetization of the sample when loading, a permanent magnet (1600 G) was constructed by placing two rare-earth ceramic magnets inside a “U” shaped iron channel such that the poles were co-linear. This magnet was placed so that its field was perpendicular to that of the Helmholtz coils and so that it was surrounding the tail of the Janis dewar, centered on the sample. The open end of the iron channel was then capped with a shallow piece of iron channel, so cut as to be symmetric with the other side. This cap ensured a more
uniform field and more efficient flux return. Before a sample was loaded, the RF coil bridge was balanced at the resonant field. The permanent magnet was then installed and the Helmholtz coils ramped up to 200+ G. The sample was frozen and inserted, as previously outlined. After the sample chamber was reflooded with liquid helium and measurements were ready to be taken, the permanent magnet was slowly and carefully removed. The 200 G field in the Helmholtz coils ensured that the sample did not pass through zero field as the permanent magnet was removed. From this point on, the initial rapid relaxation started. The field was quickly ramped to the desired holding field and automatic acquisition was initiated. Operating instructions for the software controlling this experiment are not included here but can be found in the above mentioned AFP directory on polariz02.

3.5.1 The AFP Experimental Results

Within experimental error, the results of the AFP method at 4.2 K confirmed the general results of the pulsed method. The 3 G $T_{1L}$ maximum was clearly present. Within 20\%, the $T_{1L}$ obtained from both methods (for cell 18B) were comparable for all fields up to 140 G. Data from other cells were also comparable up to the 30\% cell to cell uncertainty present in the AFP data. The kink data (taken earlier with the pulsed method) at fields higher than 150 G, however, did not correspond well with $T_{1L}$ data taken from the full relaxation curves of the AFP method. The AFP data showed a less-broad $T_{1L}$ minimum centered below 100 G and increasing sharply past 150 G. This difference was attributed to uncertainties in the kink method (see section 3.3.3). For this reason, the AFP data was considered more accurate.

For comparison, some of the results are summarized in Figures 3.18, 3.19, 3.20 and 3.21. The AFP method produced $T_{1L}$ that were on the average 10\% to 15\% longer than those of the pulsed method. Upon closer inspection, the longer $T_{1L}$ of the AFP method were clearly attributed to the nonexponential character of the long-time tail. Relaxation curves acquired by the pulsed method were typically terminated after 1200 min. In comparison, the automated AFP method typically produced curves close to 2000 min in length. As suspected, it was seen that the
Figure 3.18. Typical normalized relaxation curves for various fields obtained via the AFP method at 4.2 K.
Figure 3.19. Typical relaxation curves focusing on the early nonexponential behavior via the AFP method at 4.2 K.
Figure 3.20. Summary of relaxation times ($T_{1L}$) obtained via the AFP method at 4.2 K.
Figure 3.21. Summary of relaxation times ($T_{1L}$) detailing the 3 G maximum via the AFP method at 4.2 K.
characteristic long-time relaxation was not purely monoexponential and relaxation times were seen to gradually increase over time, even after 1200 min. If the longer relaxation curves, obtained with the AFP method, were truncated to match the curves for the pulsed method, then the results would be directly comparable.

The qualitative character of relaxation curves for both methods were also comparable. One possible exception being that the data points of the relaxation curves of the AFP method were some four times more dense during the initial rapid nonexponential section of the curve, being taken every 2 to 3 min as opposed to every 10 min with the pulsed method. As such, the AFP curves could not be fit as well with a triexponential. However, many of the AFP curves were fit very well with the diffusion model developed in Chapter 4. Also due to the ease of data collection with the AFP method, very long relaxation curves were collected, some as long as 2700 min. Trial to trial variations were of the same order in both methods (i.e., 20% variation from trial to trial). The cell to cell variation, however, with the AFP method seemed to be smaller (i.e., 20% variation from cell to cell); note that this figure reflects only two data points, namely the $T_{1L}$ for cells 18B (used for most measurements) and 39A (also enriched Xe) compared at 10 G and 3 G. A statistical uncertainty was not able to be established and so a conservative estimate of 30% cell to cell variation was assumed for the AFP method. The kink method was only done once with the AFP method, producing again comparable results to the pulsed NMR method.

Finally, the AFP method was employed to study the dependence of $^{131}$Xe isotopic concentration on $^{129}$Xe relaxation at 10 G and 4.2 K. Relaxation data were taken on cells 39A (0.1% $^{131}$Xe concentration), 39B (0.2%), 39C (0.4%) and 39D (0.6%) along with cell 38C (0.8%). See section 3.3.4 for more information on cell 38B. The results are presented in Table 3.3, Figure 3.22 and in Figure 3.23. As with the pulsed method, expected cell to cell variations as reflected in the error bars obscure any definite conclusions. However, a downward trend in $T_{1L}$ can be seen as the $^{131}$Xe concentration is raised.
Table 3.3. AFP relaxation times, $T_{1L}$, for various $^{131}$Xe isotopic concentrations at 10 G and 4.2 K.

<table>
<thead>
<tr>
<th>% $^{131}$Xe</th>
<th>$T_{1L}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1%</td>
<td>560±160</td>
</tr>
<tr>
<td>0.2%</td>
<td>431±125</td>
</tr>
<tr>
<td>0.4%</td>
<td>539±120</td>
</tr>
<tr>
<td>0.6%</td>
<td>325±100</td>
</tr>
<tr>
<td>0.8%</td>
<td>100±150</td>
</tr>
</tbody>
</table>
Figure 3.22. Comparison of relaxation curves for different isotopic concentrations at 4.2 K.
Figure 3.23. $T_{1L}$ for various isotopic concentrations.
3.6 Brief Discussion of Results

Note that even though the relaxation rate does not appear to scale directly with $^{131}$Xe concentration, cross relaxation with $^{131}$Xe could still be the dominant relaxation mechanism. Assuming that the $^{131}$Xe act as relaxation centers only where strong EFGs exist on the surface and near lattice defects (due to quadrupole effects), the relationship of nuclear relaxation to isotopic concentration is complex and has a dependence on $^{129}$Xe spin diffusion rates, crystallite size distributions and the EFG distributions in the polycrystalline sample. Such dependencies are explored by the use of a diffusion model in section 4.2. In Chapter 4, it is shown that if the regions of active $^{131}$Xe relaxation centers are far enough apart and thus spin diffusion to these remote sites is the limiting process, then increasing the strength (or equivalently the number) of the relaxation centers in such remote regions of rapid cross relaxation does not result in proportionally faster relaxation in the overall sample.

Two different experimental methods have been employed to measure nuclear relaxation of $^{129}$Xe at low fields and liquid helium temperatures: the pulsed NMR method, between the pole faces of a large electromagnet, and the AFP method, between a set of Helmholtz coils. With both methods and in both environments, the same characteristic $^{129}$Xe relaxation behavior has been seen, within experimental error, and the same field dependence has been exhibited. In particular, a $T_{1L}$ maximum at 3 G is an unmistakable, prominent feature in both methods. Thus the probability of systematic error has been reduced dramatically and it can be said with some confidence that the results presented are true characteristics of $^{129}$Xe nuclear spin relaxation in enriched samples at low fields and low temperatures.
CHAPTER 4

ANALYSIS OF RESULTS

4.1 Introduction

In this chapter, the experimental results will be analyzed and discussed. Among the most prominent are the nonexponential character of the $^{129}\text{Xe}$ relaxation curves and the distinctive $T_{1\text{L}}$ maximum that occurs at 3 G. Along with these are the sensitivity of nuclear relaxation to the solidification process and $^{131}\text{Xe}$ concentration. In this chapter a framework will be built that smoothly fits together most of the pieces of the puzzle that have been tossed on the table up to this point. A simple diffusion model will be examined that not only fits the data but also seems to fill in some of the pieces. The complete picture, however, still needs to be assembled. And yet this work, along with the others preceding, contributes to seeing the overall pattern that will aid researchers to fill in the voids.

One of Gatzke’s major thesis arguments provides the first semblance of the picture. He argued that at liquid helium temperatures, the only dominant relaxation mechanism remaining in solid Xe should be cross relaxation between $^{129}\text{Xe}$ and $^{131}\text{Xe}$. This is supported by his findings and confirmed by the present research; at high fields, where the $^{129}\text{Xe}$-$^{131}\text{Xe}$ coupling is extremely weak, the relaxation time $T_1$ of $^{129}\text{Xe}$ at 4.2 K is on the order of weeks. The $^{129}\text{Xe}$ nuclear spins in this regime form a diamagnetic insulating solid where there exists no mechanism for relaxation via exchange of nuclear angular momentum with the lattice. Such a scenario should also apply at low fields if it were possible to remove all of the $^{131}\text{Xe}$ from the solid. Unfortunately, this is not yet possible. There is always a possibility that other impurities could contribute also.

$^{131}\text{Xe}$ has its own unique identifying properties, however; it naturally exists in the lattice and has a quadrupole nuclear moment that interacts with the local elec-
tric field gradients (EFGs) present in the lattice. This interaction inhomogeneously broadens its energy spectrum (line shape) and thus enables some of the $^{131}$Xe located in the larger EFGs on the surface and near lattice defects to interact with neighboring $^{129}$Xe at low enough fields. See section 2.4.3 for details. This interaction is, of course, field dependent. The gyromagnetic ratio of $^{131}$Xe is about $1/3$ that of $^{129}$Xe and thus at higher fields the difference in Zeeman splitting between the two isotopes will energetically inhibit angular momentum exchange between allowed transitions. Warren and Norberg found that the intrinsic quadrupole energy of $^{131}$Xe in the bulk lattice of natural xenon [10] is of the same order of the Zeeman splitting of $^{129}$Xe at 7 G. Thus significant $^{129}$Xe-$^{131}$Xe cross relaxation in the bulk is possible below a field of about 7 G. This is evidenced by the results of the $^{129}$Xe cross relaxation experiment. When the field was dropped to 5 G (and below), cross polarization/relaxation in the bulk of natural xenon was seen between $^{131}$Xe and $^{129}$Xe respectively (section 3.4.1).

When the field is raised above 7 G, cross relaxation due to such thermal mixing in the bulk quickly diminishes, yet the relatively larger EFGs on the surface, on strain lines and on grain boundaries of the crystallites still allow significant cross relaxation only in these specific areas. Under such conditions, relaxation is mediated by spin diffusion which carries the magnetization in the bulk to the location of these special relaxation centers. Thus, the first visage of possible dependence on crystallite formation is encountered. In fact, under certain conditions which will be explored in this chapter, it is possible that this inhomogeneity of relaxation centers produces the nonexponential relaxation in the sample as a whole. And so some of the pieces start to fit together. In this chapter, both details and a model will be supplied that allows exploration of how they might indeed fit together.

### 4.2 The Diffusion Model

We start with the assumption that samples are pure enough so that the only relaxation mechanism available to solid $^{129}$Xe at very low fields and temperatures is cross relaxation with $^{131}$Xe mediated by spin diffusion (refer to sections 2.4.2 and
2.5.3). The pertinent macroscopic parameters are then the spin-diffusion tensor $D$, the geometric distribution of the $^{131}$Xe relaxation centers and also the average spin-relaxation rate between a $^{129}$Xe atom and a neighboring $^{131}$Xe relaxation center, $W_r$. The dipole-dipole channel for angular momentum exchange between two identical $^{129}$Xe nuclei, however, does not produce a net change in global polarization (it allows no relaxation). Such exchange, occurring at an average rate of $W_d$, is the source of spin diffusion. A “spin-up” state, therefore, is allowed to take a “random walk” through the spin lattice, changing places with spin-down states and “scattering” off the spin-up states of other $^{129}$Xe nuclei. In this light, spin diffusion is analogous to regular atomic diffusion (as seen in section 2.4.2).

As a first approximation, assume that spin-diffusion is isotropic. Then in analogy to atomic diffusion in fluids, define $n(\vec{r}, t)$ to be the polarization density and $\vec{J}(\vec{r}, t)$ to be the polarization current density associated with “flow” of this polarization as it diffuses and relaxes. Polarization, in this sense, can be construed as a physical measure of the local excess of nuclear spins (Zeeman order) that would be present along an applied field if such field were adiabatically increased to a value greatly exceeding any dipolar interactions of the nuclei. So defined, polarization still exists in smaller fields (those comparable with the dipole-dipole interactions between nuclei) in the form of local dipolar order. Diffusion of polarization, under these approximations, behaves like a fluid which diffuses through an isotropic media and is only allowed to “drain” through relaxation centers.

The velocity of the polarization flow, $\vec{v}(\vec{r}, t)$, is defined by the following relation (where $\vec{r}$ denotes the spatial coordinates):

$$n(\vec{r}, t)\vec{v}(\vec{r}, t) = \vec{J}(\vec{r}, t). \quad (4.1)$$

With this model, it is now possible to explore nuclear relaxation by considering an analogous fluid-dynamics problem. The velocity $v_r$ of polarization entering a relaxation center, for example, gives a measure of the strength of the relaxation center. Considering that spin relaxation due to a neighboring relaxation center occurs most often over the distance of approximately one lattice constant $a$, thus:
Having this tool in hand, it is instructive to find the conditions under which nonexponential relaxation is expected.

4.2.1 Nonexponential Relaxation

Nonexponential relaxation, by definition, requires that there be more than one characteristic time constant associated with the decay. Consider this scenario: suppose that relaxation centers were distributed homogeneously throughout the lattice. Then by translational symmetry, every region in the lattice must relax at exactly the same rate as every other region. Since the speed at which polarization is diminishing is always proportional to the amount of polarization left in every region, therefore, only one time constant may apply globally and monoexponential relaxation must result. To achieve nonexponential relaxation, then, there necessarily must be an inhomogeneous distribution of relaxation centers.

Now consider another scenario: suppose that spin diffusion is fast compared to the strength of the relaxation centers. Using the fluid diffusion model, this condition may be written: \( v_r \ll D/R \) where \( R \) is the average distance between relaxation centers. If the lattice initially has a uniform distribution of polarization density \( n(r,0) = \text{constant} \), then such rapid diffusion will serve to maintain (over time) a nearly uniform polarization density across the whole lattice regardless of the specific distribution of relaxation centers. This, again, assures translational symmetry. Therefore, as before, no region of the lattice can relax faster than any other region and the relaxation must be monoexponential. Only through a diffusion-limited process, where diffusion is slow compared to the strength of the relaxation centers \( (v_r > D/R) \), will nonexponential relaxation result.

Combining these two scenarios, nonexponential relaxation requires that at least two conditions be met: (1) the process is diffusion limited and (2) the relaxation centers are inhomogeneously distributed in the crystallite. As nonexponential relaxation is the normal behavior for the samples in this study, these two conditions will be generally asserted.

\[
v_r \approx a \cdot W_r. \tag{4.2}
\]
4.2.2 The Diffusion Equation

Quantitative analysis of the diffusion model will now be sought with the intention of comparing this model to the experimental data collected. For this purpose, the diffusion equation will be derived and utilized. Since no relaxation occurs in regions free of relaxation centers, polarization conservation applies in these regions:

$$\nabla \cdot \vec{J}(\vec{r}, t) = -\frac{\partial n(\vec{r}, t)}{\partial t}$$  \hspace{1cm} (4.3)

and in an isotropic diffusive media Fick’s Law also applies:

$$\vec{J}(\vec{r}, t) = -D \nabla n(\vec{r}, t)$$  \hspace{1cm} (4.4)

which states that the polarization current density is proportional to the polarization density gradient. The combination of these two equations, (4.3) and (4.4), forms the diffusion equation:

$$D \nabla^2 n(\vec{r}, t) = \frac{\partial n(\vec{r}, t)}{\partial t}.$$  \hspace{1cm} (4.5)

The general solution to the diffusion equation is well known and of the form:

$$n(r, \theta, \phi, t) = \sum_{i, l, m} J_{l+1/2}(k_{ilm}r) \left\{ \begin{array}{c} P_{lm}(\cos(\theta)) \\ Q_{lm}(\cos(\theta)) \end{array} \right\} \left\{ \begin{array}{c} \cos(m\phi) \\ \sin(m\phi) \end{array} \right\} e^{-\alpha_{ilm}^2 t}$$  \hspace{1cm} (4.6)

where $J_{l+1/2}$ are Bessel functions, $P_{lm}$ and $Q_{lm}$ are orthogonal Legendre polynomials, $k_{ilm} = \alpha_{ilm}/\sqrt{D}$ and $A_{ilm}$, $\alpha_{ilm}$ are constants. The curly brackets indicate that any linear combination of the two orthogonal functions may be used, if boundary conditions so require. This equation can be solved when given a set of boundary conditions and initial values. The realization of such requires some discussion.

4.2.3 Boundary Conditions and Initial Values

In an attempt to give some definite geometry to the distribution of relaxation centers in the lattice, the approximation will be made that relaxation centers are evenly spread over the surfaces of a set of spheres of radii $R_j$ and that no relaxation occurs anywhere except on the surface of these spheres. Spin diffusion is allowed in the interior of these spheres. Consider one such sphere of radius $R$. Applying
spherical symmetry, \( l = 0 \) and \( m = 0 \), to equation (4.6), results in the spherically symmetric general solution of the diffusion equation:

\[
n(r, t) = \sum_i A_i \frac{\sin \left( \frac{\alpha_i}{\sqrt{D}} r \right)}{r} e^{-\alpha_i^2 t}.
\]  

(4.7)

As relaxation takes place only on the surface of this sphere (where \( r = R \)), a surface boundary condition must be defined to reflect the strength of the relaxation centers there. A natural parameter for this has already been discussed. Utilizing the fluid-dynamics analogy, the parameter \( v_r \) [eqn. (4.2)] describes the velocity at which polarization disappears into the relaxation centers. This parameter can theoretically be used to control the velocity at which polarization is “drained” on the surface of the sphere.

For the purposes of this model, the individual relaxation centers can be thought of as being smeared out into a continuous relaxive surface. A fluid continuum, by definition, will be assumed everywhere. Since \( n(R, t) v_r = \vec{J}(R, t) \) on the surface of the sphere, we have from equation (4.4):

\[
n(R, t) v_r = -D \nabla n(R, t).
\]

Using the general solution (4.7) above, this reduces to the requirement that:

\[
\frac{R}{\sqrt{D}} \alpha_i \left( 1 - \frac{v_r R}{D} \right) = \tan \left( \frac{R}{\sqrt{D}} \alpha_i \right).
\]  

(4.8)

This boundary condition, therefore, determines the \( \alpha_i \).

The transcendental equation above (4.8) can be represented graphically by the intersection points of a line passing through the origin and the tangent function (see Figure 4.1). Even though this equation is not analytically solvable, values for \( \alpha_i \) may be easily calculated if the parameters \( R, D \) and \( v_r \) are known. The inverse argument is not true, however. Due to numerical instabilities near the odd multiples of \( \pi / 2 \) it is generally difficult to precisely extract these parameters from a given set of \( \alpha_i \). The method of parameter extraction from experimental results will be discussed in the following sections.
Figure 4.1. Graphical solution to Equation (4.8).

Once the $a_i$ have been determined by the boundary conditions, the only remaining task is to find the $A_i$ necessary to meet the initial conditions (the polarization density distribution at time zero). It is natural to assume that the polarization density is completely uniform throughout the crystallites before the relaxation mechanism is turned on. Thus assume $n(r, 0) = 1$ where $0 \leq r < R$:

$$n(r, 0) = \sum_i A_i \frac{\sin\left(\frac{a_i}{\sqrt{D}} r\right)}{r} = 1.$$  \hspace{1cm} (4.9)

The set of $A_i$ can be determined that most closely satisfy Equation (4.9) by utilizing a particularly potent numerical method that efficiently calculates these coefficients by means of a least squares fit over a finite number of terms in this sum. The
adaptation of this method is referred to in this dissertation as the Finite Basis Expansion Method (FBEM) and has been utilized in several of the numerical algorithms to fit data in this research. Appendix A is entirely dedicated to outlining this numerical method. Once this task is done, then by uniqueness the complete solution to the diffusion equation has been found.

A typical solution of the diffusion equation, \( n(r, t) \), for a spherical crystallite with the parameters \( D = 26 \times 10^{-14} \text{ cm}^2/\text{s} \), \( R = 5 \times 10^{-5} \text{ cm} \) and \( v_r = 1 \times 10^{-9} \text{ cm/s} \) is graphed in Figure 4.2. Notice that at \( t = 0 \text{ sec} \), the polarization density is uniform throughout the sphere, \( 0 > r > R \). As time advances, the polarization near the relaxive surface of the sphere, \( r = R \), is quickly depleted followed eventually by the polarization near the center, \( r = 0 \text{ cm} \). Having determined the \( A_i \) and \( \alpha_i \), it is now possible to calculate a theoretical relaxation for a single sphere by integrating the polarization density over the sphere to find the time dependent polarization \( P(t) \):

\[
P(t) = \int_V n(r, t) \, dV = P(0) \sum_i P_i e^{-\alpha_i^2 t}
\]

(4.10)

**Figure 4.2.** Graph of a typical radial polarization density profile over time for a spherically symmetric half-micron crystallite.
where
\[ P_i = 3A_i \left( \frac{v_r}{D - Rv_r} \right) \left( \frac{\sqrt{D}}{R\alpha_i} \right) \cos \left( \frac{R\alpha_i}{\sqrt{D}} \right). \]  

(4.11)

Notice that nonexponential behavior is possible even in the relaxation of a single sphere with a relaxive surface. It is now possible to explore the parameter space in order to better understand the expected behavior of relaxation in the various regions of this space.

### 4.2.4 Exploration of Parameter Space

The determination of the \( \alpha_i \) is of particular interest because they are directly related to the expected relaxation rates. Specifically, \( T_{1L} \), the long-time tail characteristic relaxation, can be related to the slowest rate \( \alpha_i^2 \):

\[ T_{1L} = \frac{1}{\alpha_i^2} \]  

(4.12)

where \( \alpha_1 \) is defined as the first nontrivial solution to equation (4.8). Referring to Figure 4.1, the value for \( \alpha_1 \) depends on the slope \( s \) of the line intersecting the tangent function:

\[ s \equiv \frac{1}{1 - \frac{v_rR}{D}}. \]  

(4.13)

If the relaxation centers are weak, \( v_r \ll D/R \), then \( s \) approaches 1 from the positive side. Thus \( \alpha_1 \) approaches zero and, as expected, the first term in the expansion (4.10) will dominate, producing nearly exponential relaxive behavior that is dependent on \( v_r \) but not much on \( D \); \( T_{1L} \approx R/(3v_r) \). On the other hand if the relaxation centers are strong, \( v_r \gg D/R \), then \( s \) approaches 0 from the negative side and the line intersects the tangent function near multiples of \( \pi \). Thus \( \alpha_i^2 \approx (i\pi)^2(D/R^2) \) and the relaxive behavior depends on \( D \) but not so much on \( v_r \). Nonexponential relaxation can be seen in this case with \( T_{1L} \approx R^2/(\pi^2D) \). In summary:

\[ v_r \ll D/R \quad \Rightarrow \quad T_{1L} \approx R \frac{3\alpha}{3v_r} \]  

(4.14)

\[ v_r \gg D/R \quad \Rightarrow \quad T_{1L} \approx R^2 \frac{\alpha}{\pi^2D}. \]  

(4.15)
Relating these results to the expected relaxation of solid $^{129}$Xe: At moderate fields (above 20 G), bulk relaxation in $^{129}$Xe is negligible, relaxation occurs only on the surface of the crystallite. And thus the radius of the sphere, $R$, can be estimated to be of the order of the size of a crystallite. An approximate diffusion coefficient, $D$, for solid natural xenon was estimated from theoretical calculations done in Gatzke’s doctoral dissertation [7]. For natural Xe this was found to be $D = 7.3 \times 10^{-14}$ cm$^2$/s; this must be adjusted for enriched Xe by using the assumption in Gatzke’s dissertation that diffusion scales proportionally with $^{129}$Xe concentration, $f$. Since $f_{nat} = 0.26$ and $f_{enr} = 0.86$, $D$ for enriched Xe can be found as listed below. We estimate that the radius $R$ of the sphere is on the order of the size of a crystallite, $1 \times 10^{-5}$ cm (order of magnitude). The velocity $v_r$ can be estimated by using Equation (4.2) with the experimentally determined spin-destruction rate, $W_r$, (estimated to be $1/30$ s$^{-1}$ from the $T_{1S}$ measurements at 20 G) and the lattice constant, $a$ (6.13 Å at 4 K). Given these estimates, the approximate parameter values can be summarized as follows:

\[
D \approx 2.4 \times 10^{-13} \text{cm}^2/\text{s} \\
R \approx 1 \times 10^{-5} \text{cm} \\
v_r \approx 2 \times 10^{-9} \text{cm/s} \\
D/R \approx 2 \times 10^{-8} \text{cm/s}.
\]

Since the crystallite radius $R$ is only an estimate and could vary significantly from crystallite to crystallite, it is possible that for the specific case of $^{129}$Xe, $v_r$ falls between the two extremes discussed in the last paragraph. That is to say that the possibility that $^{129}$Xe relaxation is not solely diffusion limited nor solely limited by the strength of the relaxation centers must be considered.

Thus at low fields (near 10 G), where $v_r$ is expected to be significantly larger (relaxation centers are strong), the relaxation characteristics would tend to be more nonexponential and have a much larger dependency on $D$ [Equation (4.15)]. At higher fields (over 150 G) and thus much smaller $v_r$ (relaxation centers are relatively weaker), relaxation characteristics would tend to be more exponential and limited.
by \( v_r \) [Equation (4.14)]. Between these two extremes, the spin-diffusion process \( D \) and the strength of relaxation centers \( v_r \) would be competing entities and the full problem would need to be solved. Notice that in either case, \( T_{1L} \) of a single crystallite is strongly dependent on the radius, \( R \), of the crystallite.

### 4.2.5 Crystallite Size Distribution

It is naive to assume that xenon crystallites come in just one size. Furthermore, each crystallite is isolated from the others since spin diffusion between neighboring crystallites is prohibited or severely retarded by the substantial gap in interatomic spacing over grain boundaries. Thus when considering the relaxation properties of polycrystalline \(^{129}\)Xe the global polarization should be calculated as a weighted sum of the polarizations of the individual crystallites over the distribution of crystallite sizes \( g_{\text{size}}(R) \):

\[
P_{\text{glob}}(t) = \int_R g_{\text{size}}(R) P(R; t) \, dR
\]

where the individual crystallite polarizations, \( P(R; t) \), are found by equation (4.10). In practice, it is not possible to integrate equation (4.16) directly and so discrete aliasing methods will be employed to approximate the integral. The crystallite size distribution \( g_{\text{size}}(R) \) must be determined. Since smaller crystallites can relax at a much faster rate than the larger crystallites (according to the diffusion model) knowledge of crystallite size distributions becomes crucial to understanding the overall relaxation characteristics of the solid.

Other investigators have shown by x-ray diffraction techniques [38] that Xe does indeed solidify into a polycrystalline powder (at least on all the substrates investigated). It is assumed that such is the case for the “large area deposition” method with Xe at one atmosphere on a glass substrate at liquid nitrogen temperatures. In order to better understand the crystalline structure, the condensed Xe crystallites were examined under a long-focal-length 20X microscope and seen to have a feathery dendritic structure, yet no individual crystallites could be resolved. Based on this observation, an extreme upper limit of 10 microns for the crystallite radii is reasonable.
Perhaps more revealing is the understanding gained from the x-ray diffraction techniques that both the partial pressure of Xe and the substrate temperature have an effect on crystallite growth rates and sizes [39, 40]. In a closed cell, the Xe pressure drops exponentially with time as the gaseous Xe is depleted. Also the surface temperature and coarseness of the topmost Xe layer increase with the total deposition thickness. In quench-condensed Xe films [41], a variety of crystallite parameters (thickness, density, crystallinity, texture, and surface roughness) were measured by Heilmann et al. by x-ray reflectivity and refraction. Films condensed at 15 K to 55 K had characteristic crystallite sizes of 10-200 Å. At temperatures near 55 K some annealing was observed, yet the structure was still characterized as a randomly oriented nanocrystalline powder. Such temperatures are admittedly lower than the 77 K substrate temperature of pyrex cells used in these relaxation experiments, yet similar polycrystalline structure for thus seeded bulk growth is not an unreasonable assumption.

Furthermore, when combined with the exponentially decreasing growth rates, this mimics the conditions present in the growth of the better-researched crystallization of metallic condensates prepared under inert-gas environments [42]. For nanocrystalline condensates prepared under inert gas, the grain-size distributions in general exhibit a log-normal distribution. That is to say that the logarithm of the grain size has a normal distribution. Thus, without explicit justification, it will be proposed that the crystallite sizes for the Xe condensate grown under an atmosphere of helium may also have a log-normal distribution:

\[
g_{\text{size}}(R) = \frac{1}{\sqrt{2\pi} R \ln(\sigma)} e^{-\frac{\ln^2(R/\mu)}{2\ln^2(\sigma)}}. \tag{4.17}
\]

See Figure 4.3. The results of these experiments tend to support this conjecture by the excellent data fits produced when assuming a log-normal distribution of crystallite sizes. In contrast, Gaussian or Lorentzian distributions of crystallite sizes yield poor fits.
Figure 4.3. The log-normal distribution.
4.2.6 Summary of Diffusion Model

The isotropic, spherically-symmetric diffusion equation has been solved to model spin diffusion in a spherical volume covered with a relaxive surface. Such spheres are designed to model xenon crystallites where $^{129}\text{Xe}$ spin diffusion takes place in the bulk and relaxation takes place only on the surface. Having developed a model for $^{129}\text{Xe}$ nuclear relaxation in an individual crystallite, the global relaxation curve is determined by summing this result over a log-normal distribution of crystallite sizes. Thus a quantitative model has been developed that can now be compared to experimental results. This model has only four free parameters:

1. $D$: The isotropic spin-diffusion coefficient

2. $v_r$: The speed of spin destruction on the crystallite surfaces

3. $\bar{R}$: The mean crystallite radius in the log-normal distribution

4. $\sigma$: The variance (width) of the log-normal distribution

Of these four parameters, the mean crystallite radius $\bar{R}$ and width $\sigma$ are expected to be roughly constant from sample to sample (if the method used in freezing is consistent). Thus the other two parameters, $D$ and $v_r$, are the only two parameters that could significantly vary with field. This is played out in the data fitting, being that the shape of the theoretical curve is particularly sensitive to the crystallite size distribution ($\bar{R}$ and $\sigma$).

4.3 Comparison to Experimental Results

It is now possible to compare the diffusion model quantitatively with experimental data. The data obtained from the AFP method were chosen exclusively for this task because of its much higher temporal resolution and smaller experimental uncertainties. The curve fitting process was done using the so called “Chi by eye” method. Initial guesses for the four free parameters were chosen as shown in section 4.2.4, the theoretical curve was then superimposed on the data graph and $\chi^2$ was calculated. Another set of parameters were chosen and the process repeated.
until the optimal data fit was found (minimizing $\chi^2$). This method worked very well for relaxation curves from 10-200 Gauss (at 4.2 K). Good data fits were generally found in 20 to 30 iterations with $\chi^2$ per point on the order of $10^{-3}$, the theoretical curve passing well within the error bars for most of the data points. However, for fields less than 10 G, the data fits were very poor. This was not entirely unexpected, the diffusion model outlined in this chapter does not apply when relaxation is able to take place in the bulk solid of the crystallites; recall that (in this model) relaxation is restricted to the surface of the crystallites. At fields less than 10 G, bulk cross relaxation has been observed in natural $^{129}$Xe (see section 3.4). Thus it is possible that the model is fundamentally inadequate at fields under 10 G even for enriched samples.

Automated optimization methods to fit the data tended to “run away”, especially for low-field data (around 10 G), where $v_r \gg D/\langle R \rangle$. This is due to the phenomena described in section 4.2.4. In this regime, the relaxation process theoretically becomes severely diffusion limited and the curve fit is insensitive to $v_r$ (which can be made arbitrarily large without effect). At low fields (30 G and below), $D$ became the dominant field-dependent adjustable parameter. At higher fields (around 200 G), where $v_r < D/\langle R \rangle$, the curve fit became less sensitive to changes in $D$ and more sensitive to changes in $v_r$. This trend can be easily seen in Table 4.1. See Figure 4.4 for an example of such a fit.

Error estimates were painstakingly made by varying the parameters in order to find the value of $\chi^2$ that indicates a confidence interval of 68% (as outlined

<table>
<thead>
<tr>
<th>Field (G)</th>
<th>$D$ ($10^{-14}$cm$^2$/s)</th>
<th>$v_r$ ($10^{-9}$cm/s)</th>
<th>$\langle R \rangle$ ($10^{-6}$cm)</th>
<th>$\langle R \sigma - 1 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7.9±0.4</td>
<td>&gt; 80</td>
<td>7.6±0.6</td>
<td>51±3</td>
</tr>
<tr>
<td>20</td>
<td>8.2±0.6</td>
<td>&gt; 80</td>
<td>8.4±1.0</td>
<td>34±4</td>
</tr>
<tr>
<td>40</td>
<td>19.5±0.5</td>
<td>6.9±0.4</td>
<td>2.6±0.3</td>
<td>7±1</td>
</tr>
<tr>
<td>120</td>
<td>18±1</td>
<td>6.9±0.6</td>
<td>5.1±0.4</td>
<td>35±4</td>
</tr>
<tr>
<td>140</td>
<td>24±2</td>
<td>5.2±0.1</td>
<td>5.2±0.3</td>
<td>32±4</td>
</tr>
<tr>
<td>200</td>
<td>26±1</td>
<td>1.6±0.1</td>
<td>5.5±0.2</td>
<td>35±4</td>
</tr>
</tbody>
</table>
Xe129 Relaxation at 10G and 4K
Compared to Diffusion Model

**Figure 4.4.** Typical curve fit of the diffusion model to the data.

in Numerical Recipes [54]). This was done by varying the parameters until the curve just passed outside of the error bars for most data points and then recording corresponding $\chi^2$ value. The errors for each of the individual parameters were then estimated by finding the maximum variance that kept $\chi^2$ within the 68% confidence interval. This process is often necessary when gaussian error distributions cannot be guaranteed. During the $\chi^2$ mapping process, it was found that simultaneously decreasing $\overline{R}$ and increasing $D$ slightly, resulted in little increase in $\chi^2$ when it is near the minimum. This local “shallow” region in the $\chi^2$ surface is problematic when attempting to find the absolute minimum. Practically, it means that there can be a lot of “play” in the $\overline{R}$ parameter which may not be adequately reflected in the error limits. Due to the time consuming calculations (taking about a day per parameter) a full $\chi^2$ mapping was not done, yet it will be mentioned here that $\overline{R}$ could possibly vary as much as 20% from the results posted in Table 4.1 and still remain within the 68% confidence interval.

Note that the $\sigma$ parameter in equation (4.17) is necessarily dimensionless and greater than one, being that $\ln(\sigma)$ is the standard deviation of the logarithm of the
crystallite sizes: \( \text{stdev}\{\ln(R_j/R_x); R_j = \text{radii}\} \). Thus \( \bar{R}(\sigma - 1) \) represents the spread of the crystallite sizes on the positive side of this asymmetric distribution.

It is interesting to note that above 40 G the \( \bar{R} \) and \( \sigma \) parameters stayed constant and needed very little adjustment in order to fit the data curves optimally; an exception being the 40 G relaxation curve. The other two parameters follow an interesting pattern. At the lower fields, the strength of the relaxation centers, \( \nu_r \), becomes irrelevant and the curves can be closely fit by variation of solely the diffusion coefficient, \( D \). At higher fields, however, the diffusion coefficient tends to “settle down” to a constant value while the strength of the relaxation centers, \( \nu_r \), becomes the crucial variable used to adjust the data fit. This trend is suggestive, it seems to indicate that diffusion slows down at the lower fields counteracting the possible effects of stronger relaxation centers. With a closer look, however, it is found that \( D \) is the only adjustable parameter available to fit the curves under 40 G, since \( \nu_r \) becomes irrelevant in this regime. Thus the decrease in the \( D \) parameter may reflect processes other than diffusion (such as bulk relaxation processes) that are not part of the surface relaxation model. Recall that in section 2.4.2 it was argued that spin diffusion at fields larger than 0.3 G is independent of the applied field. Thus the apparent slowdown of the diffusion may be an artifact due to the inadequacy of the model in fields below 40 G. Above 40 G where this model is expected to be valid, \( \nu_r \) (the strength of the relaxation centers) decreases monotonically with increasing field, as expected, and the other parameters remain relatively constant.

### 4.4 The \( T_{\text{1L}} \) Maximum

The most prominent feature of enriched \(^{129}\text{Xe}\) relaxation at 4.2 K and fields below 20 G is the \( T_{\text{1L}} \) maximum at 3 G, standing nearly an order of magnitude over the neighboring valleys. This feature exists in a region where \( T_{\text{1L}} \) might be expected to literally plummet due to the possible coupling between \(^{129}\text{Xe}\) and \(^{131}\text{Xe}\) in the bulk of the crystallites at very low fields (0-7 G) (section 2.5.3). It is therefore natural to question the validity of this maximum. Yet two entirely
separate experimental methods and environments (the pulsed method in a large electromagnet and the AFP method in a set of small Helmholtz coils) have produced essentially the same results.

The characteristic relaxation curve at the $T_{1L}$ maximum (3 G) for enriched $^{129}$Xe has a distinctive shape. It starts with a very rapid initial decay ($T_{1S} \approx 5$ min) which over a few tens of minutes turns into a $T_{1m}$ of several hours. After only 2 hours of relaxation, a $T_{1L}$ of about 10 hours is seen which continues to increase slowly to values close to 18 hours over a day’s time. If this decay is to be understood in light of the diffusion model, then the quick initial relaxation could be explained by the relaxation of the $^{129}$Xe atoms immediately neighboring the $^{131}$Xe relaxation centers. Even at the 0.1% $^{131}$Xe concentration in enriched $^{129}$Xe, still about 13% of the $^{129}$Xe in the lattice have a $^{131}$Xe atom within two lattice constants. The subsequent slow-down of the long-time relaxation, however, is more problematic.

In this section, several possible candidates for the mechanism behind the $T_{1L}$ maximum at 3 G in enriched xenon will be examined in light of the diffusion model and tested against experimental observations. These candidates are broken down into two general categories: (1) diffusion retardation or diffusion barriers that inhibit spin diffusion into strong bulk relaxation centers or (2) weakened bulk relaxation centers where the $^{129}$Xe-$^{131}$Xe coupling or $^{131}$Xe-lattice coupling strength is diminished. The actual mechanism may possibly be a combination of these. Each candidate must stand up to three experimental tests based on the observations that: (1) field cycling, when collecting data, does not cause significant relaxation, (2) Abrupt changes in field after many hours of relaxation at 3 G results in faster, near-exponential relaxation (kink data), and (3) Cross relaxation between $^{129}$Xe and $^{131}$Xe may exist below 7 G (at least in natural xenon). The second observation (kink data) places rather strict restrictions on the distribution of polarization after many hours of relaxation.

Both experimental data and the theoretical model show that if the polarization density were uniform at any time and at any field below 500 G, then rapid non-exponential relaxation would immediately result. This is based on the assumption
that, in every case, the polarization density is initially uniform throughout the sample before the field is turned down and rapid relaxation is initiated. Therefore, if rapid nonexponential relaxation is not seen, then the polarization density cannot be uniform. In order for near-exponential behavior to be manifest, polarization density must be depleted in such a pattern that when the field is abruptly changed and the new initial conditions are considered, the higher order terms in equation (4.10) turn out to be negligible and the smaller crystallites have already relaxed.

The diffusion parameters extracted in the last section show the beginnings of diffusion slowing at the lower fields (10-20 G). Theoretical arguments against spin diffusion slowing at these fields have already been presented in section 2.4.2. Experimental observations which further eliminate the possibility of the dependence of spin diffusion on field will now be presented. Assuming that the relaxation centers in the bulk lattice at very low fields (0-7 G) are strong and that they are also homogeneously distributed throughout, then in order to explain the slower relaxation at these fields, at least two possibilities present themselves:

1. Spin diffusion in the bulk lattice drastically slows down.

2. Spin diffusion barriers are established around relaxation centers in the bulk lattice.

Both of these cases will be examined.

Beginning with the first case, suppose that at low fields (less than 10 G) spin diffusion is slowed down in the bulk lattice to such a degree that despite the possible activation of bulk relaxation centers, overall relaxation still slows down. Due to the proximity of $^{131}$Xe relaxation centers in the bulk lattice of enriched xenon (on the average 4 lattice constants), to be consistent with observed relaxation rates requires that even on the atomic scale, spins will not diffuse more than a few lattice sites an hour. To get an estimate of the diffusion coefficient, the diffusion model will be utilized with a spherical radius of only a few lattice constants, $R \approx 12$ Å. Then with $D \approx R^2/(\pi^2 T_{1L})$ [section 4.2.4] and with $T_{1L} \approx 1000$ min, it follows that $D \approx 2 \times 10^{-20}$ cm$^2$/s. In this case, diffusion will be virtually halted on the
macroscopic scale. Furthermore, the millisecond after the field is raised beyond 7 G and the relatively rapid diffusion is re-established, the polarization will homogenize, since variations in the polarization density were on the atomic scale below 7 G. With uniform polarization again established, subsequent lowering of the field back down to the low-field value would necessarily reinitialize the quick nonexponential bulk relaxation, as already discussed, and a significant portion of the sample would be seen to relax at each field cycle. All of the data were taken using the field cycling method and no strong dependence on field-cycling frequency was seen (at times there were long irregular periods of time between field cycles due to operator fatigue).

A more convincing argument against this case, however, comes from the observed kink behavior. According to the diffusion model, if diffusion is virtually halted at 3 G and relaxation takes place only a few lattice constants around the the \(^{131}\)Xe relaxation centers in the bulk, then if the field were abruptly raised to 150 G, the initial condition of near uniform polarization would be quickly restored. This initial condition at 150 G would require that a rapid nonexponential decay occur. Since nonexponential relaxation was not seen after the kink, it must be assumed that significant relaxation near the surface relaxation centers had already occurred throughout the sample, even at 3 G, before the field was changed; in particular, the smaller crystallites must have already entirely relaxed. It therefore may be said with confidence that there is no evidence that spin diffusion is halted or drastically slowed down at 3 G. This is consistent with the theory developed in section 2.4.2 that predicts no field dependence for spin diffusion at fields larger than 300 mG.

The second case now will be examined. Suppose that spin diffusion persists in the bulk but diffusion barriers are established around the bulk \(^{131}\)Xe relaxation centers at very low fields due to, say, significant local-field inhomogeneities around the \(^{131}\)Xe sites [43]. In this case, it will also be assumed that the surface relaxation centers (on the surface, grain boundaries, lattice irregularities, etc.) have no such diffusion barrier so that relaxation can proceed in these special areas. The initial rapid decay would then be due to a combination of relaxation in the
bulk immediately around the $^{131}$Xe atoms and the more gradual depletion of the polarization around the “surface” relaxation centers on crystallite irregularities. In particular, the smaller crystallites would relax much faster, along with the crystallites with larger defect densities. During field cycling, the diffusion barriers would be removed when the field is raised and spins would be allowed to diffuse into the sites adjacent to the temporarily-inert bulk relaxation centers. When the field is again lowered, bulk relaxation would be partially reinitialized. Such an effect would be detectable and dependent on field-cycling frequency. Such an effect was not seen experimentally. On the other hand, however, the kink behavior would be expected to exhibit an exponential behavior in compliance with experimental evidence.

Thus in order to explain the $T_{1L}$ maximum, candidates which reduce or stop the effectiveness of bulk relaxation centers in enriched samples are the front runners. There is a possibility that the coupling between $^{129}$Xe and $^{131}$Xe is reduced at very low fields (0-7 G) or that $^{131}$Xe relaxation to the lattice is slowed down. Such behavior is consistent with the expected theoretical behavior discussed in section 2.5.3. This must be reconciled, however, with the observation that in natural xenon, fast cross relaxation was seen to exist in the bulk at 3 G. A clue is possibly offered by the one relaxation curve that was taken for natural xenon at 4 G and 4.2 K: $T_{1S} \approx 2$ min and $T_{1L} \approx 16$ min. With this natural sample the relaxation showed no sign of slowing after the first 10 min. In comparison, an enriched sample at 4 G and 4.2 K exhibits a drastic slow-down after the first 10 min starting with a $T_{1S} \approx 5$ min and arriving at a $T_1(10 \text{ min}) \approx 90$ min. The natural sample continued even after 50 min to have a $T_1(50 \text{ min}) \approx 16$ min, in contrast to the enriched sample with a $T_1(50 \text{ min}) \approx 130$ min that would eventually slow to a $T_{1L} \approx 800$ min. After 55 min, the signal for the natural sample was already in the noise (even though the initial signal to noise ratio exceeded 1500). This suggests that the relaxation processes for natural Xe and enriched Xe are not equivalent at low fields.

Experimentally, the $^{131}$Xe NMR signal in enriched xenon (0.1% $^{131}$Xe, 86% $^{129}$Xe) is far too weak to detect with our apparatus. Thus it is still uncertain
whether cross polarization/relaxation between the two isotopes does indeed take place in the bulk lattice of enriched xenon as it does in the natural xenon lattice (21% $^{131}$Xe, 26% $^{129}$Xe). Theoretically, the full quantum, many-body problem that one would need to solve to find the “matrix elements” related to angular momentum exchange vs. isotopic concentration is difficult in the bulk lattice, especially at low fields (where quadrupole fields are significant). And so it will remain an open question as to whether significant $^{129}$Xe relaxation takes place in the bulk lattice in enriched samples. If it does exist, however, it is obvious that bulk relaxation times greater than 1000 min at 3 G and 4.2 K would be necessary in order to be consistent with experimental results. Furthermore, no $T_{1L}$ maximum is seen in the natural samples. This evidence, though circumstantial, still indicates that there are significant differences in the relaxation characteristics at low fields and temperatures between the spin lattices of natural and enriched xenon.

To summarize, in order for the $T_{1L}$ maximum to exist and also to maintain consistency with other experimental results, relaxation in the bulk lattice must be very slow after the initial bulk cross relaxation (if any). Also effective “surface” relaxation centers must be inhomogeneously distributed and have field dependence. Relaxation centers on the surface of the crystallites at fields around 3 G must still be effective; the sample polarization, as has been discussed, must be nonuniform after several hours of relaxation in such a way that smaller crystallites have relaxed and larger crystallites still exhibit near exponential relaxation behavior when the field is abruptly changed. There is no evidence for the dependence of spin diffusion on the applied field. The exact mechanism for relaxation in the bulk crystallites, however, is still shrouded in mystery but would seem to have a dependence on gross $^{131}$Xe concentration.

4.5 Suggestions for Further Research

Some of the open questions in this thesis are related to the characteristic behavior of spin diffusion at very low fields or the interactions between $^{131}$Xe and $^{129}$Xe in the bulk lattice at low fields or the dependency of local fields on isotopic
content and lattice defects. In this section, a few brief suggestions for possible future research will be presented and then some interesting hypotheses offered for, if nothing else, entertainment.

Solid $^{129}$Xe at low temperatures is an ideal platform on which to isolate and investigate essential nuclear spin-interaction characteristics [44]. The simplicity of electron interactions in the noble gases, the ability to hyperpolarize the nuclei, the inclusion or exclusion of quadrupole effects by modifying the applied field, the possibility of ultra-high sensitivity due to relaxation times of hundreds of hours and the ability to investigate relaxation at very low fields are all huge benefits. As a bonus, if $^{129}$Xe is able to be polarized in excess of 90%, then enriched $^{129}$Xe may be even be used to directly investigate the properties highly-polarized spin lattices, such as the quenching of dipole-dipole couplings [45] or super-sensitivity to container geometries [46].

It appears that a majority of spin relaxation in enriched solid $^{129}$Xe takes place on the surface of the crystallites and the bulk relaxation has a relatively small effect. The suggestion was made to introduce an artificial diffusion barrier between the bulk and the surface in order to isolate the bulk from the more active surface regions. This could possibly be done by introducing a small “puff” of a gaseous, spinless xenon isotope into the cell after freezing the $^{129}$Xe. This would coat the exposed crystallite surfaces with several monolayers of spinless xenon atoms which would then act as a diffusion barrier, preventing the $^{129}$Xe nuclei from coming into contact with the exposed surfaces of the crystallites. Of course, lattice defects and internal grain boundaries will not be affected.

Growing a single crystal of enriched hyperpolarized $^{129}$Xe would be the most direct method of isolating bulk relaxation. This recently has become more of a possibility due to a process developed in our group to maintain steady-state polarization in liquid xenon via spin exchange optical pumping (SEOP) in an oven, convective transport to a refrigerator and subsequent phase exchange with a liquid xenon repository [47]. Polarizations near 10% could be maintained indefinitely in the liquid $^{129}$Xe while it is gradually solidified by the upward movement of a steady
temperature gradient. This could conceivably be done by sequentially turning off coaxial heaters surrounding the liquid sample in a cold finger maintained near 80 K. Even though relaxation has been shown to be fast in solid $^{129}$Xe when near the melting point over a gas-solid interface, the experiment to measure the relaxation rate of solid $^{129}$Xe over a liquid-solid interface has not yet been done.

Double resonance experiments [48] with $^{129}$Xe and $^{131}$Xe at low temperatures and fields might also be revealing; in particular, saturating the $^{131}$Xe and measuring the $^{129}$Xe relaxation response. Or possibly polarizing the $^{131}$Xe via cross polarization and then monitoring subsequent $^{129}$Xe relaxation at moderate fields (200 G). Such investigation could help clarify the cross-polarization/relaxation coupling between $^{131}$Xe and $^{129}$Xe. This experiment could also be done for samples with varying isotopic concentration. It would be advisable to spread such experiments over a wider range of isotopic concentrations, being that sample to sample variations are difficult to surmount.

Finally, investigations into spin diffusion at very low fields where dipole-dipole interactions compete with the applied field may be possible. This would need to be accomplished through magnetic shielding (at fields < 300 mG). In this regime, the exchange of angular momentum between $^{129}$Xe nuclei preserve dipolar order (entropy), but not necessarily spin polarization. It is not clear to the author whether “spin diffusion” due to such an exchange should proceed at the same rate as spin diffusion at higher fields where Zeeman order is dominant. Some interesting speculation on the topic is that diffusion may slow down in the dipolar order regime due to the same mechanism that exists during a phase change. In particular, local interaction energy minimums could form in the same fashion as, say, a glassy transition forms. In short, a “spin glass” could form, which impedes the propagation of energy through angular momentum exchange in an analogous fashion as glass impedes the conduction of heat. Of course, this is mere speculation, but it is still entertaining to consider, and perhaps it will motivate research in this area.
CHAPTER 5

CONCLUSION

Low-field investigation of longitudinal nuclear relaxation of enriched polycrystalline $^{129}$Xe at 4 K has shown that the quadrupole $^{131}$Xe isotope is a significant player if not the dominant player in the nuclear relaxation of polycrystalline $^{129}$Xe in this regime. This is clearly seen in the sharp differences between the characteristic relaxation of natural xenon (21% $^{131}$Xe, 26% $^{129}$Xe) and enriched xenon (0.1% $^{131}$Xe, 86% $^{129}$Xe) where the exclusion of $^{131}$Xe in similarly prepared solid xenon samples drastically slows the long-time relaxation rates of the $^{129}$Xe [Section 3.3.4]. Besides dependence on $^{131}$Xe concentration, $^{129}$Xe relaxation has been seen to have a strong dependence on the crystalline properties of the polycrystalline solid as well as a dependence on the applied magnetic field.

At fields above 10 G (where only the $^{131}$Xe on surface sites and near lattice defects should exhibit cross relaxation with the $^{129}$Xe), the characteristic nonexponential relaxation curves are closely fit by the theoretical curves produced by a macroscopic surface relaxation model that takes into consideration just these factors: surface relaxation and bulk spin diffusion [Section 4.3]. These curve-fits provide further insight into the details of such relaxation. The crystallite size distribution, the spin diffusion coefficient and the strength of the surface relaxation centers are parameters extracted from these curve-fits. In this model, smaller crystallites relax relatively quickly and larger crystallites relax from the outside to the inside as limited by spin diffusion [Section 4.2]. It was necessary to assume a log-normal crystallite size distribution and spherically shaped crystallites in order to realize this curve fitting [Section 4.2.5]. Without means of being able to independently determine the crystallite size distribution and geometry of the crystallites,
these parameters are only approximate; yet they are reasonable and the curve fits are extraordinarily close. The other extracted parameters are also very close to the expected values, especially the spin diffusion coefficient that has been theoretically determined, given the known lattice characteristics of solid xenon both in this work (via a twin-atom quantum model) [Section 2.4.1] and in Gatzke’s earlier work [7].

The field dependence of $^{129}$Xe nuclear relaxation at fields above 100 G at 4 K shows no significant deviation from expected behavior if $^{131}$Xe were in truth the only relaxation mechanism in this regime and follows the model presented by Gatzke in his original work [7]. The strength of the $^{131}$Xe relaxation centers decreases predictably with increasing field. However, when the field is brought below 100 G this prediction breaks down and the strength of the relaxation centers is seen to actually decrease with decreasing field [Section 3.5.1]. At fields below 10 G, not even the macroscopic surface relaxation model mentioned above would fit the experimental relaxation curves. As the field is lowered further, this slowing trend in relaxation continues to the point where at 3 G a large $T_{1L}$ maximum is seen [Section 4.4]. This $T_{1L}$ maximum occurs at a field where the strength of the $^{131}$Xe relaxation centers is expected to be strong even in the bulk lattice of the individual crystallites. It appears as if there is some mechanism that tends to decrease the effectiveness of $^{131}$Xe relaxation centers when fields are brought below 100 G. Such behavior, however, is only seen in the enriched xenon samples.

Naively, the 3 G $T_{1L}$ maximum could suggest that yet some other unexpected relaxation mechanism due to an impurity or environmental noise has been at play, the which becomes ineffective at fields approaching 3 G. This naive hypothesis still does not take into account why the $^{131}$Xe relaxation centers existing in the bulk lattice would be so ineffective at 3 G. The 3 G $T_{1L}$ maximum conflicts with the observation that in natural xenon at 5 G, the average bulk cross relaxation rate between $^{129}$Xe and a neighboring $^{131}$Xe was measured to be (at the very least) a few nuclear spins per minute [Section 3.4]. At this same rate in enriched xenon, taking normal spin diffusion into account, the $^{129}$Xe $T_{1L}$ would be on the order of 10 min. And yet the observed $T_{1L}$ at 3 G for enriched $^{129}$Xe is on the order of 1000 min;
orders of magnitude longer than expected. This suggests that instead of attempting to find a relaxation mechanism due to some unknown impurity or environmental factor, focus should be shifted to the physics of cross relaxation between $^{129}$Xe and $^{131}$Xe in the enriched xenon lattice in an attempt to understand how bulk cross relaxation could be so slow in the 3 G regime.

Due to the complexity of the many-body problem associated with the theoretical full quantum treatment of nuclear relaxation in enriched $^{129}$Xe, a simplified two-atom problem was examined [Section 2.5.3]. It was found that over several different configurations of local EFGs and nuclear orientations in applied fields less than 10 G, nuclear angular momentum exchange between an isolated $^{129}$Xe and $^{131}$Xe pair was inhibited due to the fact that all other energies at these fields (dipole-dipole and Zeeman) became dominated by the quadrupole energies of the $^{131}$Xe (as determined by the local EFGs in the bulk lattice). Although nuclear spin exchange between two isolated atoms does not fully model relaxation (as energy necessarily would also be exchanged with the lattice), it does suggest, however, that internuclear angular momentum exchange between $^{129}$Xe and $^{131}$Xe at fields less than 10 G could be inhibited by the quadrupole energies involved in the exchange. According to the two-atom calculations, accidental degeneracies (degeneracies that would facilitate cross relaxation) between an isolated pair of $^{129}$Xe and $^{131}$Xe nuclei only start to occur at fields above 3 G [Section 2.5.3]. Interestingly, this is concurrent with the observed 3 G $T_{1L}$ maximum. At fields above 10 G, quadrupole energies in the bulk lattice again start to become small compared to the Zeeman energy of the $^{129}$Xe nucleus. Thus cross relaxation is effectively shut off in the bulk lattice yet still can exist in regions where larger EFGs and thus larger quadrupole energies exist; such as regions on the surface and near lattice defects.

The larger EFGs possible on the surface and near lattice defects, as investigated by the two-atom calculations, allow significant probability of accidental degeneracies and thus angular momentum exchange between $^{129}$Xe and $^{131}$Xe nuclei on the surface of the crystallites well into the 100 G range [Section 2.5.3]. This is concurrent with the observations made when fitting the relaxation curves to
the macroscopic surface relaxation model mentioned above. It also may help explain why this specific macroscopic surface relaxation model was only able to fit relaxation curves at fields above 10 G [Section 4.3]; at lower fields relaxation centers in the bulk of the crystallites become significant. Again at fields below 10 G, the very limited range of EFGs and nuclear orientations examined by the two-atom quantum calculations, were consistent with the possibility that inhibited cross relaxation between $^{129}$Xe and $^{131}$Xe is also responsible for the 3 G maximum and the subsequent behavior of $T_{1L}$ at larger fields up until about 100 G.

There still remains an open question as to what might cause the rapid initial relaxation (short $T_{1S}$) at fields below 10 G. At fields greater than 10 G (where bulk relaxation is negligible), this rapid initial relaxation can be explained by the macroscopic surface relaxation model, where the rapid initial relaxation is related to the relatively quick relaxation times of the smaller crystallites compared to the longer relaxation times of the larger crystallites (recall that spin diffusion is the limiting factor in larger crystallites). The $T_{1L}$ long-time relaxation, therefore, mostly indicates relaxation times in the larger crystallites. If this analogy is to be extended to relaxation at 3 G, this implies that even at 3 G, surface relaxation is still relatively quick compared to bulk relaxation in the crystallites. This implication is supported by the “kink” data [Section 4.4]. The fact that the rapid initial relaxation is not repeated when the field is suddenly raised from 3 G to a point where surface relaxation dominates implies that significant relaxation must have already occurred near the surface of the crystallites and that the smaller crystallites must have already mostly relaxed when held at 3 G. Why would surface relaxation be relatively quick at 3 G? This is the open question. The two-atom quantum calculations imply that the active surface relaxation sites that would be normally active at higher fields should be shut down at 3 G (given that quadrupole energies would largely dominate the Zeeman energies at these surface sites). There may be other active relaxation sites, however. The nature and distribution of the EFGs on the surface of the crystallites is an unknown and may well be the missing information in this puzzle.

Considering the overall results, however, there was no conclusive calculation
or observation made in this thesis that eliminates the possibility that $^{131}\text{Xe}$ cross relaxation is indeed the dominant mechanism for $^{129}\text{Xe}$ at 4 K over all the applied fields examined. In fact, at fields above 10 G, the results of this investigation support $^{131}\text{Xe}$ dominated relaxation. Complete details of the expected behavior of the specific relaxation mechanisms at low fields, however, have yet to be discovered. Much work remains to be done before the physics of nuclear spin relaxation in polycrystalline $^{129}\text{Xe}$ is to be completely understood.
APPENDIX A

NUMERICAL METHODS

A.1 Finite Basis Expansion Method (FBEM)

A general procedure to fit a function, written as an expansion over a set of arbitrary basis functions, to a set of data points and conditions will be described herein. This is a particularly useful algorithm that was employed many times in this present research for linear data fitting and also as part of a hybrid nonlinear Levenberg-Marquardt data-fitting algorithm. This method was developed independently by the author yet has subsequently been found to be used extensively in the computational physics field under different names: “The Cell Discretization Method” of John Greenstadt [49], “The Best Approximation Method” of Yen and Pinder Hromadka [50], “The Pseudo Spectral Method” commonly used by many, possibly originated by Gottlieb and Orzag [51], “The Fast Multipole Method of Roklin” [52]. This idea was also used by Collatz during his illustrious career. There are many examples in most of his many books [53]. This method has been applied in many different contexts in many different areas, however, it is presented here in a generic context. A few specific applications that apply to solving the diffusion equation and data fitting will then be discussed.

Suppose that we are given a finite set of approximate basis functions \( \{ \psi_i(\vec{r}) \} \) which we believe is particularly suited to a certain problem. We have a set of boundary conditions and possibly other conditions we wish to meet. In its most general form, the solution function \( f(\vec{r}) \) could be approximated as a finite expansion over \( n \) terms:

\[
f(\vec{r}) = \sum_{i=1}^{n} q_i \psi_i(\vec{r})
\]

or in vector notation
\[ f(\vec{r}) = \vec{q}^T \cdot \vec{\psi}(\vec{r}) \]  

(A.1)

where \( \vec{r} \) is a vector of independent parameters and \( \vec{q} \) is a vector of scalar coefficients. For the sake of generality, we will relax any restrictions and say that this set of basis functions does not necessarily need to be complete or orthonormal. Our task is to find the set of coefficients \( \{q_i\} \) that most closely causes the function to fit a given set of conditions. Such conditions could be that the function passes through a set of points, or satisfies a differential equation, or meets a set of boundary conditions, etc.

A general set of \( m \) such conditions could be written in the form:

\[ L_j f(\vec{r}_j) = b_j \quad j = 1, \ldots, m \]  

(A.2)

where \( L_j \) is a linear operator (such as a differential operator or even the identity operator) and \( \{\vec{r}_j\} \) is a set of points along the boundaries (or any other place) where you wish to fit \( L_j f(\vec{r}_j) \) to the specific value \( b_j \). We can use the linear nature of (A.2) to express these conditions in the form:

\[ L_j [\vec{q}^T \cdot \vec{\psi} (\vec{r}_j)] = b_j \]

\[ \vec{q}^T \cdot L_j \vec{\psi} (\vec{r}_j) = b_j \]

or in vector notation

\[ \vec{b}^T = \vec{q}^T \cdot \{L_1 \vec{\psi}(\vec{r}_1), L_2 \vec{\psi}(\vec{r}_2), \ldots, L_m \vec{\psi}(\vec{r}_m)\} \]  

(A.3)

For now, it is assumed that \( j \) is a discrete index, and thus only a discrete set of boundary value points are to be used to enforce the boundary conditions.

We define the \( n \times m \) matrix \( \cdots \) in eqn. (A.3) to be \( \Psi \), so that in shorthand matrix notation the boundary conditions for \( f(\vec{r}) \) may be written:

\[ \vec{b}^T = \vec{q}^T \Psi. \]  

(A.4)

Written explicitly,

\[ \Psi \equiv \begin{pmatrix} L_1 \psi_1(\vec{r}_1) & L_2 \psi_1(\vec{r}_2) & \cdots & L_m \psi_1(\vec{r}_m) \\ L_1 \psi_2(\vec{r}_1) & L_2 \psi_2(\vec{r}_2) & \cdots & L_m \psi_2(\vec{r}_m) \\ \vdots & \vdots & \ddots & \vdots \\ L_1 \psi_n(\vec{r}_1) & L_2 \psi_n(\vec{r}_2) & \cdots & L_m \psi_n(\vec{r}_m) \end{pmatrix}. \]  

(A.5)
Ψ depends entirely on our choice of n basis functions and m conditions at boundary points. We will impose the condition that \( m \geq n \), implying the soft restriction that we have at least as many conditions as terms in our expansion.

By using a least squares method, we can invert \( \Psi \) to obtain the best \( \vec{q} \). One such method is to calculate the SVD \([54]\) of \( \Psi \):

\[
\Psi = U W V^T
\]  

(A.6)

where \( U \) and \( V \) are orthonormal and \( W \) is diagonal, then invert the diagonal matrix \( W \rightarrow W^{-1} \) by letting \( w_i^{-1} = 1/w_i \), and if \( w_i \) is close to zero then \( w_i^{-1} = 0 \). The best fit, in the least squares sense, is then:

\[
\vec{q}^T = \vec{b}^T V W^{-1} U^T \equiv \vec{b}^T \vec{\Psi}
\]  

(A.7)

where \( \vec{\Psi} \equiv V W^{-1} U^T \).

The function \( f(\vec{r}) \) is then found from equations (A.1) and (A.7) to be:

\[
f(\vec{r}) = q^T \cdot \vec{\psi}(\vec{r}) = [\vec{b}^T \vec{\Psi}] \cdot \vec{\psi}(\vec{r})
\]

and finally

\[
f(\vec{r}) = \vec{b}^T \cdot [\vec{\Psi} \vec{\psi}(\vec{r})]
\]  

(A.8)

or

\[
f(\vec{r}) = \vec{b}^T \cdot \vec{\phi}(\vec{r}) \ \text{where} \ \vec{\phi}(\vec{r}) \equiv \vec{\Psi} \vec{\psi}(\vec{r}).
\]  

(A.9)

Written in this form, it is easy to see that we now have a new (Green’s) basis, \( \vec{\phi}(\vec{r}) \), over which \( f(\vec{r}) \) is a linear combination of the boundary values in \( \vec{b} \). Since all the \( b_j \) are independent from one another, it can be shown that

\[
L_j \phi_i(\vec{r}_j) = \delta_{ij} \ \text{where} \ \delta_{ij} = \begin{cases} 
0, & i \neq j \\
1, & i = j
\end{cases}
\]  

(A.10)

and where the \( L_j \) and \( \vec{r}_j \) are the conditions and boundary points used in constructing \( \Psi \). Note that \( \vec{\phi}(\vec{r}) \) does not depend on the boundary values in \( \vec{b} \), so these values may then be changed without the cost of inverting \( \Psi \) again. However, \( \vec{\phi}(\vec{r}) \) does, depend on the specific set of discrete boundary points \( \vec{r}_j \) and conditions \( L_j \) that are chosen. Such choices provide effective degrees of freedom in this method.
A.2 Unspecified Boundary Values

Suppose that some of the boundary values in \( \vec{b} \) are not explicitly specified, but may be found by matching function values at a boundary or by using some other conditions that depend on matching two functions \( f_i(\vec{r}) \) and \( f_j(\vec{r}) \) over such a boundary. Let us segment \( \vec{b} \) such that we separate the values that are known (\( \vec{b}_o \), with \( m_o \) components) and those which are unknown (\( \vec{b}_u \), with \( m_u \) components):

\[
\vec{b}^T = \begin{pmatrix}
\vec{b}_o \\
\vdots \\
\vec{b}_u
\end{pmatrix}^T
\]  

(A.11)

where \( m_o + m_u = m \) as required. We then require \( m_u \) equations to solve for these unknowns. The function may be expressed in segmented form [compare with eqn. (A.9)]:

\[
f(\vec{r}) = \begin{pmatrix}
\vec{b}_o \\
\vdots \\
\vec{b}_u
\end{pmatrix}^T \begin{pmatrix}
\vec{\phi}_o(\vec{r}) \\
\vdots \\
\vec{\phi}_u(\vec{r})
\end{pmatrix}.
\]  

(A.12)

Here \( \vec{\phi}(\vec{r}) \) has also been segmented into two vectors with \( m_o \) and \( m_u \) components, respectively.

Consider the case where two functions, \( f_1 \) and \( f_2 \), which are expressible in the form of eqn. (A.12) above, interface at a set of given boundary points \( \{\vec{r}_j\} \). Conditions at the interface generally come in the form:

\[
\Omega_1 f_1(\vec{r}_j) = \Omega_2 f_2(\vec{r}_j)
\]  

(A.13)

where the \( \Omega \) are linear operators. This can be expanded [see eqn. (A.12)]:

\[
\Rightarrow \vec{b}_{u1}^T \cdot \Omega_1 \vec{\phi}_o(\vec{r}_j) + \vec{b}_{u2}^T \cdot \Omega_1 \vec{\phi}_u(\vec{r}_j) = \vec{b}_{o1}^T \cdot \Omega_2 \vec{\phi}_o(\vec{r}_j) + \vec{b}_{o2}^T \cdot \Omega_2 \vec{\phi}_u(\vec{r}_j).
\]

Isolating the \( b_u \) and then combining:

\[
\begin{pmatrix}
\vec{b}_{u1} \\
\vdots \\
\vec{b}_{u2}
\end{pmatrix}^T \begin{pmatrix}
\Omega_1 \vec{\phi}_u(\vec{r}_j) \\
\vdots \\
-\Omega_2 \vec{\phi}_u(\vec{r}_j)
\end{pmatrix} = \begin{pmatrix}
\vec{b}_{o1} \\
\vec{b}_{o2}
\end{pmatrix}^T \begin{pmatrix}
-\Omega_1 \vec{\phi}_o(\vec{r}_j) \\
\Omega_2 \vec{\phi}_o(\vec{r}_j)
\end{pmatrix}.
\]  

(A.14)

If there are enough points along the boundary, \( \{\vec{r}_j\}; \ j = 1, \ldots, n_b \geq 2m_u \), then the matrix

\[
\begin{pmatrix}
\Omega_1 \vec{\phi}_u(\vec{r}_1) & \ldots & \Omega_1 \vec{\phi}_u(\vec{r}_{n_b}) \\
\vdots & \ldots & \vdots \\
-\Omega_2 \vec{\phi}_u(\vec{r}_1) & \ldots & -\Omega_2 \vec{\phi}_u(\vec{r}_{n_b})
\end{pmatrix}
\]
can be inverted in the same fashion as $\Psi \rightarrow \overline{\Psi}$ was in the introduction and the optimal \( \left( \begin{array}{c} \vec{b}_{u1} \\ \vdots \\ \vec{b}_{u2} \end{array} \right) \) can be found.

The FBEM (Finite Basis Expansion Method) is general enough to be applicable to a plethora of problems. We will look first at an application to data fitting and then focus on methods to approximate solutions to linear differential equations and the diffusion equation, in particular.

### A.3 Linear Curve Fitting

Let us take the problem of fitting a 1-D curve through \( m \) points. An exponential basis with \( n \) terms will be used: \( \psi(x) = \{e^{-\alpha_1 x}, e^{-\alpha_2 x}, \ldots, e^{-\alpha_n x}\} \). The boundary conditions, in this case, are just that the curve \( f(x) \) passes through a set of points \( \{(x_1, b_1), (x_2, b_2), \ldots, (x_m, b_m)\} \Rightarrow f(x_i) = b_i; \quad i = 1, \ldots, m \). Therefore,

\[
\Psi = \left( \begin{array}{cccc}
e^{-\alpha_1 x_1} & e^{-\alpha_2 x_1} & \cdots & e^{-\alpha_n x_1} \\
e^{-\alpha_1 x_2} & e^{-\alpha_2 x_2} & \cdots & e^{-\alpha_n x_2} \\
\vdots & \vdots & \ddots & \vdots \\
e^{-\alpha_1 x_m} & e^{-\alpha_2 x_m} & \cdots & e^{-\alpha_n x_m} \\
\end{array} \right)
\]

where the \( \alpha_i \) are known constants.

Now if the \( x_j \) represent the independent variable data along the horizontal axis, then \( \vec{\phi}(x) \) can be computed. See equation (A.9). The \( b_j \) would then represent the dependent variable data along the vertical axis. The data fit thus could be computed: \( f(x) = \vec{b}^T \cdot \vec{\phi}(x) \). As an example (included only for demonstration), one of the relaxation curve data sets collected in the \(^{129}\)Xe relaxation experiments will be fit to a triexponential \( (n = 3) \), where an initial guess, \( \alpha_i = \{1/500, 1/80, 1/5\} \), was made by visual examination of the graph (see the initial guess in Figure A.1). Certainly, the fit can be further optimized by variation of the \( \alpha_i \). Such can be accomplished by utilizing a nonlinear fitting algorithm.

### A.4 Nonlinear Curve Fitting

The Levenberg-Marquardt nonlinear fitting algorithm is robust and efficient and thus has become very popular for use in scientific research. A brief outline of this
algorithm will be presented. Suppose that we have \( m \) data points, \( \{(x_j, y_j); \; j = 1 \ldots m\} \), that we wish to fit with a candidate function \( f(\tilde{\alpha}; x) \) having \( n \) adjustable parameters, \( \tilde{\alpha} = \{\alpha_i; \; i = 1 \ldots n\} \). Let the error \( \tilde{\epsilon}_p \) be defined in the following way:

\[
\tilde{\epsilon}_p \equiv y - \tilde{f}(\tilde{\alpha}_p) \quad \text{where} \quad \tilde{f}(\tilde{\alpha}_p) = \begin{pmatrix} f(\tilde{\alpha}_p; x_1) \\ f(\tilde{\alpha}_p; x_2) \\ \vdots \\ f(\tilde{\alpha}_p; x_m) \end{pmatrix} \quad (A.15)
\]

and the \( p \) subscript indexes the iterations. Then minimizing the square of the error \( (\tilde{\epsilon}_p \cdot \tilde{\epsilon}_p) \) by varying \( \tilde{\alpha}_p \) is the desired least-squares fitting criterion.

Taking the first-order Taylor expansion of \( \tilde{f}(\tilde{\alpha}_p) \) around \( \tilde{\alpha}_{p-1} \) yields:

\[
\tilde{f}(\tilde{\alpha}_p) = \tilde{f}(\tilde{\alpha}_{p-1}) + J_{p-1} (\tilde{\alpha}_p - \tilde{\alpha}_{p-1}) \quad (A.16)
\]
where \( J_{p-1} \) is the Jacobian matrix of \( \tilde{f}(\tilde{\alpha}_{p-1}) \). Substitution of eqn. (A.16) into eqn. (A.15) can be shown to produce:

\[
\tilde{e}_p = \tilde{e}_{p-1} - J_{p-1} (\tilde{\alpha}_p - \tilde{\alpha}_{p-1}). \tag{A.17}
\]

If the error is zero, as desired \((\tilde{e}_p = 0)\), this implies that

\[
J_{p-1} (\tilde{\alpha}_p - \tilde{\alpha}_{p-1}) = \tilde{e}_{p-1} \tag{A.18}
\]

which is a linear equation. And thus a new guess for the parameters \( \tilde{\alpha}_p \) can be found by inverting \( J_{p-1} \rightarrow \tilde{J}_{p-1} \) in the same fashion as \( \Psi \rightarrow \tilde{\Psi} \) was done previously (that is: \( \tilde{J}_{p-1} = (VW^{-1}U^T) \) where \( U, V \) and \( W \) are found by taking the standard SVD of \( J_{p-1} \)):

\[
\tilde{\alpha}_p = \tilde{\alpha}_{p-1} + \tilde{J}_{p-1} \tilde{e}_{p-1} \tag{A.19}
\]

Equation (A.19) is then iterated until small enough variation of the mean-square-error (MSE) is obtained. The method outlined thus far is commonly known as Newton’s method of iteration.

The Levenberg-Marquardt (Lev-Mar) method is an ingenious variation of Newton’s method. A similar iteration routine is employed, however, a parameter \( \lambda \) is inserted before inverting \( J_{p-1} \):

\[
\tilde{J}_{p-1} = V (W + \lambda)^{-1} U^T \tag{A.20}
\]

where the matrix \((W + \lambda)\) is formed by adding \( \lambda \) to the diagonal elements of \( W \). When \( \lambda \) is small, this method is equivalent to Newton’s method. When \( \lambda \) is large, the method approaches the “down-hill” method (following the path of steepest descent). The Lev-Mar method uses \( \lambda \) to smoothly switch between the stability of the “down-hill” method and the speed of the Newton method in the following fashion: If an iteration results in a larger MSE \((\tilde{e}_p \cdot \tilde{e}_p)\), then the step is rejected and \( \lambda \) is multiplied by 10 and the step is tried again. If, on the other hand, the MSE is reduced, then the step is accepted and \( \lambda \) is divided by 10. If \( \lambda \) gets large, there will always be a \( \lambda \) where the “down-hill” method starts reducing the MSE. If
\[ \lambda \text{ gets small, then this indicates that Newton's method is monotonically converging to a minimum.} \]

The data-fitting example started in the last section will now be continued in order to illustrate the nonlinear method just outlined. The \( \alpha_i \) in the exponential basis, for example, can be optimized by Levenberg-Marquardt (Lev-Mar) iteration. This will modify the basis functions \( \psi(x) \) and a new matrix \( \Psi \) must be calculated. The linear FBE method can then be repeated to find the optimal expansion coefficients and the nonlinear optimization repeated to find the optimal basis functions. Alternating between the linear FBE method and the nonlinear Lev-Mar method in this fashion will produce quick convergence to the optimal parameters. The resulting fit after 10 such iterations can be seen Figure A.1, thus compared to the initial guess. Such a method was also outstandingly successful in obtaining the optimal fit to data modeled by Lorenzian curves superimposed on a drifting baseline.

Consequently, equation A.19 can be used to estimate the uncertainties \( (\tilde{\alpha}_p - \tilde{\alpha}_{p-1}) \) in the fitting parameters by setting \( \tilde{\epsilon}_p \) to be the known experimental uncertainties in the data points.

### A.5 FBEM Solution to the Diffusion Equation

The general solution to the isotropic, spherically symmetric diffusion equation with diffusion coefficient \( D \) and the boundary condition of restricted flow velocity \( v_r \) through a spherical surface of radius \( R \) was derived in section 4.2.3:

\[
\begin{align*}
n(r, t) = & \sum_i A_i \frac{\sin(\frac{\alpha_i r}{\sqrt{D}})}{r} e^{-\alpha_i^2 t}, \\
\end{align*}
\]

Also mentioned was the fact that such boundary conditions completely determine the \( \alpha_i \). However, the \( A_i \) must be chosen to enforce the initial conditions; this being that the density is initially uniform, \( n(r, 0) = 1 \), inside the sphere, \( r < R \). The FBE method, as previously developed, is ideally suited for determining the \( A_i \).

The first step is to choose a set of basis functions. The first \( n = 30 \) basis functions were chosen: \( \psi_i(r) = \sin(\alpha_i r / \sqrt{D}) / r \), as shown above. The next step is
to choose a discrete set of initial points. For this purpose, \( m = 35 \) equally spaced points, \( r_j = 0.985 \frac{R(j - 0.99)}{(m - 0.99)} \), were carefully chosen so as to avoid any computational singularities. The final step is to determine the desired boundary values. In this case, the density is unity everywhere so that \( b_j = 1 \) is assigned to all the \( m \) boundary values. Using the same notation that was developed in section A.1, it is now possible to construct the \( \Psi \) matrix, invert it \( (\Psi) \) and find the optimal expansion coefficients \( (\vec{q}^T = \vec{b}^T \Psi) \). Thus the coefficients \( (A_i = q_i) \) are found which enforce the initial conditions. Figure A.2 shows the graph of \( n(r, 0) \) as found by the FBE method.

Notice that the \( A_i \) determined by FBEM cause the initial density to be near unity everywhere inside the sphere, however when \( r > R \) outside the sphere, the initial density will not be zero. It may quickly drop and even be negative. It will

![Initial Polarization Density Sum Over 30 Terms](image)

**Figure A.2.** Typical initial density distribution using FBEM \( (R=7.7e-5 \text{ cm}) \).
take the exact form necessary to insure that the velocity of the “fluid” through the surface (after $t = 0$) will be constant ($v_r$). Recall that such velocity is regulated by the magnitude of the density gradient across the surface of the sphere. Since equation (A.21) satisfies the diffusion equation and all of the boundary conditions and initial conditions, it is therefore guaranteed to be the unique solution. Incidentally, the $A_i$ may also be found by convolution with the orthogonal basis functions. The ultimate fit to the initial conditions through orthogonal expansion, however, is not nearly as good as that obtained by the FBEM. Orthogonal expansion, nevertheless, can be used to show that none of the $A_i$ are necessarily zero except the time-independent term ($\alpha_0 = 0$). With the exception that in the case where $v_r = 0$ (no loss across the surface), the time-independent term is non-zero and the other terms may indeed be zero.

**A.6 Approximate Solutions to Linear Differential Equations**

This section is included as a “general interest” section which illustrates a general method by which the FBEM can be used to solve linear differential equations even when the exact solution basis functions are not known. In the last section it was shown how the FBEM can be used to find the expansion coefficients which satisfy initial conditions to the diffusion equation when the solution basis is known. It may be difficult, however, in some cases to find a solution basis to a given differential equation. This section illustrates how to use any arbitrary basis to find an approximate solution.

Suppose that we have somehow found a complete finite basis ($\vec{\psi} = \{\psi_i\}; \ i = 1, \ldots, n$) that spans some solution space of interest. Over this basis, differential operators can be expressed as matrices. To show this, note that the derivatives of the basis functions are also in the space and may be expanded over $\vec{\psi}$:

$$\frac{\partial}{\partial x} \psi_i = \vec{q}_i \cdot \vec{\psi} \quad \Rightarrow \quad \frac{\partial}{\partial x} \vec{\psi} = \{\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_n\} \cdot \vec{\psi} \equiv D_x \vec{\psi} \quad (A.22)$$

where $x$ is an independent variable and the $\vec{q}_i$ are arrays of scalar expansion coefficients. The matrix $D_x$ in eqn. (A.22) is the matrix representation of the
differential operator. It turns out that any linear differential operator \( L_x \) can also be represented as a matrix:

\[
L_x = \sum_{j=1}^{m} a_j(x) \frac{\partial^j}{\partial x^j} \quad \text{and} \quad u = q^T \cdot \psi
\]

\[
\Rightarrow \quad L_xu = q^T \cdot \left[ \sum_{j=1}^{m} a_j(x) D_x^j \right] \psi = q^T \cdot \Lambda_x \psi
\]

where the \( a_j(x) \) are known functions and \( \Lambda_x \) is the matrix representation of the linear differential operator \( L_x \). These matrix operators are convenient to work with being that all the tools of linear algebra are at our disposal.

If \( L \) is any linear differential operator, \( \Lambda \) its matrix representation and \( f \) a known function, then we may seek a solution \( (u) \) to the following differential equation by expanding \( f \) and \( u \) over \( \psi \) with coefficients \( \tilde{q}_f \) and \( \tilde{q}_u \) respectively:

\[
Lu = f \quad \Rightarrow \quad \tilde{q}_u^T \cdot \Lambda \tilde{\psi} = \tilde{q}_f^T \cdot \tilde{\psi} \quad \Rightarrow \quad \tilde{q}_u^T \Lambda = \tilde{q}_f^T.
\]

It is immediately obvious that the particular solution to \( \tilde{q}_u \) can be found by inverting \( \Lambda \to \Lambda^{-1} \) (if it has an inverse) and thus \( \tilde{q}_u^T = \tilde{q}_f^T \Lambda^{-1} \). This particular solution then must be added to the solution of the homogeneous equation \( (Lu = 0) \) in order to finally achieve a complete solution. The solution of the homogeneous equation is not as obvious and yet it can, in principle, be found using generalized inverses, general solutions [55] or by using other methods to find the coefficients \( (\tilde{q}_u) \) which zero the residual \( (r_s) \):

\[
r_s = Lu = \tilde{q}_u^T \cdot \Lambda \tilde{\psi} = \tilde{q}_u^T \cdot \tilde{\phi}_\lambda \quad \text{where} \quad \tilde{\phi}_\lambda \equiv \Lambda \tilde{\psi}
\]

At this point, we will again relax the restriction that the finite basis is complete. We instead choose a basis that spans a function space “close” to the solution space of the differential equation of interest. Then in this space, we seek the approximate solution that is closest to the exact solution. The FBE method is designed to locate the expansion that in fact does this. It remains, however, to define the condition which determines what is meant by “close” to the solution. For this purpose, we
will define the closest solution as one that minimizes the square of the residual 
\((r^2 = (Lu)^2)\) integrated over the region of interest \((\rho)\):

\[
\frac{\partial}{\partial q_j} \int_\rho (Lu)^2 \, d\rho = 0 \quad \Rightarrow \quad q^T \cdot \int_\rho \phi_x \phi_{\lambda j} \, d\rho = 0 \quad (A.27)
\]

where the residual is minimized by variation of the \(q_j\) coefficient. Since there are as many of these equations as there are basis functions, we will always have enough equations to solve for the unknown \(q_j\).

It is often convenient to work in the Green’s basis \((\vec{\phi} = \vec{\Psi} \vec{\psi})\) that was developed in section A.1. In this basis, \(u = \vec{b}^T \cdot \vec{\phi}\) where \(\vec{b}\) holds the actual initial values or boundary values for the differential equation. Transformation to the Green’s basis is straightforward. Simply make the following replacements in this section: \(\vec{\psi} \rightarrow \vec{\phi}\), \(\Lambda \rightarrow \vec{\Psi} \Lambda \vec{\Psi}\) and \(\vec{q} \rightarrow \vec{b}\) and all arguments still hold.

Of course, convergence of this method depends strongly on the basis functions chosen and the well-conditioning of the matrices. The FBE method converges in the same sense that the Galerkin method converges. That is: when enough linearly independent basis functions are included to span the complete solution space [56] then the FBE method will, in theory, produce the unique solution.

**A.6.1 Example: Solution to a Linear Differential Equation**

As proof of principle, the approximate solution of a well known, simple differential equation will be calculated using the FBE method. Each step will be taken in detail and the solution obtained will be compared against the known solution.

To start, we choose the famous second-order differential equation:

\[
\frac{d^2}{dt^2}u(t) + \frac{\pi^2}{4}u(t) = 0 \quad (A.28)
\]

with the well known solutions \(u(x) = A \sin \left(\frac{\pi x}{2}\right) + B \cos \left(\frac{\pi x}{2}\right)\).

To apply the FBE method, we must first pick a basis: say, a fourth-degree polynomial basis, \(\vec{\psi}(t) = \{1, t, t^2, t^3, t^4\}\). The differential operators, in this basis, can be written out:
\[
D = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 \\
0 & 2 & 0 & 0 & 0 \\
0 & 0 & 3 & 0 & 0 \\
0 & 0 & 4 & 0 & 0
\end{pmatrix} \Rightarrow \Lambda = D^2 + \frac{\pi^2}{4} = \begin{pmatrix}
\frac{\pi^2}{4} & 0 & 0 & 0 & 0 \\
0 & \frac{\pi^2}{4} & 0 & 0 & 0 \\
2 & 0 & \frac{\pi^2}{4} & 0 & 0 \\
0 & 6 & 0 & \frac{\pi^2}{4} & 0 \\
0 & 0 & 12 & 0 & \frac{\pi^2}{4}
\end{pmatrix}.
\] (A.29)

There are five basis functions, so at least five conditions are required. The first two conditions could be the initial or boundary conditions for the ODE. We choose to specify the initial point \( u(0) = b_1 \) and the first derivative \( \dot{u}(0) = b_2 \) at \( t = 0 \). At least three more conditions are needed. We have the five equations from minimizing the integral of the square of the residual (by variation of \( q_1, q_2, q_3, q_4 \) and \( q_5 \)) over the region of interest [see eqn. (A.27)]. For simplicity, we pick the region of interest to be between 0 and 1 (\( t \in [0,1] \)). We now have seven conditions in order to construct \( \Psi \) which are represented by the following FBEM matrices (recall \( \tilde{\phi}(t) = \Lambda \tilde{\psi}(t) \)):

\[
\tilde{b} = \begin{pmatrix}
b_1 \\
b_2 \\
0 \\
0 \\
0 \\
0
\end{pmatrix}, \quad \Psi = \{\tilde{\psi}(0), \dot{\tilde{\psi}}(0), \int_0^1 \tilde{\phi}_1 \dot{\phi}_1 dt, \ldots, \int_0^1 \tilde{\phi}_5 \dot{\phi}_5 dt\} \quad (A.30)
\]

\[
\Rightarrow \tilde{\phi}(t) = \Psi \tilde{\psi}(t) \quad \text{and} \quad u(t) = \tilde{b}^T \cdot \tilde{\phi}(t).
\]

We now compare the approximate solution \( u(t) \), calculated above, against one of the known solutions: \( \sin \left( \frac{\pi}{2} t \right) \). At \( t = 0 \), the \( \sin \) function is zero \( (b_1 = 0) \) and its derivative is \( \frac{\pi}{2} \) \( (b_2 = \frac{\pi}{2}) \). Substituting these values into \( \tilde{b} \) and calculating gives us (see Figure A.3):

\[
u(t) = 0.0 + 1.5707962t + 0.02962057t^2 - 0.7727320t^3 + 0.1720939t^4. \quad (A.31)
\]

If more basis functions are added \( (\tilde{\psi}(t) = \{1, t, t^2, \ldots, t^9\}) \), resulting in a ninth-degree polynomial basis, then the error decreases dramatically (see Figure A.4).
Figure A.3. FBEM quartic polynomial approximation over $[0,1]$ of the ODE for $\sin(\frac{\pi}{2}t)$ (plots superimposed) [left] and plot showing the absolute error over this region [right].

In larger degree polynomials, numerical roundoff errors start to be introduced due to the large powers of $t$. We have also tried this method on several other familiar ODEs (including Bessel’s Equations) with similar results.

As a note: if $m$ (the number of conditions) is larger than $n$ (the number of basis functions) then the FBE method does not strictly enforce any of the conditions, including the initial conditions. It is straightforward to show that the variances from the initial conditions (for example: $\delta b_1 \equiv u(0) - b_1$ and $\delta b_2 \equiv \dot{u}(0) - b_2$) can be calculated in general as:

$$\delta \bar{b}^T = \bar{b}^T (\Psi \Psi - I). \quad (A.32)$$

If it is desirable to strictly enforce the initial or boundary conditions, then
Figure A.4. FBEM ninth-degree polynomial approximation over [0,1] of the ODE for $\sin(\frac{x}{2}t)$ (plots superimposed) [left] and plot showing the absolute error over this region [right].

$\Psi$ can be made square by choosing only a subset of the residual minimization equations; enough so that $m = n$. In fact, it is not even required to use any of the residual minimization equations when constructing $\Psi$. The conditions used in $\Psi$ can be chosen randomly (ex: derivatives or points somewhere along the curve). The corresponding unknown values in $\vec{b}$ can then be found by doing the following: The resulting $\Psi$ (now containing none of the residual minimization) can then be used to construct the Green’s basis ($\vec{\phi} = \nabla \vec{\psi}$) and a new differential operator ($\Lambda_{\phi} = \nabla \Lambda \vec{\psi}$). The residual minimization equations now minimize the residual by variation of the $b_j$ and appear like $\vec{b}^T \cdot \int_{\rho} (\Lambda_{\phi} \vec{\phi}) [\Lambda_{\phi} \vec{\phi}]_j \, d\rho = 0$. A linear system of equations, where all the known values (the initial conditions) remain the same ($b_1 = b_1, b_2 = b_2,$...
and where there are as many new residual minimization equations as the unknown \( b_j \), can be used to find these unknowns. (Pick the minimization equations whose \( j \)'s do not correspond to those of the known values.) And then, of course, when \( \tilde{b} \) is so calculated, the solution is: \( u = \tilde{b}^T \cdot \tilde{\phi} \).

This appendix only serves as an introduction to the method. In principle, this method should work for an immense variety of problems, for PDEs and multi-dimensional systems.
APPENDIX B

PC CONTROLLED SMALL ANIMAL VENTILATOR

B.1 Introduction

An inexpensive, robust small-animal ventilator has been designed and constructed to successfully ventilate animals (with less than 50 cc tidal volume) during MRI scanning. This ventilator is capable of injecting hyperpolarized \(^3\)He and a variable mixture of two other gases during ventilation. It is constructed from off-the-shelf parts except for the simple pneumatically-controlled breathing valve and mixing chamber that is placed in the magnet core with the animal. The fully-programmable breathing cycles are controlled by the parallel port of a PC running Windows 95 and customized software. Beside the three gas injection valves, there are the Exhale valve, two auxiliary valves, and two trigger channels. This ventilator is patterned after a small-animal ventilator built by Dr. L. Hedlund for the same purpose [57]. There are significant differences; it has been re-engineered and simplified for more capacity, flexibility, and expandability.

B.2 Hardware Design Overview

The primary function of the ventilator is to deliver the volume of gas that an animal will normally inhale with the same respiration rate and oxygen concentration; maintaining at all times safe levels of pressure and flow. Filtered and regulated gas sources (4 psi) must be provided. These gases pass through precision pressure regulators, flow control meters, several feet of tubing, a gas reservoir, and then directly into the breathing valve array that is inches from the animal’s mouth. The breathing valve array consists of four pneumatically controlled valves which can open to allow the gases to enter or leave the animal’s lungs. Three of the
valves control the injection of the gases. The fourth valve opens the lungs to the atmosphere (or an exhale reservoir) through a flow gauge. The breathing valve array is less than 2 inches wide and is metal-free and thus can be placed inside the magnet core with the animal. Figure B.1 shows a block diagram of the ventilator hardware.

Computer controlled solenoid valves inside the ventilator housing connect the pneumatic control lines of the breathing valves to either a pressurized air tank or an evacuated tank. The pressurized air or vacuum in the control lines respectively closes or opens and the pneumatic breathing valves that are in the magnet core with the animal.

**Figure B.1.** Ventilator hardware and control structure: showing gas flow lines and control lines.
B.2.1 Gas Supply

The three air delivery lines labeled “Air”, “Oxy”, and “\(\text{N}_2\)” should be filtered, regulated to 4 psi and attached to the ventilator. Inside the ventilator housing each line passes through a precision pressure regulator and a needle flow valve. A pressure gauge and sensitive flow meter measure the pressure and flow of these gas supply lines. All the control knobs and gauges are mounted on the front panel and labeled for easy access. The three regulated gas lines then pass out of the ventilator and go through several feet of tubing into gas reservoirs and then directly into the breathing valves which are in the magnet’s core a few inches from the animal’s mouth.

Initial calibration of gas pressures and flows are necessary before the ventilator can be used. This is accomplished by opening each of the respective breathing valves by placing the valve switch in the “open” position and then adjusting the precision pressure regulators and flow valves until the desired flow reading is achieved. The pressure should always read well below the maximum safe pressure allowed for the animal. Dynamic flows and pressures during breathing cycles should also be estimated and calibrated. The following sections outline the basic principles behind this dynamic flow structure.

B.2.2 Gas reservoirs and \(^{3}\text{He} \) injection

It was found that when the breathing valves were closed, enough static pressure built up behind the valves to create a significant pressure spike when the valves were opened, and yet it was necessary to have enough pressure to drive proper flow through several feet of tubing. Thus gas reservoirs with about 50 times the tidal volume were connected to the injection lines a few feet before they enter the magnet core. This allowed the driving pressure to be reduced while still maintaining smooth flow. Such an arrangement also accommodated the hyperpolarized gas. A Tedlar bag was placed inside one large plastic cylinder connected to the regulated \(\text{N}_2\) driving gas. The bag is then filled with hyperpolarized \(^{3}\text{He} \) and connected to the breathing valve. The pressure on the surrounding \(\text{N}_2\) gas then drives the HP \(^{3}\text{He} \) out of the bag. This decreases the “dead volume” the HP gas traverses to the
breathing valves and provides it with a metal-free conduit to reduce the possibility for relaxation. The Air and O\textsubscript{2} reservoirs, of course, have no bags. See Figure B.2.

An electrical analog was used to estimate good values for the driving pressure $P$ needed to regulate flow at the breathing valves $s$ as well as the capacitance $C$ of the gas reservoirs. The resistance of the long gas line $R$ and short gas line $r$ were experimentally determined by their pressure/flow ratios. The capacitance $L$ of the animal's lung was estimated using available P-V curves. The circuit in Figure B.3 expresses the model used to obtain reasonable values for the pertinent parameters.

**B.2.3 Breathing Valves**

Each breathing valve consists of a thin sheet of vinyl pressed between two acrylic blocks. A cylindrical cavity cut in the upper block is connected to a pneumatic

![Electrical analog of breathing lines, reservoirs and valve-lung interface. The switch represents inspiration and expiration cycling.](image)

**Figure B.2.** Hyperpolarized $^3$He bag inside an $N_2$-filled plastic cylinder.

**Figure B.3.** Electrical analog of breathing lines, reservoirs and valve-lung interface. The switch represents inspiration and expiration cycling.
control line in order to control the position of the vinyl sheet by either exerting pressure or vacuum. An inlet hole and outlet hole are machined into the lower acrylic block, the inlet hole has an o-ring fitted around it. See Figure B.4. When the top cavity is pressurized, the vinyl sheet is pressed against the o-ring around the inlet hole in the bottom block, effectively stopping the flow of gas. When vacuum is applied to the upper cavity, the vinyl sheet is pulled away from the inlet and outlet holes allowing gas to pass freely from the supply line into a mixing cavity which is connected directly to the animal’s lungs. The three regulated gas lines can thus be gated right at the mouth, each line delivering gas (at a regulated volume rate and pressure) when its respective breathing valve is open.

There is a fourth breathing valve called the Exhale valve. The Exhale valve opens the mixing cavity and lungs up to the atmosphere allowing gas to escape. However, before the exhaled gas is passed to the atmosphere it passes back into the ventilator where the exhale flow is measured by a flow meter. The exhaled gases then pass out of the ventilator and may be collected, if desired, or vented to the
atmosphere.

B.2.4 Control Lines, Valves and Triggers

The pneumatic control lines carry pressure or vacuum to the breathing valves in order to respectively close or open them. The pressure and vacuum tanks are inside the ventilator and are connected to each 3-way solenoid valve. When activated, the solenoid valve connects the pressure tank to its respective pneumatic control line, effectively closing the breathing valve. When not activated the vacuum tank is connected, effectively opening the breathing valve. Thus the solenoid valves effectively control the state of the breathing valves. These solenoid valves can be controlled manually by a switch or by a parallel port connection from a computer. See Figure B.5. The ventilator program running on a PC is designed to automatically control the breathing cycles invoking an easy-to-use windows-based interface. The software is designed to control the state of the eight (8) data ports of a standard PC parallel port. When the switches are in the “Comp” position (Computer), these data ports are connected via a cable to the opto-isolators and solenoid valves inside the ventilator. See Figure B.5. When a port is low (0v) the port provides an effective ground for the opto-isolator circuit and the solenoid is activated. When a port is high (+5v) the opto-isolator and solenoid is deactivated. Thus a high signal (+5v) from the computer causes the solenoid to deactivate admitting vacuum to the pneumatic control line thus opening the breathing valve and similarly a low (0v) signal admits pressure closing the breathing valve. Review Figure B.1.

The same electronics is used to set up the triggers, except the solenoid in Figure B.5 is replaced with a BNC connector and the 12V source was replaced with a variable voltage source to accommodate the possibility of different triggering arrangements.

B.2.5 Pressure Transducers

A Honeywell 1 psi differential pressure transducers was used to measure the mouth pressure of the animal during ventilation via a tube connected to the mixing
cavity in the breathing valve. A low-noise amplifier was used to supply adequate output for an oscilloscope. See Figure B.6. This pressure transducer was attached via a 4 ft. tube to the mixing chamber in the breathing valve to measure the mouth pressure of the animal during ventilation.

### B.3 Software Design Overview

Once the software is installed and run on a standard PC with Windows 3.1 or Windows 95 the data pins on the parallel port (pins 2 to 9) are assigned to eight control channels labeled “Air,” “Oxy,” “He,” “Exh,” “Aux1,” “Aux2,” “Trig1” and “Trig2” as shown on the screen. The actual state of these ports is shown on the screen in the control panel on the right by “lights” in the form of squares that are red when the port is high and white when low. See Figure B.7. The state of the valves can be directly changed by double-clicking on these squares. Clicking the “Free Breathe” button will open both the “Air” and “Exh” breathing valves and close all others. This allows air to flow into the breathing valve mixing cavity and then stream directly out the exhale line to the atmosphere. The animal can then spontaneously breathe from this stream of air; flow variations in the exhale line and pressure variations at the mouthpiece (or trachea tube) are used to measure natural respiration rates and tidal volumes. The other functions refer to computer

![Valve control electronics diagram](image)

**Figure B.5.** Valve control electronics.
controlled breathing cycles.

B.3.1 Breathing Cycles

A Breathing Cycle consists of an inhale and exhale phase. During the inhale phase, breathing valves open to inject gases into the lung. The exhale phase starts when the “Exhale” breathing valve is opened to allow the gases to escape from the lung; these two phases may overlap. The mixture of gases injected into the lung is determined by the duration of the breathing valve openings. Gas flow dynamics from any of the three supply gases have been simulated or found experimentally and thus the mixture and volume of the injected gases can be regulated. One example of a Breathing Cycle is one where all the breathing valves are closed except the “Air” valve, allowing air to enter the lungs. The “Air” valve is then closed and a forced breath-hold is sustained for a short while. Then the “Exhale” valve is opened and the animal is allowed to exhale. It takes little imagination to see that a vast variety of breathing cycles are possible. The maximum safe pressure never should be exceeded due to appropriate pressure regulator settings. All the Breathing Cycles used are stored in the Breathing Cycle database and can be brought up modified and reviewed. An index number, 1,2,3,...., a duration, and

![Bridge pressure transducer with 50X amplification](image)

**Figure B.6.** Bridge pressure transducer with 50X amplification.
A descriptive name is assigned to each cycle and then two percentages for each channel ("Air", "Oxy", "He", "Exh", "Aux1", "Aux2", "Trig1", and "Trig2") are stored. The first percentage indicates when, in the cycle duration, the valve will open and the second when it will close. Putting the closing percentage before the opening will invert the channel (it will start open, close, then open again). Thus as specified in the Breathing Cycle database, any one of the eight channels may be turned on and off once during a cycle. For example, if the duration of a Breathing Cycle is 0.5 seconds and the "Air" channel is turned On at 10% and Off at 50%. The "Air" port will turn On 0.05 seconds after the cycle starts and Off after 0.25 seconds. Refer to Figure B.7.

**Figure B.7.** Ventilator control panel screen.
B.3.2 Sequencing Breathing Cycles

Once appropriate Breathing Cycles are set up in the Breathing Cycle database, it is possible to sequence these cycles in any order desired. This is done using the Sequence database. The Sequence database stores the sequence in which the Breathing Cycles will be executed. Breathing Cycles are referenced by their index number. For example, a sequence of “1,1,4,2,1” will execute the cycles referenced in sequential order. This arrangement allows for a very flexible control strategy. There is also a “Time Scale Factor” that may be updated even when a sequence is running to globally speed up or slow down the breathing cycles. For example, a value of 100% for this factor will run the cycle durations as found in the Cycle database. A higher value will increase the cycle durations, running the cycles slower, and a lower value will run them faster. Apart from the Sequence database, there also is an Insert Sequence database which allows a sequence of cycles to be inserted during the execution of the normal sequence. The inserted sequence will be played through once just after the executing cycle completes and then the software will return control to the next cycle in the current Sequence. This feature is convenient during MRI scans. A Sequence can be designed, for example, to hyperventilate, inject a combination of gases, execute a breath-hold, trigger the scanner, then exhale after scanning is complete. This sequence can then be started with the click of the Insert Sequence button.

B.4 Dynamic Calibration

Dynamic calibration of the ventilator under simulated conditions of respiration is required for each new target animal. A simple artificial lung can be constructed by obtaining or manufacturing a glass or clear-plastic U-tube manometer with the short leg about one-half the length of the long leg. The long leg is open to atmosphere and water is poured into the short leg until it is filled a few centimeters from the top. The breathing tube from the ventilator is connected with an air-tight seal to the short leg. As the ventilator injects gas into the short leg, it will displace water and force it into the long leg. When the Exhale valve is opened air will flow the
other way. This approximates the respiratory physics of the lung.

In order to construct the artificial lung (manometer), the tidal volume \( V_t \) and P-V curve of the target animal must be known. The manometer is constructed of cylindrical tubing of diameter \( D \) such that the displacement of one tidal volume of water in the short leg of the manometer requires a relative pressure roughly equal to the lung pressure at full inspiration \( P_t \) from the P-V curve. The inner diameter should be roughly

\[
D = \frac{4}{3} \sqrt[3]{\frac{V_t}{P_t}} \quad (B.1)
\]

where \( D \) is in millimeters, \( V_t \) is in cubic centimeters, and \( P_t \) is in psi. A typical tube diameter for rats is \( D = 3 \) mm. The length of the small leg is generally about 15 cm and the long leg 30 cm. As a rule, the short leg must be long enough to accommodate 1 tidal volume of gas. The height of one tidal volume in the tube, \( h = 4V_t/\pi D^2 \), measured from the top of the column of water in the short leg down to the point of full inspiration, is marked on the short leg. The top of the column of water is also marked. These marks are then used to calibrate the ventilator.

With the ventilator connected to the artificial lung, the programmed breathing cycle is executed. When properly calibrated, the water level in the short leg should fall to near the lower mark at full inspiration and rise back up close to the top mark at full expiration. A small positive pressure offset is normal. The visual feedback of this method provides for quick calibration and adjustment. The mouth pressure waveform as seen on the oscilloscope with the model lung serves as a guideline of what to expect when the animal is ultimately connected to the ventilator.

The “Free Breathe” mode of the ventilator allows the animal to breath spontaneously while connected to the ventilator. In this mode, air is flowed continuously through the breathing valve and into the open exhale line. During spontaneous inspiration, the air diverted from this flow into the lungs will cause both mouth pressure and exhale flow to drop. During expiration, this process will be reversed. By monitoring the mouth pressure and exhale flow, it is possible, by integrating the flow over time, to make a rough estimate of the tidal volume. It is trivial to measure the relaxed respiration rate of the animal.
B.5 Conclusion

A small animal ventilator has been designed and constructed that fills the critical design requirements. This ventilator has been used successfully to ventilate a rat with a tidal volumes under 2 cc and inject desired mixtures of air and He in order to make MRI scans of the lungs. The rat was sedated with sodium pentobarbitol and a trachea tube inserted and attached to the ventilator. Spontaneous breathing sometimes slowed down to the point where mandatory ventilation was required. The free-breathing mode was used to measure the natural tidal volumes and breathing rates. When ventilation began, the rat did not fight the ventilator, allowing the ventilator to assume its respiratory function. Gas drive pressures were started low then turned up till satisfactory tidal volumes were being achieved. Calibration was easily achieved. The ventilator performed very well under all circumstances and has proven to be a useful tool for small animal MRI scans. Plans already have been made to update the software to include biological monitoring and measure tidal volumes using electronic flow meters. The total cost of the ventilator was minimal, the parts totaling to about $1,700 dollars, including the older-model pentium computer purchased.
REFERENCES