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Development and Applications of NMR
in Low Fields and Zero Field

by

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Chapter 1: Introduction

This dissertation is about nuclear magnetic resonance (NMR) spectroscopy in the absence of applied magnetic fields. NMR is usually done in large magnetic fields, often as large as can be practically attained. The motivation for going the opposite way, toward zero field, is that for certain types of materials, particularly powdered or polycrystalline solids, the NMR spectra in zero field are easier to interpret than those obtained in high field.

Zero-field NMR measures two kinds of interactions. One is the dipole-dipole interaction between nuclei that have magnetic dipole moments. Investigations of this interaction can yield information about the geometrical structure of molecules, since the dipole-dipole coupling is very sensitive to distances between the magnetic nuclei. The other interaction of interest is that of nuclei possessing electric quadrupole moments within the local electric field gradients. The electric field gradient has to do with the distribution of electronic and nuclear charges about a given point. Studies of quadrupolar interactions can thus provide information about the chemical bonding and local symmetry around a quadrupolar nucleus.

These interactions are effective regardless of the magnetic field strength. However, in the presence of a field, their analysis is complicated by a troublesome dependence on molecular orientation. This is illustrated in Figure 1.1 for the simple case of two coupled spin-1/2 nuclei. The high-field spectrum consists of two lines separated by a frequency $\Delta\omega$ that depends on both r , the internuclear distance, and θ , the angle between the internuclear vector and the

Figure 1.1 Simulated NMR spectra for a system of two dipolar-coupled spin-1/2 nuclei in high field (at left) and zero field (at right). Spectra are shown for $\theta_{ij} = 0^\circ, 45^\circ, 90^\circ$, and, at bottom, a statistically isotropic distribution of orientations; θ_{ij} is the angle between the internuclear vector and (in high field) the applied field or (in zero field) the initial magnetization. As the internuclear vector is reoriented, the high-field NMR frequencies change; in zero field, the frequencies cannot depend on orientation. Thus, for powdered or orientationally disordered samples, zero-field NMR often yields better-resolved spectra.

applied field vector;

$$\Delta\omega \propto (3\cos^2\theta - 1)/r^3.$$

In polycrystalline or powdered solids, such an orientation dependence in combination with the orientational disorder results in a spreading of spectral lines; one measures the average of all single-crystal spectra over the distribution of orientations. For two-spin systems, the resulting powder pattern is still interpretable¹. For systems involved in more complicated interactions, the powder patterns rarely have distinct features, and analysis of the spectrum is difficult if at all possible².

Figure 1.1 also shows spectra of the same two-spin system in zero field. With no external field, the spin energies are determined only by internal interactions, and cannot depend on molecular orientation. Thus all equivalent molecules yield identical splittings, and the powder spectrum is as well-resolved as a single-crystal spectrum. If the spectrum is measured via the magnetization along a particular axis, that axis is, in a sense, a preferred direction in space, and consequently the line intensities will vary as a function of crystal orientation. However this does not degrade the resolution or interpretability of the powder spectrum.

Figure 1.2 shows experimental spectra of the protons in barium chlorate hydrate, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. In this compound, the protons are closely grouped in pairs (the H_2O molecules) which are spaced relatively far from one another. This closely approximates an ideal, isolated two-spin system, as treated in Figure 1.1, and these experimental results essentially confirm those calculated results.

Figure 1.2 Experimental proton spectra of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. The protons are grouped closely in pairs, and yield spectra in good agreement with the calculated spectra of Figure 1.1.

From the measured zero-field splitting for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, the proton-proton distance within the water molecules is found to be 1.60 Å.

By the above arguments, zero-field NMR would seem useful indeed, but there are practical problems with observing NMR signals in zero field. The signal amplitude in any NMR measurement is proportional to the extent of spin ordering (e.g., magnetization), and usually proportional to the natural frequencies of the spin system. Since both of these factors increase with the field strength (in the high-field limit, both are proportional to the applied field), the application of a large magnetic field can bring about an enormous gain in the sensitivity. For this reason it is usually essential that measurements of nuclear magnetism be performed in high fields.

This dilemma, that zero-field NMR offers better resolution while high-field NMR offers better sensitivity, can be resolved by field cycling techniques^{3,4}. In such schemes, fields are applied when needed to enhance sensitivity, and are removed for some other time to allow for probing the zero-field behavior of the spin system. One approach to zero-field NMR by field cycling is shown schematically in Figure 1.3. This field cycle consists of three intervals. In the first, we prepare some initial spin magnetization; the spins are simply allowed to come to thermal equilibrium with their surroundings in a large static field. There follows a period of nominally zero field where we probe the spectrum with a low-amplitude rf magnetic field. After this, the static field is reapplied so that high-field NMR techniques can be used to detect the final magnetization. (The actual detection is not shown explicitly here.)

Assume that we keep all experimental parameters constant except

Figure 1.3 A simple representation of frequency-domain field cycling. The upper plot shows the applied magnetic field as a function of time; the lower plot shows the response of the spin system to those fields. In the preparation interval, spin magnetization is established consistent with equilibrium in the applied field. The field is removed, and then the zero-field spectrum is probed by irradiating the sample at a "search frequency". After restoring the static field, the remaining spin order can be measured by high-field NMR methods. Repetition of this sequence with different search frequencies allows one to determine the zero-field spectrum.

for the frequency of irradiation in zero field. Then, if the irradiation happens to be on resonance, transitions are induced among the spin states, reducing the spin order that we measure afterwards. When we are far from resonance, the rf field causes no decrease in spin order. To measure a zero-field spectrum, we repeat the field cycle a large number of times, incrementing the irradiation frequency from cycle to cycle, and noting the magnetization at the end of each cycle. A plot of magnetization amplitude vs. frequency then gives the spectrum. This is the essence of frequency-domain field cycling.

This and related experiments are widely used for zero-field nuclear quadrupole resonance ("pure NQR") spectroscopy^{5,6}. By replacing the zero field with a small static field (and retaining the rf field, of course), the technique is also used for low-field NMR studies^{4b,7}.

Field cycling can be used to make time-domain measurements of the zero-field NMR spectrum⁸. That is the approach taken in this dissertation. A prototypical time-domain field cycle is presented in Figure 1.4. This field cycle consists of three distinct intervals: high-field preparation, zero-field probing, and high-field detection, respectively. In this sense, it is similar to the frequency-domain field cycle. In the time-domain scheme, the probing in zero field involves a variable time period defined by sudden field shifts. After the high-field preparation interval, the field is suddenly switched to zero to initiate the evolution interval. In zero field, magnetization is not a stable form of spin order and it evolves coherently at the natural frequencies of the spin system. To begin the detection interval, the field is suddenly switched back on, at which point the

Figure 1.4 A simple representation of time-domain field cycling; the upper plot shows the applied field cycle, and the lower plot shows the concomitant response of the spin system. The applied field in the preparation interval serves to establish a magnetization. When the field is shut off suddenly, the magnetization oscillates and decays; this behavior is determined by the local nuclear interactions. Sudden reapplication of the field terminates the evolution and allows measurement of the result by high-field NMR methods. This sequence is repeated with different zero-field intervals (t_1) to measure the magnetization curve point by point. This scheme is the basis for most of the work in this dissertation.

magnetization is locked, *i.e.*, ceases to evolve, and may be measured by high-field NMR techniques. The final magnetization observed in a single field cycle corresponds to only a single point in the evolution time. To determine how the magnetization varies as a function of time, the field cycle is repeated while incrementing the length of the zero-field interval; the evolution and decay of the magnetization are thus measured point by point. The Fourier transform of that magnetization function yields the zero-field spectrum.

Figure 1.5 displays experimental results, obtained with this technique, for ^7Li nuclei in powdered lithium sulfate hydrate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. At top, the data are shown as they were obtained in the time domain; upon Fourier transformation, we get the spectrum shown at the bottom. The observation of two peaks (other than the one at zero frequency) indicates that there are two inequivalent lithium sites in this material.

The idea of time-domain field cycling was first employed by Strombotne and Hahn, who used it to study low-field NMR⁹. Our method has its differences, but it is a close descendant of their method. Field cycling, sometimes with time-domain measurements, is used to study low-field nuclear spin-lattice relaxation^{4a,b,10}. If we classify these as time-domain studies, we should still make a distinction; the term "time domain" usually implies the use of sudden field transitions to study coherent phenomena, while the relaxation work neither requires sudden field changes nor measures coherent effects.

This dissertation describes the development of some time-domain techniques for zero-field NMR, their application to the measurement of

Figure 1.5 ^7Li time-domain NQR of a polycrystalline sample of lithium sulfate hydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$). The upper plot shows the ^7Li zero-field signal as obtained in the time domain. The dots show the actual data; the curve is for visual clarity. Fourier transformation of the time-domain data yields the spectrum shown at bottom. One line (other than that at zero frequency) is expected for each chemically distinct site, and two such sites are thus indicated here.

dipole-dipole couplings and quadrupolar interactions in zero field, and the interpretation of those measurements in terms of molecular structure and motion. Chapter 2 reviews the basic theory of angular momentum, rotational properties, tensors, and nuclear spin interactions. In Chapter 3, a cursory discussion of high-field NMR is presented. Chapter 4 introduces the theory of time-domain zero-field NMR, placing emphasis on methods for predicting and analyzing experimental data. Chapter 5 describes the experimental principles, techniques, and apparatus. Chapter 6 is a detailed discussion of coupled spin-1/2 pairs; both theory and experimental data are presented there. Experimental results for coupled systems of more than two spins are presented and analyzed in Chapter 7. Chapter 8 presents some theory and experiments of nuclear quadrupole resonance; there is also a discussion of variant field cycling techniques applicable to quadrupolar systems. To conclude the dissertation, Chapter 9 surveys time-domain low-field NMR techniques, with experimental results which illustrate how NMR spectra change continuously from zero field to high field.

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Chapter 2: Angular Momentum, Rotations, and Interactions

In the literature related to NMR, there seems to be no general agreement about units. In particular, angular momentum may appear unitless or in units of $\hbar$; energies are often presented as frequencies, and these may be in either Hz (cycles/second) or s^{-1} (radians/second). In the literature, one also finds different ways to represent rotations and orientations.

Thus it seems best for us to make a number of statements which define units, conventions, notation, and terminology. That is one of the purposes of this chapter. Also this is a good place to display a few pages of pedagogical material. This Chapter outlines the theory of angular momentum, its relationship to rotations and rotational properties, and its connection to the electromagnetic moments and interactions of nuclei.

In this dissertation, by the way, angular momentum always appears in units of $\hbar$, energies remain in energy units, and frequencies are in radians/second unless given explicitly in Hz.

2.1 Angular momentum

The angular momentum operator $\vec{I}$ is a vector operator with components I_x , I_y , and I_z which satisfy the commutation relations

$$[I_x, I_y] = i\hbar I_z, \quad [I_y, I_z] = i\hbar I_x, \quad \text{and} \quad [I_z, I_x] = i\hbar I_y. \quad (2-1)$$

$[A, B] = AB - BA$ is defined as the commutator of the operators A and B;

we say A and B commute if $[A, B] = 0$.

The operator $\hat{I}^2$ is the scalar square of the angular momentum, defined as $\hat{I} \cdot \hat{I} = \hat{I}_x^2 + \hat{I}_y^2 + \hat{I}_z^2$. There is a set of eigenstates $|I, m\rangle$ common to $\hat{I}^2$ and I_z , with the eigenvalue equations

$$\begin{aligned} \hat{I}^2 |I, m\rangle &= I(I+1)\hbar^2 |I, m\rangle \\ \text{with } I &= 0, 1/2, 1, 3/2, \dots, \end{aligned} \quad (2-2)$$

$$\begin{aligned} \text{and } I_z |I, m\rangle &= m\hbar |I, m\rangle \\ \text{with } m &= -I, -I+1, \dots, I-1, I. \end{aligned} \quad (2-3)$$

There are the so-called raising and lowering operators, I_+ and I_- :

$$\begin{aligned} I_+ |I, m\rangle &= \hbar \sqrt{[I(I+1) - m(m+1)]} |I, m+1\rangle \quad \text{and} \\ I_- |I, m\rangle &= \hbar \sqrt{[I(I+1) - m(m-1)]} |I, m-1\rangle. \end{aligned} \quad (2-4)$$

The operators I_x and I_y are related to I_+ and I_- as:

$$\begin{aligned} I_+ &= I_x + iI_y \quad \text{and} \\ I_- &= I_x - iI_y. \end{aligned} \quad (2-5)$$

2.2 Nuclear spin

Every nucleus has a property called spin. The spin is an angular momentum, but one for which the quantum number I is stuck, as it were, at a particular value. We regard I as a fixed, intrinsic property of

a given nuclear species. That type of nucleus is said to have a spin of I . It has a spin state space of dimension $(2I+1)$, and all of its spin states are eigenstates of $\hat{I}^2$ with the same eigenvalue, $I(I+1)\hbar^2$. Thus we can substitute the scalar $I(I+1)\hbar^2$ for the operator $\hat{I}^2$ when it refers to a single spin.

Some nuclear species can, in fact, be produced in excited states with various values of I . Since these excited states are short-lived and not easily made, it is proper in our work to ignore them entirely

2.3 Rotations

The operator R corresponding to the rotation of a physical object by an angle α about the axis $\hat{u}$ (a unit vector, such that $\hat{u} \cdot \hat{u} = 1$) may be represented as:

$$\begin{aligned} R &= \exp[-i\alpha \hat{I} \cdot \hat{u} / \hbar] \\ &= \exp[-i\alpha (I_x u_x + I_y u_y + I_z u_z) / \hbar]. \end{aligned} \quad (2-6)$$

Here $\hat{I}$ is the operator corresponding to the angular momentum of the whole rotated object. Thus for a system of several spins, we would use $\hat{I} = (\hat{I}_1 + \hat{I}_2 + \dots)$. For rotations of our sample, but not the spins, we would use the rotational angular momentum $\hat{J}$ instead of the spin $\hat{I}$.

An initial state $|\psi_i\rangle$ and the rotated state $|\psi_f\rangle$ are related as

$$|\psi_f\rangle = R|\psi_i\rangle. \quad (2-7)$$

An initial operator W_i and the rotated operator W_f are related as

$$W_F = R W_I R^{-1} = R W_I R^\dagger. \quad (2-8)$$

Occasionally we shall consider a rotation that is described by the Euler angles α , β , and γ . This is conventionally defined as a rotation first by α about the original z-axis, then by β about the new (rotated) y-axis, and finally by γ about the final (doubly-rotated) z-axis. This is equivalent to a rotation first by γ about the original z-axis, then by β about the original y-axis, and finally by α about the original z-axis. In operator form, this is

$$R(\alpha, \beta, \gamma) = \exp(-i\alpha I_z/\hbar) \exp(-i\beta I_y/\hbar) \exp(-i\gamma I_z/\hbar). \quad (2-9)$$

The notation $R(\alpha, \beta, \gamma)$ will be reserved for this operation henceforth.

2.4 Tensors

2.4.1 Irreducible tensors defined

The operator T_k , with $k = 0, 1, 2, \dots$, is by definition an irreducible tensor operator of rank k if it is made up of exactly $2k+1$ components $T_{k,q}$, with $q = -k, -k+1, \dots, k-1, k$, that satisfy the following commutation relations with the angular momentum $\vec{I}$:

$$\begin{aligned} [I_z, T_{k,q}] &= \hbar q T_{k,q}, \\ [I_+, T_{k,q}] &= \hbar \sqrt{k(k+1) - q(q+1)} T_{k,q+1}, \\ \text{and } [I_-, T_{k,q}] &= \hbar \sqrt{k(k+1) - q(q-1)} T_{k,q-1}. \end{aligned} \quad (2-10)$$

As mentioned in Section 2.3 in connection with rotation operators, $\vec{I}$ here is the angular momentum of the object represented by T_k .

The spherical harmonics $Y_{\ell,m}$ have a set of commutators $[\vec{J}, Y_{\ell,m}]$ that are essentially the same as the commutators $[\vec{I}, T_{k,q}]$.

$$\begin{aligned} [J_z, Y_{\ell,m}] &= \hbar m Y_{\ell,m} , \\ [J_+, Y_{\ell,m}] &= \hbar \sqrt{\ell(\ell+1) - m(m+1)} Y_{\ell,m+1} , \\ \text{and } [J_-, Y_{\ell,m}] &= \hbar \sqrt{\ell(\ell+1) - m(m-1)} Y_{\ell,m-1} . \end{aligned} \quad (2-11)$$

In applications of Equation (2-11), $\vec{J}$ would be a rotational or orbital angular momentum (i.e., not a spin). The similarity between Equations (2-10) and (2-11) means precisely that there is a one-to-one correspondence between spherical harmonics and irreducible tensor operators, and that the two have the same rotational properties. They transform under rotations in the same way. This is useful for the purpose of visualizing tensors and their symmetries.

A scalar operator is an irreducible tensor operator of rank $k=0$. $\vec{I}^2$ is such an operator. It transforms under rotations just as the spherically symmetric function $Y_{0,0}$. That is, it has no angular dependence. A vector operator is an irreducible tensor operator of rank $k=1$. The operator $\vec{I}$ is an example, with I_z , $(-1/\sqrt{2})I_+$, and $(1/\sqrt{2})I_-$ as its components. These have the same rotational properties as the spherical harmonics $Y_{1,0}$, $Y_{1,1}$, and $Y_{1,-1}$ respectively. Table 2.1 shows the correspondences between angular momentum operators, tensors, and spherical harmonics for ranks 0, 1, and 2.

Table 2.1: Tensor operators and spherical harmonics

$$T_{0,0} : -\sqrt{\frac{1}{3}} \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} \longleftrightarrow Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$T_{1,0} : I_z \longleftrightarrow Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$T_{1,\pm 1} : \mp \sqrt{\frac{1}{2}} I_{\pm} \longleftrightarrow Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta \exp(\pm i\phi)$$

$$T_{2,0} : \sqrt{\frac{1}{6}} [3I_z S_z - \hat{\mathbf{I}} \cdot \hat{\mathbf{S}}] \longleftrightarrow Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$$

$$T_{2,\pm 1} : \mp \frac{1}{2} (I_z S_{\pm} + I_{\pm} S_z) \longleftrightarrow Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \exp(\pm i\phi)$$

$$T_{2,\pm 2} : \frac{1}{2} I_{\pm} S_{\pm} \longleftrightarrow Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \exp(\pm 2i\phi)$$

(Replace $\mathbf{S}$ with $\mathbf{I}$ to obtain single-spin operators which transform as $T_{0,0}$ or $T_{2,q}$.)

(θ and ϕ are standard polar coordinates.)

2.4.2 Rotation of irreducible tensors

An irreducible tensor of rank k , when rotated, is still an irreducible tensor of rank k . This can be surmised from Equations (2-10), and is the essence of the term "irreducible".

A particular component $T_{k,q}$ becomes:

$$R(\alpha, \beta, \gamma) T_{k,q} R^{-1}(\alpha, \beta, \gamma) = \sum_{p=-k}^k D_{p,q}^{(k)}(\alpha, \beta, \gamma) T_{k,p} \quad (2-12)$$

where $D^{(k)}(\alpha, \beta, \gamma)$ is the Wigner rotation matrix of rank k . Formulas and tables of the matrices $D^{(k)}$ may be found in the literature¹.

2.4.3 Scalar product of irreducible tensors

For two tensor operators U_k and V_k of the same rank k , we define the scalar product:

$$U_k \cdot V_k = \sum_{q=-k}^k (-1)^q U_{k,-q} V_{k,q} \quad (2-13)$$

When $k=1$, this is identical to the dot product of two vectors. The Hamiltonian is a scalar operator corresponding to the classical energy, yet we shall often see it expressed as the scalar product of vectors or higher-rank tensors.

2.4.4 Cartesian tensors

Occasionally we shall use Cartesian tensors. These are useful mathematical devices, like irreducible tensors but usually less convenient for our purposes. Methods exist, but are not described here², for converting between these two types of tensors. Cartesian tensors appearing in this work will be pointed out explicitly so that there may be no confusion. Otherwise a term like "k-th rank tensor" will refer to an irreducible tensor operator T_k .

All of the Cartesian tensors we are to use are 3×3 matrices T

with elements $T_{ij} = W(i,j)$ ($i,j = x,y,z$) where W is some operator with parameters i and j . For instance, the electric field gradient can be represented as

$$T : T_{ij} = \frac{\partial^2 V}{\partial i \partial j} = - \frac{\partial E_j}{\partial i} \quad (i,j = x,y,z) \quad (2-14)$$

where V is the electric potential and $\vec{E}$ is the electric field.

For a traceless symmetric Cartesian tensor T with elements T_{ij} ($i,j = x,y,z$), we define the principal axis system (PAS) as a set of orthogonal axes $\{\hat{x}, \hat{y}, \hat{z}\}$ in which the tensor is diagonal ($T_{ij} = 0$ for $i \neq j$), and which are ordered so that $|T_{xx}| \geq |T_{yy}| \geq |T_{zz}|$.

2.5 Electromagnetic moments and interactions

All nuclei with spin I greater than or equal to 0 (that is, all nuclei) possess an electric monopole moment. That means they have an electric charge. This can be represented as a tensor of rank $k=0$. Generally nuclear charge has very little to do with nuclear magnetism or spin, but it is of great importance in chemistry.

Nuclei with spin $I \geq 1/2$ possess as well a magnetic dipole moment. It is reasonable, if not accurate, to consider this as arising from a rotating nuclear charge. The dipole moment $\vec{\mu}$ is a first-rank tensor proportional to the angular momentum $\vec{I}$:

$$\begin{aligned} \vec{\mu} &= \gamma \vec{I}, \\ \mu_x &= \gamma I_x, \text{ etc.}, \end{aligned} \quad (2-15)$$

where γ is the gyromagnetic ratio of the nucleus. Electrons also have magnetic dipole moments (and spin $I=1/2$).

Nuclei with spin $I=1$ or greater have an electric quadrupole moment. This can be thought of as a non-spherically-symmetrical nuclear charge distribution, oriented with the nuclear spin. The quadrupole moment operator Q_2 is a second-rank tensor with components $Q_{2,q}$ proportional to the single-spin tensors $T_{2,q}$ referred to in Table 2.1.

As a matter of principle, we claim that nuclei with spin $I>1$ have higher-order multipole moments. Convincing theoretical treatments leave no doubt that spin-3/2 nuclei possess magnetic octupole moments, that spin-2 nuclei have electric hexadecapole moments, and so forth. Yet in NMR experiments these moments appear unimportant; they have proven quite elusive even in experiments designed for their observation³.

2.5.1 Zeeman interaction

In a magnetic field, a magnetic dipole moment prefers some orientations over others. This is the essence of the Zeeman interaction. The classical expression for the energy of a dipole moment in a magnetic field is:

$$\begin{aligned} E &= -\vec{\mu} \cdot \vec{B} \\ &= -[\mu_x B_x + \mu_y B_y + \mu_z B_z] . \end{aligned} \tag{2-16}$$

The corresponding Hamiltonian operator is similar:

$$\begin{aligned}\mathcal{H}_Z &= -\vec{\mu} \cdot \vec{B} = -\gamma \vec{I} \cdot \vec{B} \\ &= -\gamma [I_x B_x + I_y B_y + I_z B_z] .\end{aligned}\tag{2-17}$$

The symbol $\mathcal{H}_Z$ denotes the Zeeman Hamiltonian. We define the Larmor frequency as $\omega_0 = \gamma B_0$, with B_0 defined as the static field. Usually we shall orient our laboratory reference frame so that the static magnetic field is along the z axis. Then the Hamiltonian is proportional to I_z and its eigenstates are the states of definite I and m given in Equations (2-2) and (2-3). Then the energies are $E_m = -\gamma \hbar B_0 m = -\hbar \omega_0 m$, with ω_0 usually in the range of 0 to $2\pi \times 1 \text{ GHz}$.

2.5.2 Chemical shift

The Zeeman interaction is usually influenced slightly by the motion of electronic charges near the nucleus. That is, the external field induces local electric currents within atoms and molecules, and these currents produce small magnetic fields, resulting in a slight change in the strength of the Zeeman interaction (typically one part in 10^3 to 10^6). This effect is called the chemical shift.

The chemical shift is commonly represented as a second-rank Cartesian tensor σ , with the spin $\vec{I}$ and the field $\vec{B}$ taken as vectors in this context:

$$\mathcal{H}_{CS} = -\gamma \vec{I} \cdot (\sigma \vec{B}).\tag{2-18}$$

In this view, the external field $\vec{B}$ induces an internal field $\sigma\vec{B}$ with which the spin $\vec{I}$ interacts. Note that the effect is proportional to the applied field strength B . The matrix σ can be decomposed into three irreducible parts: T_0 , T_1 , and T_2 . The first-rank component has practically no effect (no effect to first order in σ), so σ is usually treated as a combination of scalar (isotropic) and second-rank (anisotropic) chemical shifts. In solid materials, both parts are effective. In liquids and gases, rapid tumbling motions of the molecules bring about an "averaging" of the anisotropic chemical shift (to zero) so that only the isotropic chemical shift is measurable.

2.5.3 Dipole-dipole interactions

A magnetic dipole moment itself produces a small magnetic field. Neighboring dipole moments can interact through these local fields. This is called the magnetic dipole-dipole interaction, or the dipolar interaction. The classical energy for the interaction between two dipoles is:

$$E_{d12} = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r_{12}^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r}_{12})(\vec{\mu}_2 \cdot \vec{r}_{12})}{r_{12}^5}, \quad (2-19)$$

where $\vec{r}_{12}$ is the internuclear vector (i.e., displacement from $\vec{\mu}_1$ to $\vec{\mu}_2$). If we define the Z axis as parallel to $\vec{r}_{12}$, then

$$E_{d12} = \frac{1}{r_{12}^3} \left[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3\mu_{1Z}\mu_{2Z} \right]. \quad (2-20)$$

The corresponding Hamiltonian operator is

$$\mathcal{H}_{d12} = \frac{\gamma_1 \gamma_2}{r_{12}^3} \left(\vec{I}_1 \cdot \vec{I}_2 - 3 I_{1z} I_{2z} \right) . \quad (2-21)$$

This can be recognized as proportional to $T_{2,0}$. Thus Equation (2-12) may be used to calculate the dipolar Hamiltonian when the internuclear vector $\vec{r}_{12}$ is rotated from the z axis (distinct from the Z axis) by $R(\alpha_{12}, \beta_{12}, \gamma_{12})$:

$$\begin{aligned} \mathcal{H}_{d12} = & - \frac{\gamma_1 \gamma_2}{2r_{12}^3} \left[\left(3 I_{1z} I_{2z} - \vec{I}_1 \cdot \vec{I}_2 \right) \left(3 \cos^2 \beta_{12} - 1 \right) \right. \\ & + 3 \left(I_{1+} I_{2z} + I_{1z} I_{2+} \right) \left(\sin \beta_{12} \cos \beta_{12} \exp(-i\alpha_{12}) \right) \\ & + 3 \left(I_{1-} I_{2z} + I_{1z} I_{2-} \right) \left(\sin \beta_{12} \cos \beta_{12} \exp(+i\alpha_{12}) \right) \\ & + \frac{3}{2} \left(I_{1+} I_{2+} \right) \left(\sin^2 \beta_{12} \exp(-2i\alpha_{12}) \right) \\ & \left. + \frac{3}{2} \left(I_{1-} I_{2-} \right) \left(\sin^2 \beta_{12} \exp(+2i\alpha_{12}) \right) \right] . \quad (2-22) \end{aligned}$$

The eigenvalues of $\mathcal{H}_{d12}$ are usually in the range of 0 to $2\pi\hbar \times 50$ kHz.

Dipole-dipole interactions are usually effective between many pairs of nuclei simultaneously. Thus we often see the N-spin dipolar Hamiltonian as a summation over all pairs of spins:

$$\mathcal{H}_d = \sum_{i=1}^N \sum_{j=i+1}^N \mathcal{H}_{dij} . \quad (2-23)$$

Dipolar interactions are usually observed only in solids (and liquid crystals). Rapid isotropic molecular motions, as tend to occur in liquids and gases, average the dipolar coupling to zero. This may be seen by integrating Equation (2-22) with $\vec{r}_{12}/r_{12}$ ranging over the entire unit sphere.

2.5.4 J couplings

Nuclear dipole moments may interact with each other through intermediary dipole moments such as electron spins. This occurs even in diamagnetic substances, where the electron spins are "paired up"; the nuclear moments perturb the electronic wavefunctions so that the electron moments may not precisely cancel in the vicinity of each nucleus. This kind of indirect internuclear dipole-dipole interaction is called the J coupling.

The J coupling has a second-rank part that is essentially like the dipolar coupling and is effective in solids; it also has a scalar part that is effective in liquids and gases as well as in solids. We shall consider only the scalar J coupling. For two spins $\vec{I}$ and $\vec{S}$, this is given by

$$\mathcal{H}_J = (J/\hbar) \vec{I} \cdot \vec{S} . \quad (2-24)$$

The frequency parameter J is typically in the range of 0 to $2\pi \times 1$ kHz

for interactions between light nuclei.

2.5.5 Electric quadrupole interactions

A nucleus with an electric quadrupole moment can interact with nearby charged particles such as the electrons and other nuclei around it. The net effect of the neighboring charges may be summed up as an electric field gradient at the site of the nucleus. If we represent the electric field gradient and quadrupole moment as irreducible second-rank tensors, V_2 and Q_2 respectively, the interaction is then given by the scalar product of the two:

$$\mathcal{H}_q \propto V_2 \cdot Q_2 \quad (2-25)$$

Traditionally V_2 is represented as a traceless symmetric Cartesian tensor; in this way, V_2 can be specified unambiguously by a principal axis system and the parameters

$$eq = V_{ZZ} \quad \text{and} \quad \eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \quad (2-26)$$

η is a measure of the deviation of the electric field gradient from cylindrical symmetry, and is called the asymmetry parameter. Note that $0 \leq \eta \leq 1$, given our definition of the principal axis system. We take eq as a simple measure of the size of V_2 , and customarily a quantity eQ is defined as the size of Q_2 .

In the principal axis system and in terms of spin operators, the

Hamiltonian for one spin is

$$\mathcal{H}_q = \frac{A_q}{\hbar^2} \left[3I_Z^2 - I(I+1)\hbar^2 + \eta \left(I_X^2 - I_Y^2 \right) \right], \quad (2-27)$$

$$\text{with } A_q = \frac{e^2 q Q}{4I(2I-1)}$$

We identify this as

$$\mathcal{H}_q = \frac{A_q}{\hbar^2} \left[\sqrt{6} T_{2,0} + \eta \left(T_{2,2} + T_{2,-2} \right) \right]. \quad (2-28)$$

If we should need $\mathcal{H}_q$ in another frame, Equation (2-12) can be used to transform each $T_{2,q}$ in it. The rotated Hamiltonian is then:

$$\begin{aligned} \mathcal{H}_q = \frac{A_q}{\hbar^2} \sum_{p=-2}^2 T_{2,p} \left[\sqrt{6} D_{p,0}^{(2)}(\alpha, \beta, \gamma) \right. \\ \left. + \eta \left(D_{p,2}^{(2)}(\alpha, \beta, \gamma) + D_{p,-2}^{(2)}(\alpha, \beta, \gamma) \right) \right], \end{aligned} \quad (2-29)$$

where the principal axis system is rotated by $R(\alpha, \beta, \gamma)$ from our laboratory reference frame.

The eigenvalues of $\mathcal{H}_q$ can be very wide-ranging, corresponding to frequencies from zero to several GHz, but we shall deal only with those relatively weak quadrupolar interactions that fall within the range of 0 to 1 MHz.

As with the dipolar interaction, *etc.*, the quadrupole interaction is usually not observed in liquids or gases.

2.5.6 Total Hamiltonian

In general, all of the spin interactions act simultaneously.

Thus we may write the total N-spin Hamiltonian as

$$\mathcal{H} = \sum_{k=1}^N \left[\mathcal{H}_{zk} + \mathcal{H}_{csk} + \mathcal{H}_{qk} + \sum_{\ell=k+1}^N \left(\mathcal{H}_{dk\ell} + \mathcal{H}_{jk\ell} \right) \right] ; \quad (2-30)$$

that is, the one-spin interactions ($\mathcal{H}_{z,cs,q}$) are summed over all nuclei and the two-spin interactions ($\mathcal{H}_{d,j}$) over all pairs of nuclei.

Occasionally we shall compare two Hamiltonians, for example, to say that they are of comparable size or that one is larger than the other. This "size" is the norm of the Hamiltonian,

$$\text{norm } \mathcal{H} = \|\mathcal{H}\| = \sqrt{\text{Tr}[\mathcal{H}^2]} = \left[\sum_i E_i^2 \right]^{1/2}, \quad (2-31)$$

where $\text{Tr}[\mathcal{H}^2]$ denotes the trace of the square of the Hamiltonian, E_i is each energy eigenvalue, and the summation goes over all i .

2.5.7 Static and time-varying interactions

Each of the interactions so far described can occur in a time-independent (static) form. Usually the eigenvalues and eigenstates of the total static Hamiltonian determine the frequencies and intensities observed in NMR spectroscopy. Each interaction can also vary in time. For example, natural molecular motions (notably rotations, vibrations,

and diffusion) make the chemical shift, dipolar coupling, J coupling, and quadrupolar interactions time-dependent. Spin relaxation can be thought of as a result of these time-varying local interactions. Another related effect is the averaging to zero of all the "second-rank" interactions in isotropic fluid phases.

In NMR, one of our best experimental tools is a time-varying Zeeman interaction. When that interaction is oscillatory, it is called the radiofrequency (rf) Hamiltonian, and is typically used to induce transitions between the various eigenstates of the static Hamiltonian. In practical terms, this implies the application of an oscillating magnetic field. In this dissertation, we also consider applied magnetic fields which are modulated to form pulses, sudden steps, or gradual field shifts.

References

1. We use the matrices given in H. W. Spiess, *NMR Basic Principles and Progress*, Vol. 15 (Springer-Verlag, Berlin/Heidelberg/New York, 1978), pp. 65-66, 202-204 (noting the sign error in $D_{0,-1}^{(1)}$ on p. 203). The reader may also find useful: M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957), pp. 48-54; U. Haeberlen, *Adv. Magn. Reson. Suppl.* 1 (1976), pp. 10-12.
2. M. Mehring, *Principles of High Resolution NMR in Solids*, 2nd ed. (Springer-Verlag, Berlin/Heidelberg/New York, 1983), pp. 8-14, 288-295; H. W. Spiess, *op. cit.*, pp. 74-75, 200-202, 204-205.
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Chapter 3: Solid-State NMR in High Magnetic Fields

Most NMR spectrometers operate with static fields in the range of 20 to 120 kG, where the Larmor frequency is typically in the range of 10 to 500 MHz. Typically (*i.e.*, excluding large quadrupolar interactions) the local interactions are much smaller than the Zeeman interaction. In theoretical analyses then, the local interactions can be treated as small perturbations on the Zeeman interaction. In this Chapter, we briefly go over the perturbation approach and its consequences in solid-state NMR spectroscopy. Following that, a superficial review of high-field solid-state NMR techniques is given.

3.1 Perturbation approach

There are four things that determine the spectrum of a system freely evolving under a static Hamiltonian: the initial condition of the system, the detected observable, and the eigenvalues and eigenstates of the Hamiltonian. In a typical NMR experiment, the initial condition and the detected operator correspond to transverse magnetization. The observed signal can then be calculated if the energies and eigenstates of the Hamiltonian are known.

Assume for now that we have a homonuclear spin system in a static field $\vec{B}_0$ along $\hat{z}$. If there are no local interactions, the eigenstates are the states $|m, k\rangle$ with energies $-\gamma\hbar B_0 m$ (k is an index to distinguish the degenerate states of a multispin system). We take these as the uncorrected (zero-order) states and energies.

When there is a local interaction acting as a perturbation, the

first-order correction to the eigenstates slightly mixes states with different values of m , but the mixing is on the order of the relative size of the perturbation. We dismiss that mixing as insignificant for now, although in low-field NMR it becomes important. For the present, we shall assume that the perturbation mixes only degenerate zero-order states. The resulting states thus have definite values of m , and this implies that only transitions with $\Delta m = \pm 1$ (and frequencies around the Larmor frequency) are observed.

For the first-order correction to the energies, and for determining what happens to degenerate eigenstates, we need only be concerned with the secular part of the perturbing Hamiltonian, which is the part that commutes with the Zeeman Hamiltonian. For homonuclear spin systems, the part that commutes with I_z is secular. If the Hamiltonian is represented in terms of spin tensors T_k , Equations (2-10) show that only the $T_{k,0}$ term commutes with I_z . We take this as the secular part (for homonuclear systems only!) and, when we have to, solve it for the first-order energies and eigenstates. The secular part of a Hamiltonian is often called the truncated Hamiltonian and given a symbol like $\mathcal{H}^0$.

As an example of first-order energy corrections, we consider a single spin with a quadrupolar interaction. Selecting out the $T_{2,0}$ component of Equation (2-29), we have:

$$\begin{aligned} \mathcal{H}_q^0 &= \frac{A}{\hbar^2} T_{2,0} \left[\sqrt{6} D_{0,0}^{(2)}(-\gamma, -\beta, -\alpha) + \eta \left(D_{0,2}^{(2)}(-\gamma, -\beta, -\alpha) + D_{0,-2}^{(2)}(-\gamma, -\beta, -\alpha) \right) \right] \\ &= \frac{A}{2\hbar^2} \left[3I_z^2 - I(I+1) \right] \left[(3\cos^2\beta - 1) + \eta \sin^2\beta \cos 2\alpha \right] . \end{aligned} \quad (3-2)$$

In Equation (3-2) and in what follows, we have used the inverse rotation $R(-\gamma, -\beta, -\alpha)$ to go from the lab frame to the principal axis system (PAS), in order to keep with the convention^{1,2} that $R(\alpha, \beta, \gamma)$ rotates the PAS into the lab frame.

The first-order corrections to the energy are

$$\begin{aligned}
 E_m^{(1)} &= \langle m | \mathcal{H}_q^0 | m \rangle \\
 &= \frac{A_q}{2} [3m^2 - I(I+1)] [(3\cos^2\beta - 1) + \eta \sin^2\beta \cos 2\alpha] .
 \end{aligned}
 \tag{3-3}$$

Thus the $\Delta m = \pm 1$ transitions appear as a group of $2I$ equally spaced lines, with a full width (in frequency units) of

$$\Delta\omega = \frac{3e^2qQ}{4\hbar I} [(3\cos^2\beta - 1) + \eta \sin^2\beta \cos 2\alpha] ,
 \tag{3-4}$$

and centered about the Larmor frequency.

In perturbation treatments of $\mathcal{H}_q$, it is often necessary to go to second order to explain the observed transition frequencies³. We do not go into that here, except to mention that the second-order energy corrections $E_m^{(2)}$ are far more complicated than the $E_m^{(1)}$ in terms of m , α , and β .

3.2 Orientation dependence and powder patterns

When the sample consists of a single crystal, spin systems at

crystallographically identical sites have local Hamiltonians with identical eigenvalues, eigenstates, and rotational properties. In a uniform high field, the truncated Hamiltonians are also identical, producing the same shifts and splittings throughout the crystal. Upon reorientation of the crystal, individual lines in the spectrum will move about in a well-defined way. The local interactions can be accurately measured by studying these "rotational patterns"^{3a,4,5}.

When the sample is powdered or polycrystalline, each grain has a spectrum of discrete lines, but one observes the sum of them all. With a large number ($\rightarrow \infty$) of grains, the sum approaches the average of all single-crystal spectra over a distribution of orientations. In such a powder average, each individual transition is spread widely across the spectrum. With this spreading comes a decrease in the peak height and thus a loss of sensitivity. Also, in the powder-averaged spectrum, generally all transitions overlap and the spectrum is much more difficult to interpret.

Powder spectra can be interpreted to the extent that they can be accurately modeled and calculated. Thus it is unfortunate that powder-averaged high-field spectra are usually difficult to calculate. In the simple case of a $3\cos^2\beta - 1$ angular dependence, e.g., for Equation (3-4) with $\eta = 0$, there is a known analytic solution⁴; for $\eta \neq 0$, the solution has been obtained in terms of complete elliptic integrals⁶. It is often the case that the transition frequencies are influenced by several local interactions, each with its own distinct orientation dependence and size. For example, there may be several dipolar couplings, or a combination of chemical shift and dipolar interactions affecting a set of nuclei. In such cases, the

calculation of powder patterns can probably be done only by numerical methods⁷.

3.3 High-field NMR techniques applicable to solids

In certain well-behaved cases, powder patterns can be artificially deconvoluted to yield sharp-line spectra with a method known as de-Pake-ing⁸. In this scheme, one assumes that the spectrum is just a superposition of several Pake patterns. In the deconvolution, each Pake-pattern component is reduced to a sharp line, so the overlapping of spectral components is much less of a problem. This has proven useful in studies of deuterium NMR^{8a,9}, where usually $\eta=0$ and broadening and shift interactions are relatively slight. In well-conditioned cases, it can be applied to other nuclear species¹⁰.

Most often, NMR spectra obtained by simple experimental methods are simply too complex or too poorly resolved to interpret. Thus NMR spectroscopists have invented a great assortment of clever experimental techniques to simplify the spectra. The usual method is to make some interaction (or set of interactions) time dependent in a way that nearly averages its effect to zero^{2,11-19}.

In studies of abundant spins, e.g., protons in organic compounds, it is often desirable to eliminate the homonuclear dipole-dipole couplings so that the chemical shift can be more accurately measured. A number of multiple-pulse techniques have been developed for this purpose¹². When observing rare spins, e.g., ¹³C in organic compounds, chemical shift spectra are best obtained when the heteronuclear dipole-dipole couplings are removed. The simplest approach to this is

to apply a strong, continuous irradiation near the resonance of the abundant spins¹³. The rf field can also be modulated or pulsed to decouple heteronuclear spins^{13c,14}. In one class of experiments on heteronuclear systems, the abundant spins are decoupled from one another while preserving couplings between rare spins and their abundant spin neighbors to some extent¹⁵. The dipole-dipole spectrum of the rare spin species is simplified somewhat, and geometrical information can thus be more readily extracted.

The effects of anisotropy of an interaction can be eliminated by rapid rotation or reorientation of the sample. With magic angle spinning, for example, spectroscopists routinely measure isotropic chemical shift spectra in solids; the spinning reduces the chemical shift anisotropy powder pattern to a set of sharp lines resembling the spectrum of a liquid¹⁶. Magic angle hopping produces a similar result by discrete reorientations in a two-dimensional experiment¹⁷.

When magic angle spinning involves sample rotation at frequencies on the order of the spectral width, the spectrum is broken up into sidebands. Where only one anisotropic interaction is present, the sideband intensities give a direct measure of the anisotropy. More fun can be had where two anisotropic interactions are present; in certain cases, for example, the spinning sidebands can be analyzed to yield the relative orientation (*i.e.*, correlation) of the chemical shift anisotropy tensor and dipole-dipole tensor¹⁸. Synchronous sampling, *i.e.*, time-domain sampling at multiples of the sample rotation period, which is tantamount to summation of all the spectral sidebands, can be used for isotropic chemical shift measurements¹⁹.

For half-integer quadrupolar spins, nature simplifies the spectra

somewhat by providing the relatively narrow central transition, $m = -1/2 \leftrightarrow +1/2$, which in high field is shifted only to second order by the quadrupolar interaction³. When this quadrupolar shift is sufficiently small, the spectrum can yield chemical shift information. On the other hand, when the second-order shift is large, the shape of the powder pattern offers some information about the quadrupolar interaction, and information can be extracted by observing how the pattern changes with respect to rf field strength and pulse length²⁰.

For spin-1 nuclei, the $\Delta m = \pm 2$ transition is shifted only to second order by the quadrupolar interaction. In a sense, this situation is like that of the central transition for half-integer spins, except that here we have a normally forbidden transition. For deuterium, this transition can be accessed by double-quantum NMR²¹, and the resulting spectra are interpretable in terms of the chemical shift. For ^{14}N , the $\Delta m = \pm 2$ transition is directly observable by overtone NMR spectroscopy²²; this is not feasible unless the quadrupolar interactions are large, so the resulting spectra are affected by both the quadrupolar shift and chemical shift.

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Chapter 4: General Aspects of Zero-Field NMR Theory

4.1 Density operator formalism

The state $|\psi\rangle$ of a physical system is in principle describable as a linear combination of states $|\phi_i\rangle$ comprising a complete orthogonal normalized basis set. That is,

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle, \quad (4-1)$$

with c_i complex and $\sum_i c_i^* c_i = 1$.

Generally we do not know the coefficients c_i . What we know is what we can measure, and that is limited to the expectation values of observable operators. Let us calculate the expectation value $\langle W \rangle$ of an observable operator W :

$$\begin{aligned} \langle W \rangle &= \langle \psi | W | \psi \rangle \\ &= \left[\sum_j \langle \phi_j | c_j^* \right] W \left[\sum_i c_i |\phi_i\rangle \right] \\ &= \sum_i \sum_j c_j^* c_i \langle \phi_j | W | \phi_i \rangle = \sum_i \sum_j c_j^* c_i w_{ji}. \end{aligned} \quad (4-2)$$

According to this, all measurable properties of the state $|\psi\rangle$ are specified by the set of products $c_j^* c_i$. This set constitutes a matrix,

$$\rho : \rho_{ij} = c_j^* c_i, \quad (4-3)$$

which we call the density matrix. The ρ_{ij} are matrix elements of the so-called density operator:

$$\begin{aligned}\rho &= |\psi\rangle\langle\psi| \\ &= \sum_i \sum_j c_i |\phi_i\rangle\langle\phi_j| c_j^*.\end{aligned}\tag{4-4}$$

For an ensemble of identical systems in various states $|\psi^{(k)}\rangle$, we have a related group of sums:

$$\begin{aligned}\langle W \rangle &= \sum_k \langle \psi^{(k)} | W | \psi^{(k)} \rangle \\ &= \sum_i \sum_j \sum_k c_j^{*(k)} c_i^{(k)} w_{ji},\end{aligned}\tag{4-5}$$

and averages:

$$\overline{\langle W \rangle} = \sum_i \sum_j \overline{c_j^* c_i} w_{ji},\tag{4-6}$$

$$\left. \begin{aligned}\bar{\rho} : \bar{\rho}_{ij} &= \overline{c_j^* c_i}, \\ \text{and } \bar{\rho} &= \sum_i \sum_j \overline{c_j^* c_i} |\phi_i\rangle\langle\phi_j|,\end{aligned}\right\}\tag{4-7}$$

where the overbar indicates an ensemble average (i.e., over k). In the experiments discussed in this work, we are limited to making averaged measurements on large ensembles of systems. Therefore it is

appropriate to use the averaged density operator $\bar{\rho}$, since its matrix elements $\overline{c_j^* c_i}$ determine the observed properties of the ensemble. From this point on, any reference to the density operator implies ensemble averaging; also the average density operator, $\bar{\rho}$, will appear simply as ρ , so that I do not have to type all those overbars.

The density operator has a number of useful properties which are outlined below:

The expectation value $\langle W \rangle$ of an observable operator W is

$$\langle W \rangle = \text{Tr}[\rho W] = \text{Tr}[W \rho] . \quad (4-8)$$

$\text{Tr}[X]$ denotes the trace of the matrix X . In operator notation,

$$\text{Tr}[X] = \sum_i \langle \phi_i | X | \phi_i \rangle . \quad (4-9)$$

The evolution of the density operator proceeds according to the Liouville equation,

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}] , \quad (4-10)$$

where $\mathcal{H}$ is the Hamiltonian acting on the system. If $\mathcal{H}$ is time-independent, this can be integrated to obtain

$$\rho(t) = \exp(-i\mathcal{H}t/\hbar) \rho(0) \exp(i\mathcal{H}t/\hbar) . \quad (4-11)$$

Hence also in the basis set of eigenstates $|i\rangle$ of the Hamiltonian $\mathcal{H}$,

the diagonal elements ρ_{ii} are stationary, while in general the element ρ_{ij} evolves as

$$\begin{aligned}\rho_{ij}(t) &= \rho_{ij}(0) \exp[i(E_j - E_i)t/\hbar] \\ &= \rho_{ij}(0) \exp(i\omega_{ij}t),\end{aligned}\quad (4-12)$$

where $\omega_{ij} = (E_j - E_i)/\hbar$. The elements ρ_{ii} are called populations, and each ρ_{ii} can be taken as the probability of finding the system in the state $|i\rangle$. The ρ_{ij} for $i \neq j$ are called coherences. The density matrix representing a system at thermal equilibrium at a temperature T is given by

$$\rho_{eq} = \frac{\exp(-\hat{H}/kT)}{\text{Tr}[\exp(-\hat{H}/kT)]} = \frac{\exp(-\hat{H}/kT)}{Z}, \quad (4-13)$$

where Z is the partition function and k is the Boltzmann constant.

When the transition energies are all much less than the available thermal energy, that is, when every $|E_j - E_i| \ll kT$, Equation (4-13) can be rewritten as

$$\rho_{eq} \approx \frac{1 - \hat{H}/kT}{\text{Tr}[1]}, \quad (4-14)$$

where 1 is the unit operator. This is called the high-temperature approximation. It is usually accurate in NMR for temperatures above about 1 K. The trace of 1 (as in the denominator) is simply the number of linearly independent states of the system, for example, $(2I+1)^N$ for a system of N spins I . The unit operator in the numerator

does not correspond to anything interesting; it is unaffected by rotations and evolution, and is not observable in any conventional way, so we shall henceforth use a reduced form of Equation (4-14):

$$\rho_{eq} \approx \frac{-\mathcal{H}/kT}{\text{Tr}[\mathbf{1}]} , \quad (4-15)$$

and when the proportionality constant is unimportant, we may shorten this even to $\rho_{eq} \approx \mathcal{H}$.

4.2 Signal calculation for sudden field shift to zero

At equilibrium in zero field, we expect there to be no magnetization in any direction:

$$\begin{aligned} \langle I_u \rangle_{eq} &= \text{Tr} [\rho_{eq} I_u] \\ &\propto \text{Tr} [\mathcal{H}_l I_u] = 0 , \end{aligned} \quad (4-16)$$

where $\mathcal{H}_l$ is $\mathcal{H}_d$, $\mathcal{H}_j$, or $\mathcal{H}_q$, or any combination of them, and $\mathbf{u}$ is any unit vector. The local interactions are zero-rank and second-rank tensors, and as such can not alone generate any first-rank order such as magnetization. However there is nothing to keep us from producing a nonequilibrium state that has a magnetization. (We would need a first-rank tensor interaction to do this.) Such states tend to evolve or relax toward the equilibrium state, so zero-field magnetizations are always transient.

The usual way to produce a magnetization is to apply a magnetic field. If, after doing that, we suddenly remove the field, then for a time we will have a magnetization in zero field. In this section, we use the density operator formalism to see what we should expect after the sudden removal of the applied field.

Figure 4.1 shows a simple field step. The field is:

$$\begin{aligned} \vec{B} &= \hat{z}B_0 & \text{for } t < 0, \\ \text{and } \vec{B} &= 0 & \text{for } t \geq 0. \end{aligned} \quad (4-17)$$

Our hypothetical sample consists of a large number of identical and independent spin systems. The total Hamiltonian for each system is $\mathcal{H}_z + \mathcal{H}_l$, the sum of Zeeman and local interactions. Assuming the sample has come to equilibrium before $t=0$, and using the high-temperature approximation, the initial density operator is:

$$\rho(0) = \frac{e^{-(\mathcal{H}_z + \mathcal{H}_l)/kT}}{\text{Tr}[\mathbf{1}]} . \quad (4-18)$$

At this point, we make two assumptions to simplify the remaining calculation:

- we have a homonuclear system, so $\mathcal{H}_z \propto I_z$, and
- $\mathcal{H}_z \gg \mathcal{H}_l$, so that $\rho(0) \propto I_z$.

(In Section 4.5, we shall consider the heteronuclear case and the case where the initial Zeeman interaction is not dominant.) Thus the density operator for $t \geq 0$ is, according to Equation (4-11),

Figure 4.1 Field step (at top) and its effect on the nuclear spin magnetization (at bottom). For signal calculations, we assume the spins are at equilibrium in high field before $t=0$; thus there is a net alignment of spins along the applied field. The field is removed sufficiently suddenly so that during the transition the spins are unable to appreciably realign. Only the local fields remain. The spins respond by precessing coherently about these local fields.

$$\rho(t) \propto \exp(-i\tilde{H}_\ell t/\hbar) I_z \exp(i\tilde{H}_\ell t/\hbar) . \quad (4-19)$$

Now we want an expression for the magnetization, or magnetic moment, μ_z , which is proportional to I_z :

$$\langle \mu_z \rangle(t) = \gamma \langle I_z \rangle(t) = \gamma \text{Tr} [\rho(t) I_z] \quad (4-20)$$

$$\langle \mu_z \rangle(t) \propto \text{Tr} [\exp(-i\tilde{H}_\ell t/\hbar) I_z \exp(i\tilde{H}_\ell t/\hbar) I_z] .$$

The exponential operators are most easily dealt with in the basis set of eigenstates of the Hamiltonian $\tilde{H}_\ell$, where $\tilde{H}_\ell$ and $\exp(\pm i\tilde{H}_\ell t/\hbar)$ are diagonal. Then it is straightforward to multiply the matrices to get the argument of the trace, here presented as a matrix element between eigenstates of $\tilde{H}_\ell$:

$$\begin{aligned} & \langle i | \exp(-i\tilde{H}_\ell t/\hbar) I_z \exp(i\tilde{H}_\ell t/\hbar) I_z | k \rangle \\ &= \sum_j \exp(-iE_i t/\hbar) \langle i | I_z | j \rangle \exp(iE_j t/\hbar) \langle j | I_z | k \rangle . \end{aligned} \quad (4-21)$$

Then the signal (i.e., trace) we are after is:

$$\begin{aligned} \langle \mu_z \rangle(t) &\propto \sum_i \sum_j \exp[i(E_j - E_i)t/\hbar] |\langle i | I_z | j \rangle|^2 \\ &\quad \exp(i\omega_{ij}t) |\langle i | I_z | j \rangle|^2 . \end{aligned} \quad (4-22)$$

For every term with $\exp(i\omega_{ij}t)$, there is one just like it with the complex conjugate, $\exp(i\omega_{ji}t)$. The imaginary parts of these cancel,

and the real parts are equal, so we obtain:

$$\langle \mu_z \rangle(t) \propto \sum_i \sum_j \cos(\omega_{ij}t) |\langle i | I_z | j \rangle|^2. \quad (4-23)$$

The signal is real and all frequency components are in phase at $t=0$.

When one desires a signal normalized at $t=0$, Equation (4-23) can be used to obtain

$$\begin{aligned} S(t) &= \frac{\sum_i \sum_j \cos(\omega_{ij}t) |\langle i | I_z | j \rangle|^2}{\sum_i \sum_j |\langle i | I_z | j \rangle|^2} \\ &= \sum_i \sum_j \cos(\omega_{ij}t) |\langle i | I_z | j \rangle|^2 / \text{Tr}[I_z^2]. \end{aligned} \quad (4-24)$$

This form conveniently removes all of the proportionality constants, and we shall make some use of it in later calculations. In applications of Equation (4-24), it may be useful to note that $\text{Tr}[I_z^2] = \frac{1}{3} \text{Tr}[\vec{I} \cdot \vec{I}]$.

4.3 Orientation dependence and powder averaging

In zero field, we might say that space is isotropic; there is no special or unique direction as far as the sample is concerned. As far as the theoretician is concerned, however, direction makes a big difference, particularly in the way operators and spin states are expressed as matrices. The theoretician has to express these things in terms of a basis set of spin states, and the basis set is defined

in terms of a reference frame with some particular orientation. If he or she chooses a different reference frame, the basis set and the matrix expressing each operator or spin state will change.

So far in this chapter, we have been able to avoid this sort of trouble. The various operators and eigenstates have been implicitly dependent on orientation, but we had not considered that orientation as variable. In this section we now consider what happens when the Hamiltonian or I_z is reoriented. In particular we calculate the signal from a powder, where I_z is fixed and there is a distribution (among powder grains) of orientations of the Hamiltonian.

These calculations are to be done with reference to a molecular reference frame consisting of axes labeled $\hat{x}$, $\hat{y}$, and $\hat{z}$. These axes are selected so that the expression of the total dipolar and quadrupolar Hamiltonian in terms of I_x , I_y , and I_z is independent of molecular orientation. The importance of this is that the eigenstates are thus fixed; that is, in the molecular frame, the only orientation dependence is in the operator I_z .

It should be noted that the above definition of molecular frame is ambiguous, and moreover the frame thus defined is not unique. Yet it is just sufficient for the general work that follows. When dealing with a particular Hamiltonian with a known symmetry (as in Chapter 6), then it would be appropriate to choose molecular frame axes coinciding with some of the symmetry axes.

Let θ and ϕ be the polar angles, representing declination and azimuth, respectively, of $\hat{z}$ in the molecular frame. Thus

$$I_z = \cos\theta I_z + \sin\theta \cos\phi I_x + \sin\theta \sin\phi I_y. \quad (4-25)$$

Substituting Equation (4-25) into Equation (4-24), and defining

$U(t) = \exp(-i\mathcal{H}_0 t/\hbar)$ for brevity, one obtains

$$\begin{aligned}
 S(\theta, \phi, t) = & 3 \cdot \text{Tr} \left\{ \cos^2 \theta \quad U(t) \quad I_Z \quad U^\dagger(t) \quad I_Z \right. \\
 & + \sin^2 \theta \cos^2 \phi \quad U(t) \quad I_X \quad U^\dagger(t) \quad I_X \\
 & + \sin^2 \theta \sin^2 \phi \quad U(t) \quad I_Y \quad U^\dagger(t) \quad I_Y \\
 & + \cos \theta \sin \theta \cos \phi \left[U(t) \quad I_Z \quad U^\dagger(t) \quad I_X + U(t) \quad I_X \quad U^\dagger(t) \quad I_Z \right] \\
 & + \cos \theta \sin \theta \sin \phi \left[U(t) \quad I_Z \quad U^\dagger(t) \quad I_Y + U(t) \quad I_Y \quad U^\dagger(t) \quad I_Z \right] \\
 & \left. + \sin^2 \theta \cos \phi \sin \phi \left[U(t) \quad I_X \quad U^\dagger(t) \quad I_Y + U(t) \quad I_Y \quad U^\dagger(t) \quad I_X \right] \right\} / \text{Tr}[\tilde{\mathbf{I}} \cdot \tilde{\mathbf{I}}].
 \end{aligned} \tag{4-26}$$

The powder average is obtained by integrating Equation (4-26)

with $\tilde{\mathbf{r}}$ ranging over the unit sphere:

$$S(t)_{\text{powder}} = \frac{1}{4\pi} \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi \, S(\theta, \phi, t). \tag{4-27}$$

The terms with odd powers of $\cos \phi$ or $\sin \phi$ integrate to zero. Thus after integrating and reexpressing the traces, we are left with

$$\begin{aligned}
 S(t)_{\text{powder}} = & \sum_i \sum_j \cos(\omega_{ij} t) \left[| \langle i | I_X | j \rangle |^2 \right. \\
 & \left. + | \langle i | I_Y | j \rangle |^2 + | \langle i | I_Z | j \rangle |^2 \right] / \text{Tr}[\tilde{\mathbf{I}} \cdot \tilde{\mathbf{I}}]. \tag{4-28}
 \end{aligned}$$

Equation (4-28) provides a practical prescription for the calculation of zero-field powder spectra for experiments based on

preparation and detection of a Zeeman polarization I_z . The zero-field Hamiltonian is calculated and diagonalized. The energies and transition frequencies are thus obtained. Then the angular momentum operators I_x , I_y , and I_z are expressed in the basis set of zero-field eigenstates. The relative intensity of each transition is obtained by summation of the absolute squares of corresponding matrix elements of I_x , I_y , and I_z . Equation (4-28) has proven useful for analytic calculations of zero field spectra of small spin systems, and it is also the essence of the computer program DBZINT, which we have used for numerical simulations of zero-field powder spectra of systems of coupled spin-1/2 nuclei. The program DBZINT is given at the end of Chapter 7.

4.4 General one-dimensional free-evolution experiment

The derivation of Equation (4-23) can be generalized to cover any initial condition $\rho(0)$, and any detected observable W . The general result is:

$$\langle W \rangle(t) = \sum_i \sum_j \exp(i\omega_{ij}t) \langle i | \rho(0) | j \rangle \langle j | W | i \rangle. \quad (4-29)$$

If we interchange i and j in any single term, we get the complex conjugate of the original term. Therefore the sum $\langle W \rangle$ is always real, although in general it can have terms in both $\sin(\omega_{ij}t)$ and $\cos(\omega_{ij}t)$; that is, in this case, different frequency components can have different phases at $t=0$.

This result turns out to be useful for a wide variety of time-

domain experiments, namely those involving a single variable interval of free evolution. During the evolution interval, any static Hamiltonian is allowed, although we shall usually consider $\mathcal{H} = \mathcal{H}_d, \mathcal{H}_j$, or $\mathcal{H}_q$. Two applications are outlined here:

(1) When the spin system includes two distinguishable types of spins, I and S, the initial condition might be $\rho(0) = \rho_{eq} \propto \gamma_I I_z + \gamma_S S_z$. The experimenter can easily arrange things to get the more general $\rho(0) = a I_z + b S_z$. The detected operator might be $W = I_z$, or $W = S_z$, or $W = \mu_z = \gamma_I I_z + \gamma_S S_z$. We shall investigate this more fully in Chapter 6.

(2) When the Zeeman interaction for $t < 0$ is not really dominant, one would take $\rho(0) \propto \mathcal{H}_z(t < 0) + \mathcal{H}_d$. The detected operator, however, would still be $W = \mu_z$. Using Equation (4-29), one obtains for the homonuclear case

$$\begin{aligned} \langle \mu_z \rangle(t) &\propto \text{Tr} \left[\exp(-i\mathcal{H}_d t/\hbar) (\mathcal{H}_z + \mathcal{H}_d) \exp(i\mathcal{H}_d t/\hbar) I_z \right] \\ &= \text{Tr} \left[\exp(-i\mathcal{H}_d t/\hbar) \mathcal{H}_z \exp(i\mathcal{H}_d t/\hbar) I_z \right] \\ &\quad + \text{Tr} \left[\exp(-i\mathcal{H}_d t/\hbar) \mathcal{H}_d \exp(i\mathcal{H}_d t/\hbar) I_z \right] . \end{aligned} \quad (4-30)$$

The second term is zero, so we are left with the same signal we calculated in Section 4.2. Note however that the assumptions that $\rho(0) \propto \mathcal{H}(t < 0)$ and $W = \mu_z$ are not necessarily true in field-cycling experiments.

4.5 Adiabatic and sudden field changes

Zero-field NMR experiments are usually done with field-cycling techniques, which are to be described in the next Chapter. Field cycling of course involves a change, i.e., time dependence, of the magnetic field. Theoretical considerations of time-dependent spin interactions are often excruciatingly difficult, but there are special or limiting cases where the theory produces a simple result. Two such cases, known by the terms adiabatic and sudden, are particularly relevant to field cycling. We usually design our experiments so that every field change can be accurately modeled as either adiabatic or sudden, and, in so doing, we simplify the theory and spectral interpretation.

4.5.1 Rotating eigenvector model

Assume that the Hamiltonian undergoes a change between times t_0 and t_1 (with $t_0 < t_1$), and that the change is continuous. Assume also that each eigenstate changes continuously. This continuity of individual eigenstates defines a one-to-one correspondence between the initial and final eigenstates:

$$\begin{array}{lll} \mathcal{H}(t_0) & \longrightarrow & \mathcal{H}(t_1) \\ \text{and } |i(t_0)\rangle & \longrightarrow & |i(t_1)\rangle \text{ for each eigenstate } |i\rangle. \end{array} \quad (4-31)$$

The various eigenstates can be thought of as orthonormal vectors in a Hilbert space. As $\mathcal{H}(t)$ changes, the vectors undergo a

corresponding change which is describable as a rotation, within the Hilbert space, of the complete set of eigenvectors such that they remain orthogonal at each instant in time. Figure 4.2 shows this evolution in a simplified view. For any pair of states, say $|i\rangle$ and $|j\rangle$, we define

$$\alpha_{ij} = \langle j(t) | \frac{d}{dt} | i(t) \rangle. \quad (4-32)$$

This is the rotational velocity of $|i(t)\rangle$ towards $|j(t)\rangle$.

4.5.2 Adiabatic

The basic requirement for adiabaticity is that the eigenvectors rotate slowly in comparison to the natural frequencies of the system. More specifically,

$$|\alpha_{ij}|^2 \ll \omega_{ij}^2 \quad (4-33)$$

throughout the interval $t_0 \leq t \leq t_1$ and for every transition $i \rightarrow j$. Thus sufficiently slow magnetic field shifts are usually adiabatic.

In terms of the density operator, adiabatic transformations leave the populations unchanged:

$$\langle i(t_1) | \rho(t_1) | i(t_1) \rangle = \langle i(t_0) | \rho(t_0) | i(t_0) \rangle \text{ for each } i. \quad (4-34)$$

Also adiabatic transformations do not convert populations into

Figure 4.2 Schematic view of the eigenvectors of the instantaneous Hamiltonian $H(t)$. α_{ij} is the rotational velocity of $|i(t)\rangle$ toward $|j(t)\rangle$. When $\alpha_{ij} \ll \omega_{ij}$, the change of Hamiltonian is adiabatic, i.e., does not induce transitions between $|i(t)\rangle$ and $|j(t)\rangle$. The state of the system thus follows the eigenstates of the Hamiltonian. When $\alpha_{ij} \gg \omega_{ij}$, the change is sudden in the quantum mechanical sense; i.e., as the eigenstates of the Hamiltonian change, the state of the system does not, and indeed can not, change similarly.

coherences, so that if $[\rho(t_0), \mathcal{H}(t_0)] = 0$, then $[\rho(t_1), \mathcal{H}(t_1)] = 0$.

Note that there is a problem if an energy level crossing occurs. Then $\omega_{ij} = 0$, and any motion of the eigenvectors $|i(t)\rangle$ and $|j(t)\rangle$ will be nonadiabatic. Adiabaticity is dependent also on other conditions: a general smoothness and nonresonance of the external field change, and continuity and differentiability of the eigenstates within the interval $t_0 \leq t \leq t_1$.

4.5.3 Sudden

In the limit of suddenness, i.e., as $t_1 - t_0 \rightarrow 0$, a change of the Hamiltonian leaves the state of the system unchanged:

$$\rho(t_1) = \rho(t_0) . \quad (4-35)$$

During a sudden change, the spin interactions cannot alter the spin states fast enough to keep up with the changing eigenstates. This degree of rapidity is assured if

$$|(t_1 - t_0)\omega_{ij(\max)}| \ll 1 , \quad (4-36)$$

where $\omega_{ij(\max)}$ is the largest natural frequency occurring during the transition interval.

For zero-field NMR, the above condition is needlessly strict, and we may restate the criterion for rapidity as follows:

$$|(t_1 - t_0)\omega_{ij(\max, \text{zero field})}| \ll 1 , \quad (4-37)$$

where $\omega_{ij}(\text{max, zero field})$ is the largest natural frequency of the spin system in zero field. This condition assures that the local interactions do not cause significant evolution during the field shift; evolution may still occur, but it only amounts to a rotation around the field axis (or, for heteronuclear systems, a different rotation of each spin species) according to the Zeeman interaction.

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Chapter 5: Practical Techniques and Apparatus

5.1 The basic technique

5.1.1 Field switching requirements

While the idealized field cycles shown in Figures 1.4 and 4.1 feature instantaneous field transitions, practical schemes require finite times to bring about changes in the applied field. There is no problem with that as long as the rapidity of the field switching meets two natural constraints. First, the field switching time τ_s should be short in comparison to the spin-lattice relaxation time T_1 ,

$$\tau_s \ll T_1, \quad (5-1)$$

in order that the magnetization produced in high field not be lost during the field cycle. A second constraint governs the switching time when the instantaneous applied field is comparable in magnitude to the local fields (that is, when the Zeeman energy is comparable to the dipolar or quadrupolar energy). Then the switching time should be short relative to the natural periods (i.e., $1/\omega$) of the zero-field evolution:

$$\tau_s \ll 1/\omega_{\max} \quad (5-2)$$

where $\omega_{\max}$ is the largest zero-field frequency of the spin system. Field transitions less rapid than this may bring about a partial disordering of the spins (or a transformation of spin order such as

adiabatic demagnetization) resulting in some loss and probable distortion of the observed zero-field signal. We refer to Equation (5-2) as a condition of suddenness although, as mentioned in Section 4.5.3, it is not strictly equivalent to quantum-mechanical suddenness. Since T_1 is always longer than $1/\omega_{\max}$, Equation (5-1) is satisfied whenever Equation (5-2) holds.

Field cycling experiments where the entire field transition is sudden, in keeping with Equation (5-2), are not feasible in practice. For most spin systems of interest, the zero-field evolution periods are on the order of microseconds. To obtain adequate sensitivity, the fields used for preparing and detecting the magnetization are necessarily large and uniform ($\geq 10^4$ G and relative homogeneity $\leq 10^{-5}$ over ~ 1 cm³), and as such can not be easily switched on or off in a matter of microseconds. (This is discussed further in Section 5.1.3.) However it is generally unnecessary to carry out the entire field transition with such rapidity since Equation (5-2) is important only when the applied field is within a limited range. It is therefore reasonable and more practical to execute each field cycle in two steps, as illustrated in Figure 5.1. In this scheme, the field is changed relatively slowly between the high field level and an intermediate field level, subject only to the first constraint of the spin-lattice relaxation time. Sudden field switching in keeping with the second constraint of suddenness is attempted only between the intermediate field level and zero, where it is more feasible. As long as the intermediate field is somewhat larger than the local fields, the more practical field cycle of Figure 5.1 and the simple one of Figure 1.4 should have identical effects on the nuclear spins.

Figure 5.1 Schematic representation of a practical time-domain field cycle. Here we have modified the simpler field cycle of Figure 1.4 by adding adiabatic field shifts to and from an intermediate field. With this, much higher preparation and detection fields ($\geq 10^4$ G) become feasible.

5.1.2 Intermediate field level

In the two-step cycle of Figure 5.1, the size of the intermediate field is important because it determines the type of spin order which is to be prepared before and detected after the zero-field interval. When the Zeeman interaction in the intermediate field is much larger than the local interactions, the field cycle serves to prepare and then detect spin states which are approximately eigenstates of the Zeeman Hamiltonian. Such states are generally nonstationary in zero field, and their evolution gives information about the zero-field Hamiltonian. When the intermediate field is small compared to the local fields, the spin states which are prepared and subsequently detected are more like the zero-field eigenstates. As a result, some fraction of the detected signal is nonevolving. This not only results in a loss of useful signal, but also an increase in the background signal. Moreover the signal loss is not generally uniform across the spectrum. Relative line intensities are affected, and so it becomes more difficult to analyze the results. It is desirable to avoid such problems by making the intermediate field at least a few times as large as the local fields.

By equating the Larmor frequency to the highest natural frequency of the spin system in zero field, and solving for the field, we obtain a useful definition of the marginal intermediate field, where the Zeeman and local interactions are of the same magnitude:

$$B_{\text{mar}} = \omega_{\text{max}} / \gamma \quad (5-3)$$

where B_{mar} is the marginal intermediate field, ω_{max} is the largest zero-field frequency, and γ is the gyromagnetic ratio of the nuclear species of interest. The marginal field, thus defined, is the highest field at which we can find an energy level crossing (or avoided crossing) involving states that, in high field, have different values of the quantum number m . Where heteronuclear dipolar couplings are significant, the lowest of the values of γ should be used.

Typical values of the marginal field range from about 10 gauss, corresponding to some dipolar-coupled systems, to a few thousand gauss or more for nuclei with moderately large quadrupolar interactions and small γ . In the apparatus to be described, the intermediate field is nominally 100 G, which is generally appropriate for dipolar-coupled spin systems. The apparatus can be adapted to other intermediate field levels, although beyond 1000 G alternative methods may prove more feasible.

5.1.3 Rapid field switching

Sudden field switching appears to be most conveniently done by means of switchable electromagnets. The practical limitations on electromagnet switching often result from limitations of the power which can be transferred between the electrical power supply and the magnet. For an ideal electromagnet, the electrical power transferred while switching is simply the rate of change of magnetic energy with respect to time. For an approximate calculation, assume the intermediate field B is uniform over the sample volume V and zero

elsewhere, and that the field transitions are exponential with time constant τ_s . Then the peak electrical power P_{peak} is

$$P_{\text{peak}} = B^2 V / 2\mu\tau_s \quad (5-4)$$

in rationalized MKS units and where μ is the magnetic permeability of the sample. When no ferromagnetic materials are present, $\mu \sim \mu_0$, the permeability of free space, and we shall assume this henceforth. Using Equations (5-2) to (5-4), an equation for the marginal power requirement is obtained in terms of the characteristics of the sample and spin system:

$$P_{\text{peak}} = \omega_{\text{max}}^3 V / 2\mu_0 \gamma^2 \quad (5-5)$$

For a typical quadrupolar-coupled deuterium spin system with $\omega_{\text{max}} = 2\pi \times 200$ kHz and $\gamma = 2\pi \times 654$ Hz/G, and a sample volume of 1 cm^3 , this power amounts to about 470 W. The marginal field in this case is 310 G. The actual power required is generally greater than that given in Equation (5-5) since the switched field is not precisely uniform and localized about the sample as assumed above. Additionally one may opt to use intermediate fields and switching times better than marginal, in which case the power requirements are much higher.

5.1.4 A practical technique

When the natural constraints imposed by the nuclear spins are considered along with the practicalities of magnets and of

electronics, several reasonable methods of instrumentation can be devised. The method described in this section is one of the easier ways to adapt an ordinary pulsed NMR spectrometer to do zero-field NMR, but there are interesting and useful alternative methods, some of which are mentioned in Section 5.4.

In our apparatus, the high-field portions of the experiment take place in a 43 kG persistent superconducting solenoid which has a room-temperature bore. In the following discussion, the superconducting solenoid is called the "main coil". There is a simple pneumatic shuttle system which can transport the sample in ~ 0.15 s between the center of the main coil and a point outside, where the fringe field due to the main coil is about 100 G. In that intermediate field region, the zero-field interval could be provided by simply applying a current pulse to an electromagnetic shielding coil. That coil would have to be rapidly switchable and also capable of precisely canceling the fringe field in the region of the sample. For practical reasons, it is difficult to combine both functions in a single apparatus. Rather we use a set of two switchable electromagnet coils (in addition to the main coil) in the arrangement shown schematically in Figure 5.2. In this scheme the characteristics of high speed and high precision are separated into two functionally independent magnet systems optimized for either characteristic separately. This considerably eases the design of the coils and of the associated switching electronics.

The coil labeled B_1 and its power source can be only slowly switched (in a few milliseconds) but are made to very accurately cancel the fringe field of the main coil B_0 . In the 100-G fringe

Figure 5.2 Shown schematically at left, the arrangement of magnet coils and the sample shuttle system. B_0 represents a superconducting solenoid which is left on continuously. B_1 and B_2 are switchable room-temperature magnet coils. B_1 is designed to accurately cancel the external fields. B_2 applies an extra field during the switching transients of B_1 , and provides the sudden field shifts needed for the zero-field experiment. The timing diagram at right shows the sequence of sample shuttling and field switching which is used to form the field cycle. The labels (1) to (6) refer to the more detailed description in the text.

field, the coil B_1 (the "shielding coil") can consistently null the field to less than 100 mG. The coil B_2 (the "auxiliary coil") and its power source are not as accurate or well regulated, but instead are made to switch very rapidly. B_2 is used to apply an extra field during the switching transients of the coil B_1 , and it provides the sudden field transitions needed for time-domain studies. In our apparatus, the field produced by B_2 is 100 ± 10 G. Its switching transitions are nearly exponential with a time constant of 300 ns.

The sequence used for going from high field to zero field and back is illustrated in Figure 5.2 and described below:

- (1) The sample is moved from the main coil to the fringe field. During this period, both low-field coils are shut off.
- (2) Both coils are turned on. B_2 turns on quickly, maintaining a field at least as large as 100 G at the sample while B_1 is settling into its steady-state current.
- (3) After the current in B_1 settles, B_2 is turned off. Then the sample is in zero field.
- (4) The zero-field interval ends when B_2 is switched back on. B_1 is turned off at the same time.
- (5) After B_1 settles down, B_2 is turned off, and only the fringe field remains.
- (6) The sample is then moved back into the main coil for the detection of the final magnetization.

Note that this field cycle includes two extra field transients [at steps (2) and (5)] which are not necessary from a theoretical perspective but which arise because of the different switching speeds of B_1 and B_2 . When the intermediate field is much larger than the

local fields, the extra field transients will have almost no effect, since the spin eigenstates do not change appreciably then. When this is not the case, it is expected that the extra field transients will cause some loss of signal. This could be remedied by shaping the auxiliary coil current pulses so that their rise and fall at steps (2) and (5) matches the rise and fall of the shielding coil current pulses.

The high-field detection can be done by any method which results in a signal proportional to the nuclear magnetization. Figure 5.3(a) depicts the simplest detection sequence, which consists of the application of a strong 90° rf pulse to the sample, followed by the measurement of the initial amplitude of the free induction decay. In solids it is often preferable to record the signal amplitude after a spin-echo sequence¹, as shown in Figure 5.3(b). This can eliminate the problems associated with the pulse recovery time of the probe and receiver. The spin-echo sequence may often be extended to generate a train of spin echoes², as Figure 5.3(c) depicts. This can be used to improve the overall signal-to-noise ratio, since it allows rapid sampling of the magnetization as many as thousands of times for every field cycle.

In zero-field experiments, we usually observe slow drifts of the signal baseline, occurring over minutes or hours, which introduce errors in the measurements. This is due to slow variations in the spectrometer characteristics, which are possibly correlated to changes in the line voltage and ambient temperature. To compensate for this, we use a technique termed phase cycling. In its simplest form, this means replacing each field cycle with a pair of field cycles which

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Figure 5.3 Simple rf pulse sequences (rf magnetic field vs time) for detecting the nuclear magnetization at the end of each field cycle. The Gaussian curves represent the resulting free induction decays (fids) and spin echoes; optimally the signal would be recorded at the peaks of these curves. In (a), a single pulse produces an fid. The spin echo sequence, shown in (b), offers the technical advantage that the signal appears well after the applied pulses and can therefore be measured more accurately. The optimal pulse angle θ depends on the rf field strength and the details of the local spin interactions, but is usually between 45° and 90° . If a series of spin echoes is formed, as shown in (c), signal averaging over the entire echo train may yield a large increase in sensitivity.

differ only in the phase of the initial 90° rf pulse, with a phase difference of 180° . This inverts the signal that would ideally be obtained, however the baseline is not inverted. Therefore, when the two resulting data sets are subtracted, the baseline (plus its drift) is canceled. One could perhaps do better by taking periodic reference measurements along with the zero-field data, and then calculating baseline, amplitude, and phase corrections afterwards.

5.2 The instrument

5.2.1 Basic NMR spectrometer

The design and construction of our zero-field apparatus is based on a preexisting homebuilt NMR spectrometer described in detail elsewhere³. Since any existing solid-state NMR spectrometer can be similarly adapted, we merely list the essential characteristics:

The magnet (the main coil) is a persistent superconducting solenoid contained in a Dewar vessel which has a room-temperature bore of 89 mm inner diameter. The field at the center is approximately 43 kG, corresponding to a proton Larmor frequency of 185 MHz, and is homogeneous to the extent of about 1 ppm over the sample volume used (approximately 6-mm-diameter, 8-mm-long cylinders) without room-temperature shims.

The transmitter section is capable of producing spectrally pure rf pulses with rise and fall times of about 50 ns and with an amplitude precision better than 1 dB. Four phases, set 90° apart ($\pm 1^\circ$), are available. The available pulse (peak) power is at least 1000 W at the Larmor frequencies of ^2D , ^{13}C , and ^{27}Al , and at least

600 W for protons. With our NMR probes, this is sufficient to obtain 90° pulse times of a few microseconds for each of these nuclei.

The receiver section has an overall noise figure of 3 dB or better at the frequencies of interest. After the application of strong rf pulses, the receiver appears to fully recover in about 20 to 25 μ s. This interval includes the ringdown time of the resonant probe circuit and the saturation recovery time of the receiver electronics. A phase-sensitive superheterodyne detector is used to mix down the NMR signal, yielding two audio-frequency channels which correspond to two orthogonal phases of the rf signal. The signal is then converted by two 10-bit analog-to-digital converters and stored in a digital memory system. The data can be converted and stored at any rate up to 1 point (two 10-bit numbers) per 3 μ s.

The rf pulsing, data acquisition, magnet pulsing, and sample shuttling are all controlled by a homebuilt, high-speed multichannel programmable digital pulse generator⁴ (pulse programmer) which is capable of timing and producing sequences of many thousands of pulses, if necessary. The pulse lengths and delays can be set in increments of 100 ns.

5.2.2 Overview of the field cycling apparatus

The arrangement of the high-field and low-field magnets, shuttle system, and NMR probe is shown in Figure 5.4. The Dewar vessel which contains the main coil is supported 75 cm above the floor. This allows easy access to the low-field apparatus placed below the Dewar, while permitting service of the NMR probe from above. All mechanical

Figure 5.4 Overview of the field cycling apparatus. The Dewar vessel and main coil are supported about 75 cm above the floor. The low-field apparatus is placed below the main coil. The NMR probe is accessible from above the Dewar vessel.

support structures in the low-field region are made of aluminum or brass except the coil forms, which are made of plastics. The rf coil of the NMR probe is of the "saddle shaped" configuration and is placed about the center of the main coil, wherever the field is found to be the most uniform. The low-field coils are centered about a point on the axis of the main coil, where its fringe field is 100 G.

5.2.3 Sample shuttle system

The sample is contained in a short plastic tube, which is shown in Figure 5.5. After the sample has been packed into the tube, a close-fitting plug is put on the open end, and then the plug may optionally be held in place by a diametrical pin (not illustrated). All parts of the sample holder must be made out of an impact-resistant material. Nylon and kel-F work well in this regard. For samples that are air-sensitive, or for liquid samples, the plug can be adapted to hold an elastomeric (e.g., rubber) O ring. The O-ring variant sample holder is also useful for fine powders that may be able to slip past a simple plastic plug.

The sample holder travels in the "shuttle tube", which runs between the high- and low-field regions. At least at its ends, the shuttle tube itself must be electrically insulating, since time-varying magnetic fields are to be applied and eddy currents must be avoided. For satisfactory shuttling, the bore of the tube must be uniform. We have used ordinary thin-walled glass tubing, which seems suitable in both regards.

The sample is moved up and down within the shuttle tube by air

Figure 5.5

Sample holder for the air-driven sample shuttle system.

pressure. Two simple pneumatic circuits for this are shown schematically in Figure 5.6. In the first [Figure 5.6(a)], the sample is driven up into the main coil by compressed air [about 6 psi (40 kPa) above atmospheric pressure] and down by a partial vacuum [about 10 psi (70 kPa) below atmospheric pressure] applied to the lower end of the shuttle tube. The upper end of the shuttle tube vents freely to the atmosphere. This scheme needs only one interface to the shuttle tube, but requires a vacuum source. In the second scheme [Figure 5.6(b)], the sample is propelled in either direction by directing compressed air to one end of the shuttle tube while venting the other end at atmospheric pressure. This scheme does not require a vacuum source. It does, however, require connections at both ends of the shuttle tube.

The driving air and vacuum are switched through commercial solenoid-actuated valves (e.g., Automatic Switch Co., Catalog No. 8320A89). The solenoid power is controlled by a simple semiconductor switching circuit. Two such circuits, for dc and ac operated solenoids respectively, are shown in Figures 5.7(a) and (b). For most experiments, ac powered valves are suitable. Where the spin-lattice relaxation times are short, reproducibility of the sample shuttling is very important, and in such cases dc operated valves perform better as they tend to have more reproducible switching delay times. At this time it is routine in our lab to operate ac solenoids with dc power supplies, yet a word of warning is in order: this runs a risk of overheating the solenoid. The solenoid current in ac operation is limited by the inductance and resistance, but in dc operation only by the resistance. Thus one finds that a dc voltage comparable to the

Figure 5.6 (a) Schematic diagram of a single-ended air-driven sample shuttle system. By applying compressed air or a partial vacuum to the lower end of the shuttle tube, the sample is moved up or down through the tube. The upper end of the shuttle tube is at atmospheric pressure. (b) Diagram of a double-ended pneumatic circuit. To move the sample one way, compressed air is applied to one end of the shuttle tube while the other end is vented to the atmosphere; the pressures are reversed to move the sample in the opposite direction.

Figure 5.7 In (a), a simple dc circuit to power solenoid-actuated devices; in (b), a circuit suitable for ac solenoids. Either of these may be used with solenoid valves to control the sample shuttling for zero-field NMR, although the ac arrangement is often undesirable since the oscillatory solenoid current introduces a slight uncertainty in the valve response time.

rated ac voltage will promptly burn up the coil. A much smaller dc voltage suffices to actuate the valve, and one should not far exceed this sufficient voltage.

A drawing of the NMR probe and the upper end of the shuttle tube is presented in Figure 5.8. At the upper end of the shuttle tube, upward motion of the sample is stopped by a thin-walled nylon or kel-F tube which extends down into the shuttle tube and is attached to the body of the NMR probe. The length of this stop is chosen so that the sample is accurately positioned within the rf coil during the detection sequence. The upper stop also serves in part to position the shuttle tube along the axis of the main coil. When necessary, the top of the probe support tube is connected to the pneumatic switching system; otherwise it is left open to the atmosphere.

At the lower end, the shuttle tube is attached to a glass-compatible T fitting (e.g., Cajon Co., Ultra-Torr model). Figure 5.9 shows this in the context of the low-field part of the apparatus. The driving air or vacuum is applied to the central branch of that fitting. To stop the sample in the low-field region, a thin nylon rod extends up into the shuttle tube and is attached to the lower branch of the T fitting by a screw which allows adjustment of the vertical position of the stop.

During the shuttle cycle, a considerable mechanical impulse is delivered to each of the shuttle stops. It is therefore important that the NMR probe body and the T fitting, to which the stops are attached, are securely anchored to some steady supports.

Figure 5.8 Framework of the high-field NMR probe. The rf coil is of the saddle-shaped configuration, and is rigidly mounted to the probe body. The position of the upper stop is adjusted so that the sample is centered within the rf coil during the detection sequence.

Figure 5.9 • Low-field apparatus, including low-field coils and shuttle hardware. The sample can be removed or replaced through the lower branch of the T fitting. The position of the lower stop is adjusted so that the sample is centered within both coils during the zero-field interval.

5.2.4 Shielding coil system

5.2.4.1 Background

In order to cancel the external field effectively, the shielding coil must match that field not only at a point but everywhere in the sample volume. That is to say that we must cancel the field and, to some degree, its gradients as well. The cancellation of field gradients is usually difficult, but in this case a simplification arises from the near symmetry of the external field. That field comes primarily from the main coil, which is a solenoid, so the external field is very nearly cylindrically symmetric in the region of interest. This has the practical consequence that we can cancel the field well with a cylindrically symmetric coil aligned coaxially with the main coil. Also, given cylindrical symmetry, the field gradients at a point may be described completely by the set of axial derivatives of the axial component of the field, e.g., $\partial^n B_z / \partial z^n$.

At the low-field sample position in our apparatus, the external field is characterized by these components (to third order):

$$B_z = 100.0 \text{ G} ,$$

$$\frac{\partial B_z}{\partial z} = 3.9 \text{ G/cm} ,$$

$$\frac{\partial^2 B_z}{\partial z^2} = 0.2 \text{ G/cm}^2 , \quad (5-6)$$

$$\frac{\partial^3 B_z}{\partial z^3} = 0.01 \text{ G/cm}^3 \text{ (estimated)} ,$$

where the z axis is taken as parallel to the axis of the main coil. In these units, the derivatives grow rapidly smaller as the order of the derivative goes higher. The practical significance of this is that for samples on the order of 1 cm length and width, the higher-order gradients are far less important in terms of their contribution to the field around the sample. Thus for many experiments, we need only cancel B_z and $\partial B_z / \partial z$ at the sample center; the most demanding experiments may require that we cancel the second derivative too.

5.2.4.2 Coil design model

There are a great many ways to vary the geometry of a magnet coil to achieve certain characteristics in its magnetic field. Even given the limitations of cylindrical (i.e., $C_{\infty v}$) symmetry, one has an infinite number of geometrical parameters to vary. Therefore before we start designing a coil we have to narrow the field a lot, somewhat arbitrarily selecting a few adjustable parameters, and fixing all others.

Figure 5.10 shows one such selection, in fact the one that we use. We have chosen to consider magnets consisting of two coaxial solenoids of the same radius, with negligible radial thickness, and with uniform current distribution. Figure 5.10 also depicts the essential geometrical parameters of this model: the coil radius, r ; the axial positions of the coil edges, a , b , c , and d , such that $a \geq b \geq c \geq d$; the origin, 0, where we presume our sample is located and Equations (5-6) apply; the cylinder axis of the coil, $\hat{z}$; the current density (current per unit length), J , assumed uniform along each solenoid segment. The magnetic field along the z -axis is:

$$B_z(z) = \frac{\pi}{5} J \left\{ \left[\frac{(a-z)}{\sqrt{r^2 + (a-z)^2}} - \frac{(b-z)}{\sqrt{r^2 + (b-z)^2}} \right] \quad (\text{coil } a \rightarrow b) \right. \\ \left. + \left[\frac{(c-z)}{\sqrt{r^2 + (c-z)^2}} - \frac{(d-z)}{\sqrt{r^2 + (d-z)^2}} \right] \right\}, \quad (\text{coil } c \rightarrow d) \quad (5-7)$$

where length is in units of cm, current in amps, and field strength in gauss. Figure 5.10 includes a plot of this axial magnetic field.

5.2.4.3 Coil design procedure

Our model coil has six independent parameters: a , b , c , d , r , and J . A general optimization procedure would involve varying all of those parameters independently to obtain the best quality field. This approach is difficult, since it amounts to a general search through a six-dimensional parameter space. In the design presented here, we simplified the search by fixing or restricting some parameters

Magnet Coil Model

Figure 5.10 Design model for magnet coils. The field produced by the coil depends on the six parameters a , b , c , d , J , and r , which can be adjusted to yield the desired field profile.

arbitrarily, and by making some parameters dependent on others.

The overall coil size is determined by the length, $l=a-d$, and the radius, r . These can be selected rather arbitrarily, but there are related practical concerns: as the coil is made larger, there are potentially troublesome increases in the coil resistance, coil inductance, magnetic force between the shielding coil and the main coil, and transient currents induced in nearby metallic objects. As the coil is made smaller, we must worry instead about increases in the higher-order gradients introduced by the shielding coil, inductive coupling to the auxiliary coil, and sensitivity to alignment errors. Regarding these considerations, we made an effort to be reasonable but made no attempt at rigorous optimization. We chose $l=13.34$ cm (5.25 inch) and $r=5.72$ cm (2.25 inch).

We intended for our shielding coil to match the external field and its first derivative at the origin, and to contribute nothing to the second derivative there. Here we treat the second-derivative problem first:

The calculations are simplified if we require that each coil segment ($a-b$ or $c-d$) produces no second derivative at the origin. Breaking Equation (5-7) into halves, differentiating twice, and setting them equal to zero at $z=0$, we have the following equations to solve:

$$a [r^2 + a^2]^{-5/2} - b [r^2 + a^2]^{-5/2} = 0 \quad (5-8)$$

$$\text{and } c [r^2 + c^2]^{-5/2} - d [r^2 + d^2]^{-5/2} = 0 .$$

If a is known, the first of these can be solved to find b . Likewise if d is known, the second equation can be solved for c . There are multiple solutions, some of which are not of practical interest, e.g., $a=b$ and $c=d$. However it appears that with the constraints

$$a > r/2 > b > 0$$

(5-9)

$$\text{and } 0 > c > -r/2 > d ,$$

each of Equations (5-8) can be solved for a unique and useful value of one variable, given the other variable. This establishes a number of dependences among our parameters. The parameters b , c , and d may, for example, be considered functionally dependent on r , l , and a .

There remains the problem of producing the correct field and first derivative. We took the following iterative approach:

- (0) Keep r and l fixed. (We used 5.72 and 13.34 cm.)
- (1) Choose a value of a consistent with Constraints (5-9).
- (2) Calculate $d = a - l$.
- (3) Using Equations (5-8), solve for b and c . This was done numerically, by Newton's method.
- (4) Using the parameters obtained so far, adjust J to produce $B_z(z=0) = 100.0$ G.
- (5) Calculate $\partial B_z / \partial z$ ($z=0$) and compare to 3.9 G/cm. Go to step (1) to try for a better result, if necessary.

After a modest number of iterations, we arrived at:

$$a = 8.05 \text{ cm} ,$$

$$b = 0.54 \text{ cm} ,$$

$$c = -1.27 \text{ cm} ,$$

$$d = -5.29 \text{ cm} ,$$

$$\text{and } J = 134 \text{ amp/cm}.$$

Finally we wanted to use these parameters to make a coil that would operate at less than 10 amps and less than 20 volts. The gauge of wire used, and the extent of layering, must be determined accordingly. We found that two layers of closely-wound 18-AWG (0.112 cm diameter) insulated copper wire would do it.

A rigid polymethacrylate tube with about 11.4-cm outer diameter and about 15 cm length was threaded with a pitch of 0.127 cm along its entire length. Then two layers of wire (18 AWG) were wrapped tightly over the threads. Through a sequence of careful taping, gluing, and cutting, the following arrangement was produced:

Inner layer:	60 turns of wire	(larger segment)
	14 empty turns	(gap)
	32 turns of wire	(smaller segment)
Outer layer:	59 turns of wire over the 60	
	31 turns of wire over the 32.	

All of the coil windings are connected together in series. The field gradients are optimized about a point on the axis, within the gap, and about 5 mm below the upper (larger) coil segment. This coil geometry is shown in Figure 5, along with plots of the external field and the field produced by the shielding coil. The coil resistance is about 0.9Ω , its inductance is on the order of 1 mH, and it requires about 8.5 amps to cancel the 100 G external field.

Figure 5.11 Shielding coil (above) and field profiles (below). This coil is designed to match the fringe field and its slope at the origin, where the sample is situated during the zero-field interval. The shielding coil is also designed to make a negligible contribution to the second derivatives of the field at the origin.

5.2.4.4 Electronics, shims, and ac fields

The current through the shielding coil is controlled by a simple feedback network as shown in Figure 5.12. A logic-controlled switch allows shunting of the current control signal, and thus the current may be switched on and off. With this circuit, the resistance of the magnet coil must be low enough that the steady-state coil voltage drop ($V = IR$) is less than about 20 V.

If one desires to improve the transient response, the feedback capacitor (1 nF in Figure 5.12) may be adjusted. A larger capacitance there tends to stabilize the response (i.e., reduce oscillations and overshoot) and lengthen the settling time.

When a single coil is used to cancel the external field, it is found that a relatively large residual field may arise from errors in the alignment and axial positioning of the coil. To correct for such errors, we use a set of unswitched shim coils; shims to adjust B_x and B_y can correct for small alignment errors, and a symmetric first-order gradient shim can correct for errors in the axial position. These shims are placed around the outside of the shielding coil, and are not shown in the Figures.

The shielding coil described here cancels only the static external field. No attempt has been made to cancel time-varying (ac) fields, but this has not caused us any serious problems since the ac field around our apparatus is relatively small (≤ 5 mG).

Figure 5.12 Schematic diagram of the shielding coil power source. This circuit features a simple feedback network to regulate the current. The output current is adjustable from 7.50 to 10.00 amps for magnet coil loads of 0 to 2 Ω . The relative precision of the output current is about 10^{-4} . The basic feedback circuit is modified by the addition of a shunting transistor so that the output may be switched. The capacitor labeled C may be needed (with a value in the range of μF) to obtain a satisfactory transient response for the +30V supply.

5.2.5 Auxiliary coil system

The auxiliary coil system must be rapidly switchable but need not produce a field of such accuracy or spatial uniformity as the shielding coil system. Therefore the enclosed volume of the auxiliary coil may be relatively small, and the coil current regulation relatively simple (i.e., without feedback). Both of these measures are used in our design to minimize the technical difficulty of rapid field switching.

The auxiliary coil can be made in the form of a simple solenoid. We have used one consisting of 20 turns of 28 AWG (0.038 cm diameter) insulated copper wire wound uniformly in one layer on a threaded nylon tube with an outer diameter of 1.2 cm and a pitch of 0.0397 cm (giving about 0.8 cm length). The field which this produces is relatively inhomogeneous. When that is a problem, it is better to use a double solenoid with parameters optimized for field uniformity. In pulsed NQR experiments, we have used such a coil with $r=a=-d=0.60$ cm, and $b=-c=0.12$ cm, and a pitch of 0.0397 cm (referring to Figure 5.10).

The current through the auxiliary coil is switched by the circuit shown in Figure 5.13. One must use proper caution with this circuit since life-threatening voltages (about 200 V) are present. The use of the optical isolator is important mainly for reasons of safety. It allows the magnet coil to be at low voltages most of the time, thereby reducing the risk of inadvertent electrical shock. Field-effect transistors were chosen as the switching elements because of their relatively high speed. For the current-limiting and current-sensing resistors [25 and 0.5 Ω respectively in Figure 5.13(c)], ordinary

Figure 5.13 Auxiliary coil power source: (a) Overview. One should be cautious when servicing or using a device such as this, since life-threatening voltages (~ 200 V) are present. The indicated separation of the driver and switch circuits is important for the dynamic stability of the overall circuit. The capacitor labeled C may be needed (in the range of μF) to obtain an acceptable transient response for the 180-V power supply.

b) Driver

c) Switch

Figure 5.13 Auxiliary coil power source: (b) Interface and driver for the power transistor, and (c) Power transistor section.

wirewound resistors are to be avoided because of their relatively large inductances. However commercial "noninductive" wirewound resistors appear satisfactory.

The successful operation of the high-speed pulser circuit appears to depend strongly on the manner of construction. Problems arise because the circuit has large amounts of gain and a small amount of feedback. The feedback is not part of the design, but arises from stray mutual inductances and capacitances within the circuit. Feedback between the driver and switch sections of the circuit is the most troublesome. Feedback directly from the drain to the gate of the FET is also significant. If there is too much feedback, the circuit becomes unstable and continuous rf oscillations result which may damage the power transistor. As a remedy, it appears best to isolate the driver and switch sections by spatially separating them, avoiding (when possible) shared panels or cables, and avoiding unnecessarily long wires or large loops within each separate section.

The stability and transient response of this circuit are further enhanced by the liberal use of small capacitors (0.001 to 0.1 μF) near sensitive circuit components. The placement of these capacitors rather close to associated circuit elements is important in order to minimize the effects of lead inductances. Three such capacitors are shown in Figure 5.13(b) and (c). There are additionally (not shown) $\sim 0.1 \mu\text{F}$ capacitors in parallel with the 5-V supply and each of the 12-V supplies. These capacitors are required to maintain nearly constant supply voltages in the face of rapidly changing supply currents. They should be placed near points of current demand.

Concern is warranted also in the way the power transistor is

mounted. The transistor case voltage is rapidly time-varying, and this can cause trouble (in the form of oscillatory behavior) if the power transistor case is placed too near a grounded surface. Thus mounting the transistor directly on the chassis (of course, with the customary insulating hardware) is unacceptable. Mounting it on a printed circuit board with a groundplane has also proven unsatisfactory. The power transistor should be mounted on a small heat sink which may be electrically connected to the transistor case and which should be placed no less than 1 cm from any chassis panel or groundplane.

5.3 Operation

5.3.1 Setup

In addition to the equipment mentioned in Section 5.2, it is also necessary to have an instrument for measuring the magnetic field in the low-field region. This is especially important when setting up the apparatus. A Hall effect gaussmeter (e.g., F. W. Bell Inc., model 811A gaussmeter) is recommended. In the small and inhomogeneous fields encountered, Hall effect instruments are probably more useful than instruments which employ NMR or ferromagnetic effects for magnetic field detection.

Before construction of the shielding coil and the low-field support structures, it is necessary to measure the field and characterize the field gradients in the low-field region. Later, when the coil and its supports are in place, the coil current and alignment must be set. This is most readily done if one can measure the

magnitude and direction of the residual field $\vec{B}_0 + \vec{B}_1$. A residual field oriented along the axis of the coil indicates an error in the shielding coil current; a residual field perpendicular to the coil axis indicates an error in the orientation of the shielding coil; a residual field gradient which is first order and axially symmetric suggests that an error exists in the axial position of the shielding coil relative to the main coil.

Whenever operating the apparatus, even during setup, some care must be taken to avoid operating the shielding and auxiliary coils with an excessive "duty factor" (fraction of time when current is on). At duty factors of ~ 0.1 , the shielding coil system may suffer a slight and temporary loss of accuracy due to heating of the magnet coil and the current-sensing resistor (from the coil to ground in Figure 5.12). At yet higher duty factors, the current-limiting resistor in the auxiliary coil power source may burn out, and permanent damage to the coils or their forms may result from resistive heating in the coil windings.

Once the setup adjustments are finished, the residual field can be characterized by means of zero-field NMR experiments. This is sometimes helpful, but not usually necessary. Solid samples with relatively weak local nuclear interactions show a slight spreading or splitting of the spectral lines when there is a moderate residual field. Zero-field spectra of liquid samples, with J couplings or without, are more sensitive to slight residual fields since the natural linewidths are smaller. One may of course use such measurements to make further adjustments and refinements of the residual field.

5.3.2 Routine operation

As mentioned earlier, many field cycles must be performed in order to measure the zero-field magnetization decay curve, since each field cycle tells us about only one point on that curve. Each field cycle should begin with a high-field polarization period at least as long as T_1 so that the initial magnetization is large. The values of the zero-field interval t_1 are best chosen as regularly incremented times starting with $t_1 = 0$. This is not necessary but makes computation of the Fourier transform convenient. The time increment Δt_1 should be short enough that there is no aliasing of the signal, that is, $\Delta t_1 < \pi/\omega_{\max}$, in keeping with the sampling theorem. An estimate of this time increment may be derived from the high-field spectrum, since generally the zero-field frequencies are on the order of the width of the high-field powder pattern.

The technique so far described requires a spin-lattice relaxation time constant T_1 not much shorter than the minimum time required to execute the field cycle (essentially the round-trip shuttle time, about 300 ms). If the T_1 is less than that, it may be difficult or impossible to obtain the zero-field spectrum since little evolved magnetization will survive to the end of the field cycle. This is the constraint given in Equation (5-1). Thus before attempting this technique with any sample, it is advisable to determine the suitability of the T_1 . The high-field T_1 can be conveniently measured by, for example, saturating the nuclear spins and monitoring their recovery toward the equilibrium polarization. With some samples, the

zero-field signal vanishes or is greatly reduced during the field cycle, even though the high-field T_1 is sufficiently long. In some cases that is merely because the spin-lattice relaxation is too rapid in the lower fields. In other cases the signal may be lost through heteronuclear spin-spin relaxation processes, which can be very rapid at certain intermediate field strengths⁵.

When short sample T_1 's are a problem with the experimental technique discussed here, one should consider alternative techniques, which are our subject in the next section.

5.4 Variant techniques

5.4.1 Pulsed fields

For many quadrupolar spin systems, the field cycle of Figure 5.1 may be difficult to use because the required intermediate field and switching speed are both high, and so the electrical power requirements are excessive. Other field cycling schemes may then be technically more feasible. One promising option is to initiate and terminate the evolution interval with short field pulses instead of field steps. This is described in more detail in Section 8.4 and in some recent papers⁶.

In comparison to the field-step scheme of Figure 5.1, field-pulse schemes suffer from the disadvantage that their results are more difficult to analyze theoretically. However pulsed field cycling is technically easier since the auxiliary coil pulser has to provide current for typically only a few microseconds instead of milliseconds. To be specific, this allows operation of the auxiliary pulser at

higher currents, i.e., up to the pulsed-current rating instead of the continuous-current rating of the transistors.

In pulsed-field experiments, it is sometimes desirable to apply pulses of either polarity along a coil axis. To accomplish this, we have used the bidirectional magnet pulser circuit depicted in Figure 5.14. It is related to the auxiliary coil pulser described in Section 5.2.5; the guidelines and cautionary remarks presented there are no less important here. This circuit features four FET switches; one pair of switches is activated to produce a coil current in each direction. Because of the symmetry of the circuit (when similar components are reasonably well matched), the pulse shape and magnitude are nearly independent of polarity. In this design, with no external current-limiting resistor, the pulse length must be less than 300 μ s, and the duty factor less than 0.0025, to avoid damaging the power transistors or internal current-limiting resistors.

5.4.2 Ferromagnetic shielding

In the technique discussed so far, a coil is used to shield the sample from external fields. This shielding can be done as well, and perhaps better, by an enclosure made of ferromagnetic materials. With such an enclosure, the ferromagnetic walls tend to gather the external magnetic flux, thus diverting it from the enclosed region⁷. Fields on the order of milligauss are readily obtained in this fashion. We have used this idea successfully in a study of J couplings in liquids in zero field, and other workers have used the idea for pulsed zero-field NQR experiments^{6b}. The possible advantages of ferromagnetic shielding

a) Overview

Figure 5.14 High-speed bidirectional pulser: (a) Overview. This circuit is similar in many respects to the auxiliary coil pulser described in Section 5.2.5; the cautionary remarks there regarding high voltages and possible dynamic instabilities apply here as well. This design is particularly useful for zero-field NQR experiments where short pulses are to be applied to demagnetized spin systems.

b) Drivers

Figure 5.14 High-speed bidirectional pulser: (b) Driver network.

c) Switches

Figure 5.14 High-speed bidirectional pulser: (c) Switching network.

derive in part from the fact that, within a certain range of fields, the ferromagnetism responds closely to changes in the external field. Thus the external field and its gradients do not have to be very accurately known beforehand, and the shield automatically cancels time-varying fields as well as static fields. This may make the construction and setup procedures much easier, and would increase the reliability and stability of the apparatus.

5.4.3 Switchable main coil

Instead of moving the sample between the center and the fringe of the main coil in order to remove and restore the high field, one may obtain the same effect by keeping the sample stationary and varying the current through the main coil. Such a technique is used for field-dependent T_1 studies⁸. The switching of very large magnetic fields at moderate speeds (~ 400 kG in ~ 5 ms) has been applied to other sorts of magnetic studies⁹. This kind of magnet switching may allow more rapid field cycling than mechanical sample shuttling; thus it would be useful where spin-lattice relaxation times are short. It may prove useful also in studies of fragile samples such as liquid crystals or single crystals, where it is important to avoid stressing, stirring, or pulverizing the sample. It may also be useful in variable-temperature zero-field studies, where it is best to keep the sample localized in a thermally insulated region near a heating or cooling device. Disadvantages of this scheme arise from the mechanical strain of the main coil due to the time-varying magnetic fields and resistive heating. These effects tend to limit the

constancy (both short term and long term) and homogeneity of the high field. These in turn degrade the efficiency and accuracy of the detection sequence.

5.4.4 Direct detection

In most NMR experiments, the signal is picked up by a magnet coil in accordance with Faraday's Law:

$$|\mathcal{E}| = \frac{d\Phi}{dt} = \omega M_z, \quad (5-10)$$

where $\mathcal{E}$ is the electromotive force associated with the magnetic flux Φ , ω is the characteristic frequency, and M_z is the magnetization to be detected. Since the measured voltage or current is usually proportional to $|\mathcal{E}|$, the measured signal amplitude is proportional to the signal frequency. This frequency dependence contributes to the sensitivity problem of observing NMR directly in zero field. There are alternative detection devices which do not suffer from this strong frequency dependence. The most promising alternatives at this time involve superconducting quantum interference devices (SQUIDS). These may be used as magnetic flux detectors (the resulting electrical signal is proportional to Φ , not $d\Phi/dt$), and are known to be effective for monitoring nuclear magnetizations at low frequencies.¹⁰

In zero-field NMR studies using SQUID detectors, the zero field magnetization decay might be measured directly and in its entirety, rather than indirectly and pointwise. An appropriate field cycle

includes a sudden field shift, going from some preparation field level to zero, with free evolution and detection occurring simultaneously in zero field. A single field cycle, rather than a series of many, is thus sufficient to measure the entire magnetization decay curve. Possible advantages of this scheme, relative to the schemes discussed previously, include that it may yield more rapid measurements in some cases, and it may allow zero-field experiments to be done with a simpler and smaller apparatus. The field cycles used for direct detection schemes may include a simple or a two-step field shift, as in Figure 4.1 or the first half of Figure 5.1 respectively. Alternatively one could apply a short dc or rf pulse to a demagnetized sample in order to create a transient magnetization.

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Chapter 6: Spin-1/2 Pairs in Zero Field

Spin-1/2 pairs are the simplest of all coupled spin systems, and that makes them the starting point in our exposition of dipolar couplings in zero field. In this Chapter, the theoretical methods of Chapter 4 are applied to predict and interpret the zero-field spectra of these two-spin systems. For now, the operators and spin states will be expressed as matrices, so that this Chapter may have a practical and pedagogical flavor. Experimental results are presented to illustrate and confirm the theory.

6.1 Molecular frame and spin states

In Section 4.3 we defined a molecular frame $(\hat{x}, \hat{y}, \hat{z})$ rather arbitrarily, as if it did not matter which particular frame we chose. Actually it does not matter, except that we can sometimes avoid some unpleasant work by selecting a good molecular frame. For two-spin systems, it helps to align the molecular frame along principal axes of the spin interaction when there are definite principal axes. When that is done, the zero-field solution involves the following set of spin states:

$$\begin{aligned}
 |x\rangle &= (1/\sqrt{2}) [| - - \rangle_{\hat{z}} - | + + \rangle_{\hat{z}}] , \\
 |y\rangle &= (1/\sqrt{2}) [| - - \rangle_{\hat{z}} + | + + \rangle_{\hat{z}}] , \\
 |z\rangle &= (1/\sqrt{2}) [| + - \rangle_{\hat{z}} + | - + \rangle_{\hat{z}}] , \\
 \text{and } |s\rangle &= (1/\sqrt{2}) [| + - \rangle_{\hat{z}} - | - + \rangle_{\hat{z}}] .
 \end{aligned}
 \tag{6-1}$$

Here the symbol $|+\rangle_z$, for example, represents an eigenstate of I_{1z} and I_{2z} with eigenvalues $\hbar/2$ and $-\hbar/2$ respectively, with z denoting the molecular z axis. It is useful to note that

$$\begin{aligned} |X\rangle &= (1/\sqrt{2}) [|+\rangle_x + |-\rangle_x] , \\ \text{and } |Y\rangle &= (1/\sqrt{2}) [|+\rangle_y + |-\rangle_y] . \end{aligned} \quad (6-2)$$

$|X\rangle$, $|Y\rangle$, and $|Z\rangle$ are symmetric with respect to interchange of spins 1 and 2, and are known as triplet states; the state $|S\rangle$ is antisymmetric and is called the singlet state.

We shall often need to use another basis set that consists of $|+\rangle_z$, $|-\rangle_z$, $|+\rangle_z$, and $|-\rangle_z$; it is to be called the laboratory (or lab) basis set. These are eigenstates of the operators I_{1z} and I_{2z} , which describe spin alignment along the laboratory frame axis $\hat{z}$. We define $\hat{z}$ as the direction of the external magnetic field when such a field is applied (i.e., for preparation and detection). Also by definition, θ and ϕ are the polar angles (declination and azimuth, respectively) of $\hat{z}$ in the molecular frame. Figure 6.1 illustrates this arrangement. For reorientations of a single spin-1/2 nucleus, the following relations are known¹:

$$\begin{aligned} |+\rangle_z &= \cos(\theta/2)\exp(-i\phi/2)|+\rangle_z + \sin(\theta/2)\exp(i\phi/2)|-\rangle_z , \\ \text{and } |-\rangle_z &= -\sin(\theta/2)\exp(-i\phi/2)|+\rangle_z + \cos(\theta/2)\exp(i\phi/2)|-\rangle_z . \end{aligned} \quad (6-3)$$

With some algebraic work, these can be made to yield the following

Figure 6.1 Molecular reference frame (X, Y, and Z) with the lab frame z axis. The detected magnetization and the applied field (when there is an applied field) are along the lab z axis. In this Chapter, we assume that a rotation $R(\phi, \theta, 0)$ would rotate the molecular frame to the lab frame. Thus the lab y axis is in the XY plane, while the lab x axis is in the Zx plane.

matrix by which the two-spin lab and molecular basis sets are related:

$$\begin{array}{cccc}
 (+ +)_Z & (+ -)_Z & (- +)_Z & (- -)_Z \\
 \frac{1}{\sqrt{2}} \begin{bmatrix}
 i \sin\phi - \cos\theta \cos\phi & \sin\theta \cos\phi & \sin\theta \cos\phi & i \sin\phi + \cos\theta \cos\phi \\
 -i \cos\phi - \cos\theta \sin\phi & \sin\theta \sin\phi & \sin\theta \sin\phi & -i \cos\phi + \cos\theta \sin\phi \\
 \sin\theta & \cos\theta & \cos\theta & -\sin\theta \\
 0 & 1 & -1 & 0
 \end{bmatrix} & \begin{matrix} X \\ Y \\ Z \\ S \end{matrix} \\
 = U. & (6-4)
 \end{array}$$

The columns of U are vectors representing the kets $|+ +\rangle_Z$, $|+ -\rangle_Z$, $| - +\rangle_Z$, and $| - -\rangle_Z$ in the molecular basis set. The rows of U are vectors representing the bras $\langle X|$, $\langle Y|$, $\langle Z|$, and $\langle S|$ in the lab basis set. An operator W can be expressed in either basis set as a matrix; calling these matrices W^{mol} and W^{lab} , we have the relation

$$W^{\text{mol}} = U W^{\text{lab}} U^\dagger. \quad (6-5)$$

6.2 Homonuclear two-spin system

For the case of a static dipole-dipole coupling, we define $\hat{Z} \parallel \hat{r}_{12}$, with $\hat{X}$, $\hat{Y}$, and $\hat{Z}$ mutually perpendicular. This definition leaves $\hat{X}$ and $\hat{Y}$ somewhat ambiguous, but this is appropriate since the static dipolar coupling is cylindrically symmetric.

$|X\rangle$, $|Y\rangle$, $|Z\rangle$, and $|S\rangle$ are eigenstates of the dipolar Hamiltonian, with energies $-\frac{1}{2}\hbar\omega_d$, $-\frac{1}{2}\hbar\omega_d$, $\hbar\omega_d$, and 0, respectively, where $\omega_d = \gamma^2 \hbar / r_{12}^3$. This may be verified using Equation (2-21).

The operator corresponding to the prepared and detected spin order is I_z . In the lab basis set, it is simply expressed as

$$I_z = \hbar \begin{matrix} & \begin{matrix} (+ +)_z & (+ -)_z & (- +)_z & (- -)_z \end{matrix} \\ \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} & \begin{matrix} (+ +)_z \\ (+ -)_z \\ (- +)_z \\ (- -)_z \end{matrix} \end{matrix} \quad (6-6)$$

With Equations (6-3) and (6-4), we can transform this matrix into the molecular basis set, where it is more usable:

$$I_z = \hbar \begin{matrix} & \begin{matrix} X & Y & Z & S \end{matrix} \\ \begin{bmatrix} 0 & -i \cos \theta & i \sin \theta \sin \phi & 0 \\ i \cos \theta & 0 & -i \sin \theta \cos \phi & 0 \\ -i \sin \theta \sin \phi & i \sin \theta \cos \phi & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} & \begin{matrix} X \\ Y \\ Z \\ S \end{matrix} \end{matrix} \quad (6-7)$$

Evidently the operator I_z does not "connect" triplet and singlet states. This can be shown also in terms of symmetry, noting that the I_z operator and the triplet states are symmetric with respect to spin interchange, while the singlet state is antisymmetric.

Taking Equation (4-24) we have the normalized signal,

$$S(t) = \sum_{\substack{i,j = \\ X,Y,Z,S}} \cos(\omega_{ij}t) |\langle i | I_z | j \rangle|^2 / \text{Tr}[I_z^2], \quad (6-8)$$

which can be evaluated directly to get

$$S(t) = [\cos^2 \theta \cos(\omega_{XY} t) + \sin^2 \theta \cos^2 \phi \cos(\omega_{YZ} t) + \sin^2 \theta \sin^2 \phi \cos(\omega_{XZ} t)] \quad (6-9)$$

$$= \cos^2 \theta + \sin^2 \theta \cos\left(\frac{3}{2} \omega_d t\right) . \quad (6-10)$$

Upon complex Fourier transformation, this yields three lines, at $-\frac{3}{2}\omega_d$, 0, and $\frac{3}{2}\omega_d$. The intensity distribution between the outer peaks and the center peak is orientation dependent; the frequencies are of course independent of orientation in zero field.

Experimental spectra showing this type of behavior appear in the first two plots of Figure 6.2. These are zero-field proton spectra of single crystals of barium chlorate hydrate, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. The H_2O groups in this compound closely approximate isolated two-spin systems, and all intramolecular proton-proton vectors are parallel within the crystal. For two different orientations, we indeed observe different relative intensities. The values of θ given in the Figure are determined only from the spectra; that is, we did not determine the crystal orientation independently by any other means.

Computation of the powder-averaged signal amounts to integration of Equation (6-10) over the unit sphere, as in Equation (4-27), with the result

$$S(t)_{\text{powder}} \approx \frac{1}{3} + \frac{2}{3} \cos\left(\frac{3}{2} \omega_d t\right) . \quad (6-11)$$

Figure 6.2 Zero-field proton spectra of barium chlorate hydrate. At top and center are spectra of single crystals with different orientations. When the internuclear vector is parallel to the initial magnetization (i.e., $\theta = 0^\circ$), Equation (6-10) predicts that all of the signal should appear at zero frequency; for $\theta = 90^\circ$, all of the signal should appear at $\omega = \pm 3\omega_d/2$. In the powder spectrum, shown at bottom, one observes the powder-averaged line intensities.

The Fourier transform of this has three lines of equal intensity, as shown experimentally at the bottom of Figure 6.2.

We can calculate the powder average by Equation (4-28) instead of (4-27). In that approach, we simply perform a discrete average of the single crystal signals for three orthogonal orientations [e.g., for $(\theta, \phi) = (0,0)$, $(\pi/2,0)$, and $(\pi/2,\pi/2)$].

6.3 Heteronuclear spin-1/2 pairs

Where there are spins of two different species (conventionally labeled I and S), the magnetization of each spin species (e.g., I_z or S_z) can be prepared and detected independently of the other. In terms of the density operator method of Sections 4.2 and 4.4, we can prepare $\rho(0) = aI_z + bS_z$ and detect $W = cI_z + dS_z$, with a, b, c and d independently variable (within practical limits).

In going from homonuclear to heteronuclear spin-1/2 pairs, some things stay the same. For instance, the eigenstates and energies for the heteronuclear case are still $|X\rangle$, $|Y\rangle$, $|Z\rangle$, and $|S\rangle$, with energies $-\frac{1}{2}\hbar\omega_d$, $-\frac{1}{2}\hbar\omega_d$, $\hbar\omega_d$, and 0, respectively, but now we slightly redefine $\omega_d = \gamma_I\gamma_S\hbar/r_{IS}$.

The prepared and detected spin order are arbitrary linear combinations of I_z and S_z , which are particularly simply expressed in the lab basis set:

$$I_z = \hbar \begin{bmatrix} & (+ +)_z & (+ -)_z & (- +)_z & (- -)_z \\ \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} & \begin{bmatrix} (+ +)_z \\ (+ -)_z \\ (- +)_z \\ (- -)_z \end{bmatrix} \end{bmatrix}$$

and

$$S_z = \hbar \begin{bmatrix} & (+ +)_z & (+ -)_z & (- +)_z & (- -)_z \\ \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} & \begin{bmatrix} (+ +)_z \\ (+ -)_z \\ (- +)_z \\ (- -)_z \end{bmatrix} \end{bmatrix} \quad (6-12)$$

With Equations (6-3) and (6-4) these may be transformed into:

$$I_z = \frac{\hbar}{2} \begin{bmatrix} X & Y & Z & S \\ \begin{bmatrix} 0 & -i \cos \theta & i \sin \theta \sin \phi & \sin \theta \cos \phi \\ i \cos \theta & 0 & -i \sin \theta \cos \phi & \sin \theta \sin \phi \\ -i \sin \theta \sin \phi & i \sin \theta \cos \phi & 0 & \cos \theta \\ \sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta & 0 \end{bmatrix} & \begin{bmatrix} X \\ Y \\ Z \\ S \end{bmatrix} \end{bmatrix}$$

and

$$S_z = \frac{\hbar}{2} \begin{bmatrix} X & Y & Z & S \\ \begin{bmatrix} 0 & -i \cos \theta & i \sin \theta \sin \phi & -\sin \theta \cos \phi \\ i \cos \theta & 0 & -i \sin \theta \cos \phi & -\sin \theta \sin \phi \\ -i \sin \theta \sin \phi & i \sin \theta \cos \phi & 0 & -\cos \theta \\ -\sin \theta \cos \phi & -\sin \theta \sin \phi & -\cos \theta & 0 \end{bmatrix} & \begin{bmatrix} X \\ Y \\ Z \\ S \end{bmatrix} \end{bmatrix} \quad (6-13)$$

Using Equation (4-39), we have this expression for the signal:

$$\langle W \rangle(t) = \sum_{\substack{i,j= \\ X,Y,Z,S}} \exp(i\omega_{ij}t) \langle i | aI_z + bS_z | j \rangle \langle j | cI_z + dS_z | i \rangle, \quad (6-14)$$

which can be directly evaluated to get

$$\begin{aligned} \langle W \rangle(t) = \frac{\hbar^2}{2} \{ & (a+b)(c+d) [\cos^2\theta \cos(\omega_{XY}t) \\ & + \sin^2\theta \cos^2\phi \cos(\omega_{YZ}t) \\ & + \sin^2\theta \sin^2\phi \cos(\omega_{XZ}t)] \\ & + (a-b)(c-d) [\cos^2\theta \cos(\omega_{ZS}t) \\ & + \sin^2\theta \cos^2\phi \cos(\omega_{XS}t) \\ & + \sin^2\theta \sin^2\phi \cos(\omega_{YS}t)] \} \end{aligned} \quad (6-15)$$

$$\begin{aligned} = \frac{\hbar^2}{2} \{ & (a+b)(c+d) [\cos^2\theta + \sin^2\theta \cos(\frac{3}{2}\omega_d t)] \\ & + (a-b)(c-d) [\cos^2\theta \cos(\omega_d t) + \sin^2\theta \cos(\frac{1}{2}\omega_d t)] \} . \end{aligned} \quad (6-16)$$

The powder average, obtained via Equation (4-27) or (4-28), is

$$\begin{aligned} \langle W \rangle(t)_{\text{powder}} = \frac{\hbar^2}{2} \{ & (a+b)(c+d) [\frac{1}{3} + \frac{2}{3} \cos(\frac{3}{2}\omega_d t)] \\ & + (a-b)(c-d) [\frac{1}{3} \cos(\omega_d t) + \frac{2}{3} \cos(\frac{1}{2}\omega_d t)] \} . \end{aligned} \quad (6-17)$$

The Fourier transform of this consists of seven equally spaced lines. The scale factor of $\hbar^2/2$ may be a bit unusual, but it is merely due to the arbitrary units ($\hbar$) of our choices of $\rho(0)$ and W .

Figure 6.3 shows experimental spectra displaying this kind of

Figure 6.3 Zero-field spectra of polycrystalline ^{13}C -enriched β -calcium formate, measured by proton detection and with preparation sequences yielding initial conditions, $\rho(0)$, as noted next to each spectrum. The ^{13}C - ^1H pairs in the formate ion yield seven lines with relative intensities dependent on the initial condition. These results follow closely the behavior predicted by Equation (6-16).

behavior. The sample is polycrystalline ^{13}C -enriched β -calcium formate. Each formate ion contains a ^{13}C - ^1H spin pair, and the dipolar coupling within the pair is strong in comparison to the intermolecular couplings. We observed the protons (I spins) in high field, so we take $W = I_z$ as the detected operator (i.e., $d = 0$). We were able to control the initial condition, $\rho(0) = aI_z + bS_z$, by techniques to be described below. Thus, from Equation (6-17), we expect to see one set of lines (at 0 and $\pm \frac{3}{2}\omega_d$) with intensity proportional to the sum of polarizations, $a+b$, and another set of lines (at $\pm \frac{1}{2}\omega_d$ and $\pm \omega_d$) with intensity proportional to the polarization difference, $a-b$. This is precisely what is observed.

In these experiments, we had to prepare the ^{13}C nuclei in some known polarized state, but we had at our disposal an NMR probe capable of manipulating only the protons in high field. The protons, with a T_1 of a few seconds, could be repeatably and conveniently polarized by waiting for equilibration in high field. The same idea applied to the ^{13}C nuclei would be most inconvenient, since they have a T_1 of several minutes. The sequence we developed is the following:

- (1) Both spins are depolarized (such that $\langle I_z \rangle = \langle S_z \rangle = 0$) by suddenly removing the field for 10 ms, a period sufficient for the zero-field signal to decay to a negligible level. The field is then suddenly restored.
- (2) A proton polarization is established by waiting 10 seconds in high field. At this point, we have $\rho \propto I_z$.
- (3) The field is suddenly removed for 32 μs , which is $\frac{4\pi}{3\omega_d}$ for this compound, and then suddenly reapplied. This zero-field

interval brings about a polarization transfer from the protons to the carbon nuclei which is independent of molecular orientation.

[This may be verified using Equation (6-15), with $d=0$ to monitor I_z , or $c=0$ to monitor S_z .] We expect the carbons to receive 0.75 of the initial proton polarization during this interval, but in our experiments, the ^{13}C nuclei end up with only ~ 0.40 of the proton polarization.

(4) The protons are repolarized by waiting 10 seconds in high field. At this point, we have $\rho \propto I_z + 0.4S_z$.

(5) To adjust the amount of I_z order, one may irradiate the protons in high field. Applying a strong θ pulse on resonance, and then waiting for high-field coherences to decay, one would get $\rho \propto I_z \cos\theta + 0.4S_z$. In Figure 6.3, the pulse flip angles were 0° , 66° , 90° , 114° , and 180° , in order from top to bottom.

(6) A field cycle with variable zero-field time is now executed.

Sequence (1) to (6) is repeated for every sampling of the zero-field signal. If the initial condition $\rho(0) \propto I_z$ is desired, then steps (3) to (5) should be omitted.

6.4 Asymmetric dipolar couplings in spin-1/2 pairs

Molecular motions which are not symmetric can introduce an asymmetry into the time-averaged dipolar coupling. In that case, we define the molecular frame axes as the principal axes of the averaged dipolar interaction, in analogy to our treatment of the asymmetric quadrupolar interaction. That is, the $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes are chosen so

that the averaged interaction can be expressed as

$$\overline{H}_d = (\omega'_d/\hbar) [3I_{1Z}I_{2Z} - \vec{I}_1 \cdot \vec{I}_2 + \eta(I_{1X}I_{2X} - I_{1Y}I_{2Y})] \quad (6-18)$$

with $0 \leq \eta \leq 1$

and ω'_d dependent on the details of the motion. This is analogous to Equation (2-27).

In such a molecular frame, the eigenstates and energies are

$$\begin{aligned} |X\rangle &: -\left(\frac{1-\eta}{2}\right)\hbar\omega'_d, \\ |Y\rangle &: -\left(\frac{1+\eta}{2}\right)\hbar\omega'_d, \\ |Z\rangle &: \hbar\omega'_d, \end{aligned} \quad (6-19)$$

and $|S\rangle : 0$.

For a homonuclear spin system, we may use Equation (6-8) to get the signal for a single orientation:

$$\begin{aligned} S(\theta, \phi, \tau) &= \cos^2\theta \cos(\eta\omega'_d\tau) \\ &+ \sin^2\theta \cos^2\phi \cos\left(\frac{3+\eta}{2}\omega'_d\tau\right) \\ &+ \sin^2\theta \sin^2\phi \cos\left(\frac{3-\eta}{2}\omega'_d\tau\right). \end{aligned} \quad (6-20)$$

After powder averaging, we get

$$S(\tau)_{\text{powder}} = \frac{1}{3} \left[\cos(\eta\omega'_d\tau) + \cos\left(\frac{3+\eta}{2}\omega'_d\tau\right) + \cos\left(\frac{3-\eta}{2}\omega'_d\tau\right) \right]. \quad (6-21)$$

When $\eta=0$, this reduces to the signal obtained in Equation (6-10).

For a heteronuclear spin-1/2 pair, a similar calculation can be done with Equation (6-14) as the starting point. Then we get

$$\begin{aligned}
 \langle W \rangle(\theta, \phi, t) = \frac{\hbar^2}{2} \{ & (a+b)(c+d) \left[\cos^2 \theta \cos(\eta \omega'_d t) \right. \\
 & + \sin^2 \theta \cos^2 \phi \cos\left(\frac{3+\eta}{2} \omega'_d t\right) \\
 & + \sin^2 \theta \sin^2 \phi \cos\left(\frac{3-\eta}{2} \omega'_d t\right) \left. \right] \\
 & + (a-b)(c-d) \left[\cos^2 \theta \cos(\omega'_d t) \right. \\
 & + \sin^2 \theta \cos^2 \phi \cos\left(\frac{1-\eta}{2} \omega'_d t\right) \\
 & + \sin^2 \theta \sin^2 \phi \cos\left(\frac{1+\eta}{2} \omega'_d t\right) \left. \right] \} , \quad (6-22)
 \end{aligned}$$

and $\langle W \rangle(t)_{\text{powder}} =$

$$\begin{aligned}
 \frac{\hbar^2}{6} \{ & (a+b)(c+d) \left[\cos(\eta \omega'_d t) + \cos\left(\frac{3+\eta}{2} \omega'_d t\right) + \cos\left(\frac{3-\eta}{2} \omega'_d t\right) \right] \\
 & + (a-b)(c-d) \left[\cos(\omega'_d t) + \cos\left(\frac{1-\eta}{2} \omega'_d t\right) + \cos\left(\frac{1+\eta}{2} \omega'_d t\right) \right] \} . \quad (6-23)
 \end{aligned}$$

This reduces to Equation (6-15) in the special case where $\eta=0$. These results are summarized pictorially in Figure 6.4.

6.5 Scalar-coupled spin-1/2 pairs in liquids

In the case of scalar J couplings in zero field, the choice of molecular frame is arbitrary. The eigenstates and energies of the J-coupling Hamiltonian can be expressed as

Homonuclear

Heteronuclear

Figure 6.4 Energy level diagrams indicating observable transitions for spin-1/2 pairs in zero field. For homonuclear pairs, only transitions within the triplet manifold are observable. For heteronuclear pairs, transitions are also allowed between the singlet and the triplet states. The energy difference between the X and Y states is proportional to the asymmetry parameter η , which vanishes in the absence of molecular motion.

$$\begin{aligned}
 |X\rangle &: \quad \hbar J/4, \\
 |Y\rangle &: \quad \hbar J/4, \\
 |Z\rangle &: \quad \hbar J/4, \\
 \text{and } |S\rangle &: \quad -3\hbar J/4.
 \end{aligned}
 \tag{6-24}$$

For a homonuclear spin-1/2 pair, we only see transitions among the triplet states, and all those transitions appear at zero frequency [using Equation (6-8) for example]. For a heteronuclear spin-1/2 pair, we can also see transitions between triplet and singlet states at $\omega = \pm J$. We may use Equation (6-14) to obtain the signal function:

$$\langle W \rangle(t) = (\hbar^2/2) \left[(a+b)(c+d) + (a-b)(c-d) \cos(Jt) \right]. \tag{6-25}$$

Figure 6.5 shows an experimental spectrum of neat diethyl phosphite in zero field. The phosphite group ^{31}P - ^1H coupling is much larger than all the other couplings (those involving the ethyl protons). The spectrum shows lines at 0 and ± 692 Hz, which is consistent with our theoretical analysis.

To make an independent determination of the J couplings, we measured the high-field ($B_0 = 70$ kG) ^{31}P spectrum of diethyl phosphite, shown in Figure 6.6. That spectrum shows a clear pattern of two groups of five peaks each. The splitting between the groups, 687.6 ± 0.5 Hz, is the J coupling between the phosphorus nucleus and the phosphite proton. The splitting within the quintets is 9.2 ± 0.5 Hz, and this is the J coupling between the phosphorus and each methylene proton. The couplings from the phosphorus to the

Figure 6.5 Zero-field spectrum of neat diethyl phosphite liquid, monitoring the ^{31}P signal. Both spin species were allowed to come to equilibrium in high field, and then the ^{31}P polarization was inverted in high field immediately before shuttling down to zero field. This enhances the intensity of the outer lines, which appear at $\pm 692\text{ Hz}$ in this spectrum.

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Figure 6.6 High-field ^{31}P NMR spectrum of neat diethyl phosphite. The major splitting (~ 688 Hz) is due to the phosphite $^{31}\text{P}-^1\text{H}$ coupling. The minor splitting (~ 9 Hz) arises from couplings between the phosphorus nucleus and the methylene protons.

methyl protons are not resolved but probably account for some of the linewidth. That they are unresolved puts an upper bound of approximately 1 Hz on that coupling.

The high-field and zero-field measurements of the phosphite coupling are reconciled if we take into account a slight residual field. This is the subject of the next Section.

6.6 J-coupled spin-1/2 pair with a Zeeman interaction

Our zero-field experiments with diethyl phosphite were the most demanding of all, in terms of the quality of the nominally zero magnetic field. The natural linewidth is small (~ 1 Hz), so that small fields (~ 1 mG) can have a significant effect on the spectra. Here we study the case where there is a nonzero residual field; the emphasis is on practical concerns about the spectral quality.

The problem of two spin-1/2 nuclei with a J coupling in a magnetic field is most easily analyzed in the lab basis set with $\hat{z}$ parallel to the applied field $\vec{B}_0$. The Hamiltonian then appears as

$$\begin{array}{cccc}
 (+ +)_z & (+ -)_z & (- +)_z & (- -)_z \\
 \hline
 \left[\begin{array}{cccc}
 \frac{J}{4} - \frac{B_0}{2}(\gamma_I + \gamma_S) & & & \\
 & -\frac{J}{4} - \frac{B_0}{2}(\gamma_I - \gamma_S) & \frac{J}{2} & \\
 & \frac{J}{2} & -\frac{J}{4} + \frac{B_0}{2}(\gamma_I - \gamma_S) & \\
 & & & \frac{J}{4} + \frac{B_0}{2}(\gamma_I + \gamma_S)
 \end{array} \right] & \begin{array}{l} (+ +)_z \\ (+ -)_z \\ (- +)_z \\ (- -)_z \end{array} \\
 \hline
 = \hat{H} & (6-26)
 \end{array}$$

The states $|+\rangle_z$ and $|-\rangle_z$ are eigenstates of the total Hamiltonian, and their energies are shifted to first order in the applied field strength. To get the energies of the other two states, we have to diagonalize² the 2x2 submatrix in the center of Equation (6-26):

Define $\tan\chi = J/[B_0(\gamma_I - \gamma_S)]$ with $0 \leq \chi \leq \pi$. Thus $\chi = \pi/2$ corresponds to the zero field case, and $\chi = 0$ or π corresponds to the high-field limit. The states that derive continuously from $|Z\rangle$ and $|S\rangle$ (of the zero-field basis set) are called $|Z'\rangle$ and $|S'\rangle$, respectively, with energies $E_{Z'}$ and $E_{S'}$, respectively. Then we have:

$$\begin{aligned}
 |Z'\rangle &= \sin\frac{\chi}{2} |+\rangle_z + \cos\frac{\chi}{2} |-\rangle_z : \\
 E_{Z'} &= \hbar J \left[-\frac{1}{4} + \frac{1}{2 \sin\chi} \right] = \hbar J \left[-\frac{1}{4} + \frac{1}{2} \left\{ 1 + \left[\frac{B_0}{J} (\gamma_I - \gamma_S) \right]^2 \right\}^{1/2} \right] , \\
 \text{and } |S'\rangle &= \cos\frac{\chi}{2} |+\rangle_z - \sin\frac{\chi}{2} |-\rangle_z : \\
 E_{S'} &= \hbar J \left[-\frac{1}{4} - \frac{1}{2 \sin\chi} \right] = \hbar J \left[-\frac{1}{4} - \frac{1}{2} \left\{ 1 + \left[\frac{B_0}{J} (\gamma_I - \gamma_S) \right]^2 \right\}^{1/2} \right] .
 \end{aligned}
 \tag{6-27}$$

The other two states and their energies are simply

$$\begin{aligned}
 |+\rangle_z : E_{(+ +)} &= \hbar \left[\frac{J}{4} - \frac{B_0}{2} (\gamma_I + \gamma_S) \right] \\
 \text{and } |-\rangle_z : E_{(- -)} &= \hbar \left[\frac{J}{4} + \frac{B_0}{2} (\gamma_I + \gamma_S) \right] .
 \end{aligned}
 \tag{6-28}$$

In low field, the transition $S' \leftrightarrow Z'$ is shifted only to second order in the field strength. It is observable as an oscillating component of magnetization parallel to the applied field. The transition

$(+)_z \leftrightarrow (-)_z$ is not directly observable. The remaining four transitions are split to first order in the field strength and are observable as oscillating magnetizations perpendicular to the applied field. Figure 6.7 summarizes the energies as a function of field strength, and the allowed transitions.

In practical terms, the above discussion has these implications for zero-field NMR of two-spin J-coupled systems:

(1) When there is a uniform and small residual field parallel to the initial magnetization, the line at zero frequency is essentially unchanged, and the $\omega = \pm J$ zero-field lines are shifted to slightly higher frequency. For $B_0(\gamma_I - \gamma_S) \ll J$, the frequency becomes

$$\omega = \pm J \left\{ 1 + \frac{1}{2} \left[\frac{B_0}{J} (\gamma_I - \gamma_S) \right]^2 \right\} + O(B_0^4) . \quad (6-29)$$

(2) When the residual field is perpendicular to the initial magnetization, all zero-field lines are split by an amount nearly proportional to the residual field strength. The frequencies are

$$\begin{aligned} \omega &= +J \pm \frac{B_0}{2} (\gamma_I + \gamma_S) + O(B_0^2) , \\ \omega &= -J \pm \frac{B_0}{2} (\gamma_I + \gamma_S) + O(B_0^2) , \\ \text{and } \omega &= 0 \pm \frac{B_0}{2} (\gamma_I + \gamma_S) + O(B_0^2) . \end{aligned} \quad (6-30)$$

(3) For arbitrarily oriented residual fields, some linear combination of (1) and (2) is observed.

(4) When there is an inhomogeneous residual field, one can expect

Figure 6.7 Energy levels as a function of field strength for a scalar-coupled spin-1/2 pair. Allowed transitions are indicated by vertical lines (solid : transverse, dotted : longitudinal).

to see a superposition of broad lines and sharp lines, corresponding to (1) and (2) taken over a distribution of fields within the sample. The spectrum in Figure 6.5 shows such a pattern, with broad lines of low intensity at ± 90 Hz around the center line. This indicates [by Equation (6-30)] that there was a moderately inhomogeneous residual field of 30 mG during that experiment. Plugging this value of B_0 with the high-field value of J (687.6 Hz) into Equation (6-29), we get $\omega_{Z'S'} \approx 691.8$ Hz. This is consistent with our observation of a sharp line at 692 Hz in the nominally-zero-field experiment.

References

1. C. Cohen-Tannoudji, B. Diu, and F. Lal, *Quantum Mechanics*, Vol. 1 (Wiley, New York, 1977), pp. 393-395.
2. *Ibid.*, pp. 420-423.

Chapter 7: Zero-Field NMR of Multispin Dipolar-Coupled Systems

7.1 Line broadening by dipolar couplings

In solids, one is unlikely to find a spin system that is truly isolated. As an example, consider hydrated salts. There we may say that we have a good approximation to a two-proton system in each H_2O molecule. To be exact, each proton is coupled strongly to one other proton, weakly to several other nuclei (e.g., those in nearest-neighbor H_2O molecules), still more weakly to the next-nearest-neighbor nuclei, and so on. The cumulative effect of the many weak couplings is a broadening of each line in the spectrum¹. This is known as dipolar broadening. With all other factors equal, the dipolar broadening is proportional to the number of spins per unit volume, since the individual dipolar couplings scale as r^{-3} .

Figure 7.1 illustrates this with the high-field and zero-field proton spectra of two hydrated salts, barium chlorate hydrate and calcium chloride dihydrate. Each compound shows approximately what we would expect: a Pake pattern in high field and a three-line pattern in zero field. The two compounds differ, however, in the extent of dipolar broadening, both in zero and high field. In $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, the water molecules are about 2.5 times as densely packed as they are in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.² We find about the same factor relating the zero-field proton linewidths (for the lines at ± 40 kHz, the ratio of FWHM's is ~ 2.2).

The same dipolar couplings that account for line broadening can also, in principle, yield weak resonances at multiples or combinations

Figure 7.1 Experimental high-field and zero-field proton spectra of barium chlorate hydrate and calcium chloride dihydrate. The proton pairs are more closely packed in the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and as a result the dipolar broadening is greater, both in high field and zero field.

of the fundamental dipolar frequencies³. This might be taken to explain the harmonic peaks at ± 84 kHz in the zero-field spectrum of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, but then one has to wonder why such harmonic peaks are absent in the zero-field spectrum of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, where the intermolecular couplings are more effective. Even for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, the harmonic peaks are not reproducible⁴. This suggests that they are, to some extent, experimental artifacts. Alternatively, they may be due to some minor, so far overlooked, detail of the spin interactions.

7.2 Methyl groups

After spin-1/2 pairs, the three-spin systems present in methyl ($-\text{CH}_3$) groups are the next simplest case. The three protons are identical and equidistant, so that all of the dipolar couplings are equal. Moreover, the rapid rotational motions of the methyl group about its C_3 axis make the effective dipolar couplings coaxial⁵. This high degree of spatial symmetry results in a spectrum which is uniquely simple among three-spin systems.

The rotations of the methyl group make its dipolar interactions time-dependent. However, because the motion is extremely rapid (at least at room temperature), it is correct for us to pay attention only to the time-averaged interaction and treat it the same as a static interaction. The time-averaged Hamiltonian is

$$\overline{H}_d = \frac{\gamma^2}{2r^3} [\vec{I}_1 \cdot \vec{I}_2 - 3I_{1Z}I_{2Z} + \vec{I}_2 \cdot \vec{I}_3 - 3I_{2Z}I_{3Z} + \vec{I}_3 \cdot \vec{I}_1 - 3I_{3Z}I_{1Z}] \quad (7-1)$$

where we define $\hat{Z}$ parallel to the molecular rotation axis. The factor of 1/2 in this equation is the result of evaluating $(3\cos^2\theta - 1)/2$ where θ is the angle ($\pi/2$ in this case) between each $\vec{r}$ and the Z axis. We find the following energies and eigenstates of $\overline{H}_d$:

$$\begin{aligned} E_1 &= 3\omega_d\hbar/4 & : & \quad |1\rangle = |++\rangle_Z \\ E_2 &= -3\omega_d\hbar/4 & : & \quad |2\rangle = [|+-\rangle_Z + |-+\rangle_Z + |--\rangle_Z] / \sqrt{3} \\ E_3 &= -3\omega_d\hbar/4 & : & \quad |3\rangle = \overline{|2\rangle} \\ E_4 &= 3\omega_d\hbar/4 & : & \quad |4\rangle = \overline{|1\rangle} \\ E_5 &= 0 & : & \quad |5\rangle = [|+-\rangle_Z + \exp(2\pi i/3)|-+\rangle_Z + \exp(4\pi i/3)|--\rangle_Z] / \sqrt{3} \\ E_6 &= 0 & : & \quad |6\rangle = -\overline{|5\rangle} \\ E_7 &= 0 & : & \quad |7\rangle = |5\rangle^* \\ E_8 &= 0 & : & \quad |8\rangle = -\overline{|5\rangle}^* \end{aligned} \quad (7-2)$$

where $\omega_d = \gamma^2\hbar/r^3$. The asterisk indicates complex conjugation of the coefficients, and the overbar indicates inversion of each spin in the state; e.g., $\overline{|-+-\rangle} = |+-\rangle$. In this basis set, the operators I_X , I_Y , and I_Z are particularly simple:

$$I_X = \frac{\hbar}{2} \begin{matrix} & \begin{matrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \end{matrix} \\ \begin{matrix} 0 & \sqrt{3} & & & & & & \\ \sqrt{3} & 0 & 2 & & & & & \\ & 2 & 0 & \sqrt{3} & & & & \\ & & \sqrt{3} & 0 & & & & \\ & & & & 0 & 1 & & \\ & & & & 1 & 0 & & \\ & & & & & & 0 & 1 \\ & & & & & & 1 & 0 \end{matrix} & \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \end{matrix} \end{matrix} \quad (7-3a)$$

$$I_Y = \frac{\hbar}{2} \begin{matrix} & \begin{matrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \end{matrix} \\ \begin{matrix} 0 & -i\sqrt{3} & & & & & & \\ i\sqrt{3} & 0 & -2i & & & & & \\ & 2i & 0 & -i\sqrt{3} & & & & \\ & & i\sqrt{3} & 0 & & & & \\ & & & & 0 & -1 & & \\ & & & & i & 0 & & \\ & & & & & & 0 & -1 \\ & & & & & & i & 0 \end{matrix} & \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \end{matrix} \end{matrix} \quad (7-3b)$$

$$I_Z = \frac{\hbar}{2} \begin{matrix} & \begin{matrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \end{matrix} \\ \begin{matrix} 3 & & & & & & & \\ & 1 & & & & & & \\ & & -1 & & & & & \\ & & & -3 & & & & \\ & & & & 1 & & & \\ & & & & & -1 & & \\ & & & & & & 1 & \\ & & & & & & & -1 \end{matrix} & \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \end{matrix} \end{matrix} \quad (7-3c)$$

Most of the zero matrix elements are left blank for visual clarity.

Note that, as far as dipole matrix elements are concerned, the states $|1\rangle$ to $|4\rangle$ are like an isolated spin-3/2 particle, states $|5\rangle$ and

$|6\rangle$ are like an isolated spin-1/2 particle, and states $|7\rangle$ and $|8\rangle$ are like another isolated spin-1/2 particle.

Using Equations (4-28) and (7-3), the signal is found to be

$$S(t)_{\text{powder}} = [2 + \cos(3\omega_d t/2)] / 3 . \quad (7-4)$$

Experimental spectra of sodium acetate (as $\text{CH}_3\text{CO}_2\text{Na} \cdot 3\text{D}_2\text{O}$) are presented in Figure 7.2. The samples were made from mixtures of normal anhydrous sodium acetate and its perdeuterated analog ($\text{CD}_3\text{CO}_2\text{Na}$) dissolved in D_2O and then recrystallized. Had we used H_2O as the solvent instead, the hydrate protons would have produced an intolerable line broadening. In the top spectrum, with all of the methyl groups protonated, the intermolecular couplings are still large enough to wash out the expected splittings. The resolution improves as we dilute the $-\text{CH}_3$ groups with $-\text{CD}_3$ groups, and in the most dilute case the spectrum comes close to our theoretical expectation. The observed splitting corresponds to an internuclear distance of 1.89 Å.

Figure 7.3 shows high-field and zero-field proton spectra of protonated dimethylterephthalate diluted to 16% in its perdeuterated analog. The outside pair of lines arises from the methyl groups. From their splitting, we calculate a proton-proton distance of 1.83 Å within the methyl group. The inner pair of lines is associated with the proton pairs on the aromatic ring with a separation of 2.49 Å.

Figure 7.2 Zero-field proton spectra of $-\text{CH}_3$ groups in polycrystalline sodium acetate (as $\text{CH}_3\text{CO}_2\text{Na}\cdot 3\text{D}_2\text{O}$), diluted to different extents in the perdeuterated form ($\text{CD}_3\text{CO}_2\text{Na}\cdot 3\text{D}_2\text{O}$). At top, with all methyl groups protonated, the dipolar broadening is too large to clearly resolve the couplings within individual methyl groups. As the $-\text{CH}_3$ groups are diluted with $-\text{CD}_3$ groups, the spectrum becomes increasingly well resolved, approaching the pattern expected of isolated methyl groups.

Figure 7.3 High-field and zero-field proton spectra of polycrystalline dimethylterephthalate, diluted to 16% in its perdeuterated analog. In the zero-field spectrum (at bottom), the outer pair of lines arises from the methyl groups, and the inner pair from the aromatic ring protons.

7.3 General features of larger spin systems

As the number of strongly interacting spins increases, we expect the complexity of the spectrum to increase very rapidly. For a system of N spin-1/2 nuclei, there are $N(N-1)/2$ distinct couplings. If we could measure each of these couplings, it would be a simple matter to solve for the geometry. For this N -spin system, there are 2^N linearly independent spin states. In the absence of spatial and spin symmetry in zero field, there is not in general any degeneracy, and the selection rules are not very discriminating. Thus we expect the system to have $2^N(2^N-1)/2$ distinct transition frequencies [or $2^N(2^N-1)$ lines for $-\infty < \omega < \infty$], and most likely all of these transitions will be allowed. Relatively few couplings can thus give rise to an enormous number of line frequencies.

A similar problem is confronted in high-field NMR studies of small molecules oriented in liquid-crystalline phases. In high field, multiple-quantum NMR can be used to select small subsets of the transitions, thus enhancing interpretability⁶. However, at this time, no such selective experimental technique exists for zero-field NMR.

When N is an odd number, there is a certain symmetry which reduces the number of transitions from our estimate above. From Kramer's theorem, and as a consequence of time-reversal symmetry, for N odd, all eigenstates of the zero-field Hamiltonian are at least doubly degenerate⁷. This reduces the number of transition frequencies by about a factor of four. To be precise, we have the following upper bounds on W , the number of lines in the range $-\infty < \omega < \infty$:

$$\begin{aligned}
 W &= 2^N(2^N - 1), & N &= 2, 4, 6, \dots, \\
 W &= 2^{N-1}(2^{N-1} - 1) + 1, & N &= 3, 5, 7, \dots
 \end{aligned}
 \tag{7-5}$$

The extra line that appears for N odd is at zero frequency and represents transitions between degenerate states.

Other symmetries can markedly reduce the actual number of lines observed. For example, for two spins, the formula above predicts 12 lines. Yet in Chapter 6 we saw that as few as 3 lines are observed when there is sufficient spatial (e.g., cylindrical) symmetry combined with a spin symmetry (e.g., prepared and detected states symmetric with respect to interchange of the spins). For the methyl group also, the symmetry leads to a very simple spectrum.

For large spin systems, spectral complexity is an awesome problem in itself, but matters are usually made worse by the finite resolution of the NMR experiment. Individual lines in the zero-field spectrum of a solid are usually ≥ 1 kHz wide, and the entire dipolar spectrum is typically ~ 50 kHz wide. Being very optimistic, we might expect to resolve a spectrum of up to about 50 individual lines. Beyond that, lines would merge and the spectrum would look like a continuous absorption band. As we shall see in the next Section, individual transitions are not resolved for $N \geq 4$ in known cases.

7.4 Experimental results for four-spin systems

Figure 7.4 shows, in schematic form, the structure of 1,2,3,4-tetrachloronaphthalene-bis(hexachlorocyclopentadiene) adduct. The compound is synthesized by a Diels-Alder addition of

**1,2,3,4-Tetrachloronaphthalene-
bis (hexachlorocyclopentadiene) adduct**

Figure 7.4 Schematic molecular structure of 1,2,3,4-tetrachloronaphthalene bis(hexachlorocyclopentadiene)adduct. The protons are shown here; all other sites are chlorinated.

hexachlorocyclopentadiene to 1,2,3,4-tetrachloronaphthalene. Thus it is known⁸ that the hydrogen sites marked 1 and 2 (in the Figure) are *cis* (i.e., both on the same side of the central ring); sites 1' and 2' are also *cis*. As the molecule comes together, steric effects probably prohibit the formation of a product with all four sites on the same side of the central ring.

This compound has a compact cluster of four protons roughly centered within the relatively large molecular framework. It is to be expected that couplings within the four-spin cluster here are important among the dipolar interactions, but we did not know *a priori* whether the proton-chlorine couplings or intermolecular couplings would complicate the spectrum. It turns out that these extra couplings yield only a small linebroadening, so that we were able to accurately model the system simply as a group of four protons.

In view of the abundance of ³⁵Cl and ³⁷Cl nuclei in 1,2,3,4-tetrachloronaphthalene-bis(hexachlorocyclopentadiene) adduct, a few comments about the proton-chlorine dipolar couplings are in order: The chlorine nuclei have relatively small magnetic moments; the gyromagnetic ratios of both species are less than a tenth that of the proton. Thus the proton-chlorine couplings are moderately small in any case. Additionally, all of the chlorine sites, being covalently bonded, have large quadrupolar interactions. These reduce the couplings further by, in effect, partially truncating the heteronuclear dipolar interactions^{1d}. Finally, if the chlorine spin-lattice relaxation is sufficiently rapid [i.e., if $T_1 \ll \omega_{d(H-Cl)}^{-1}$; we do not know if this is the case], their dipolar interactions will be averaged toward zero.

The zero-field proton spectrum of polycrystalline 1,2,3,4-tetrachloronaphthalene-bis(hexachlorocyclopentadiene) adduct is shown in Figure 7.5(a). For $N=4$, Equation (7-5) predicts the possibility that 240 discrete lines might be observed in the zero-field spectrum. Obviously we do not observe that number here; many of the lines are merged or overlapping because of their finite linewidths. Nevertheless, some information remains; though no individual transitions can be resolved, there is a distinctive and moderately complex intensity pattern which allows us to interpret the spectrum and extract a molecular structure.

To interpret the spectrum, we used this iterative method:

- (1) Choose a hypothetical geometry. In this case, this was done by specifying the coordinates of the four protons in a molecular frame.
- (2) Calculate the discrete spectrum. We did this by computer.
- (3) Convolute the spectrum with a hypothetical lineshape.
- (4) Compare to the experimental spectrum. We did the comparison visually, although it can be done by computation.
- (5) Go back to (1) and try for a better fit, if necessary.

After several (~ 20) iterations, the hypothetical geometry converged to within $\pm 0.05 \text{ \AA}$ of an optimum structure which has a C_2 symmetry which relates the two innermost (1 and 1') and the two outermost (2 and 2') proton sites. Because of this symmetry, only four distances characterize the structure: $r_{11'} = 2.83 \text{ \AA}$, $r_{12} = 2.22 \text{ \AA}$, $r_{12'} = 4.34 \text{ \AA}$, and $r_{22'} = 5.01 \text{ \AA}$. The simulated spectrum for this structure is shown in Figure 7.5(b). Note that this approach yields a structure in terms of proton-proton distances only.

For the next part of part of our analysis, we derived the

Figure 7.5 (a) Experimental and (b) simulated zero-field proton spectra of 1,2,3,4-tetrachloronaphthalene bis(hexachlorocyclopentadiene) adduct. The simulation, obtained by fitting to the experimental spectrum in an iterative approach, yields proton-proton distances within the four-spin cluster and indicates that the cluster has a C_2 symmetry axis.

hypothetical proton coordinates from hypothetical carbon-skeleton structures. This connection, although unnecessary, is nice because it lends some insight into the overall structure of the molecule. Figure 7.6 shows a series of simulated spectra which illustrate this idea. For these we assumed that the central ring has a D_{3d} symmetry (same as the cyclohexane chair conformation), and that the bonding around each central-ring carbon has a C_{2v} symmetry. Then the ring is describable by only four parameters: two distances and two angles. We assumed 1.54 Å for C-C bond lengths, 1.10 Å for C-H bond lengths; the C-C-C and H-C-H angles were assumed equal, with angles given in the Figure. The spectrum marked 120° , corresponding to a completely flattened cyclohexane, is the one of this series to best match the experimental spectrum. Several more series of simulations were done along these lines: smaller angle increments were sampled, we tried structures with the H-C-H angle fixed (at 109.5°) instead of variable, boat conformations with various degrees of flattening were tested, and we tried structures with all four protons on the same side of the central ring. Of all the cyclohexane-derived structures we tried, none yielded a spectrum which fit the experimental spectrum substantially better than the one shown at the center of Figure 7.6. This suggests that the flat central ring structure and corresponding proton arrangement are nearly correct.

A similar approach was made toward the analysis of spectra of bis(μ -hydrido)decacarbonyltriosmium, $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. Figure 7.7 shows the molecular structure of this compound. Neutron (and x-ray) diffraction studies⁹ indicate that the molecules are packed end-to-end

Figure 7.6 Zero-field NMR simulations of four-proton systems, with proton positions derived from the cyclohexane ring structures shown alongside the spectra. The center spectrum, corresponding to a flat ring, matches many of the features of the experimental spectrum of 1,2,3,4-tetrachloronaphthalene bis(hexachlorocyclopentadiene)adduct. This suggests that the central ring in that compound has a similar, nearly planar, conformation.

Figure 7.7 Structure of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. At top, the approximate molecular geometry is shown. In the solid state, the molecules are stacked together in pairs to yield well-isolated clusters of four proton spins, as shown in a simplified view at bottom. Sites 1 and 2 are related to sites 1' and 2' by an inversion center.

within the crystal, such that the proton pairs are themselves paired to yield well-defined four-proton clusters. Most of the natural line broadening is due to couplings between protons in separate clusters. As for the other nuclei, carbon, oxygen, and osmium have magnetic species, but all are moderately low abundance and low γ . In our analysis, we modeled the compound simply as a four-spin system with some artificial line broadening. The crystallographic studies indicate that the four-spin system has an inversion symmetry, which we assumed in our spectral analysis. Given this symmetry, the geometry is determined by three linearly independent distances.

The zero-field spectrum of powdered $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ is shown at the top of Figure 7.8. Below it are two simulations. The first is our best fit to the experimental spectrum, obtained by the iterative method described earlier in this Section. The second is the spectrum calculated from the structure determined by single-crystal neutron diffraction at 110 K^{9c}. The two simulated spectra are clearly different, even though the assumed structures are quite similar. The difference between those two structures is primarily in the intermolecular spacing, and this difference can reasonably be attributed to thermal expansion of the crystal lattice between 110 K and room temperature.

Experimental and simulated high-field spectra of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ are shown in Figure 7.9; the high-field simulations are based on the same structures used for the zero-field simulations. It appears that high-field NMR, in comparison to zero-field NMR, is much less sensitive to minor structural differences, at least when measuring dipole-dipole couplings.

Figure 7.8 Zero-field proton spectra of polycrystalline $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. The upper plot shows the experimental spectrum. The center plot shows a computer simulation which is our best fit to the experimental spectrum. The lower plot is a simulation based on the proton-proton distances reported in Reference 9(c).

Figure 7.9 High-field proton spectra of polycrystalline $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. At top, the experimental spectrum is shown. At center and bottom, simulations based on the same structures as in Figure 7.8 are displayed. The proton-proton distances assumed in these simulations are given in the following Table:

Proton Pair	Simulation A	Simulation B
1-1'	2.94	2.81
1-2	2.38	2.38
1-2'	5.28	5.17

All distances are in Å. Given the assumed inversion symmetry of the unit cell, all other proton-proton distances are uniquely determined.

Figure 7.8

Figure 7.9

7.5 Zero-field NMR as $N \rightarrow \infty$

The zero-field proton spectrum of polycrystalline squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) is shown in Figure 7.10. Single-crystal diffraction studies¹⁰ indicate that, at room temperature, the protons are arranged in long, nearly linear arrays with a spacing of $\sim 2.7 \text{ \AA}$ along the chain and $\sim 4.0 \text{ \AA}$ between chains. Our experimental observation of a narrow peak superposed on a relatively broad peak is consistent with this kind of spatial structure. For any number of spins in an isolated linear array, the cylindrical symmetry results in the appearance of at least 1/3 of the total intensity at zero frequency. With $\hat{z}$ defined as the line axis, the total dipolar Hamiltonian commutes with I_z , and so the Z component of magnetization cannot evolve. Another way to look at this is that a completely coaxial set of dipole-dipole interactions exerts no torque along the axis, as would be required to change the axial component of angular momentum. In squaric acid, the proton chains deviate slightly from linearity, and there are small couplings between chains, so this theoretical idea applies only approximately.

Figure 7.11 shows the zero-field proton spectra of three ammonium salts: Ammonium thiocyanate, NH_4SCN ; ammonium nitrate, NH_4NO_3 ; ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. At room temperature, the ammonium groups tumble rapidly so that dipolar couplings within the group are essentially averaged to zero¹¹. The width and shape of the observed patterns are then primarily due to couplings between protons on separate NH_4 groups. This is essentially the reverse of cases appearing earlier in this Chapter, where couplings within clusters are

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Figure 7.10 Zero-field ^1H spectrum of polycrystalline squaric acid.

Figure 7.11 Zero-field proton spectra of ammonium salts. The relatively narrow line is indicative of the rapid tumbling motions of the ammonium groups at room temperature. The linewidth is due mostly to intermolecular couplings. For each of these compounds, the measured linewidth (FWHM), and density of NH_4 clusters reported in References 12, are listed:

NH_4SCN	:	21.5 kHz,	0.0171 equivalents/ cm^3 ,
NH_4NO_3	:	27.0 kHz,	0.0215 equivalents/ cm^3 ,
$(\text{NH}_4)_2\text{SO}_4$	:	31.7 kHz,	0.0268 equivalents/ cm^3 .

larger than those between clusters. We find that the linewidths for these compounds are nearly proportional to the proton densities¹², as predicted in Section 7.1. Some data indicating this correlation are given in Figure 7.11.

Kubo and Toyabe have introduced a lineshape theory¹³ which may be applicable to zero-field NMR of crowded spin systems of low symmetry. In their approach, the dipolar broadening is treated as a static local Zeeman interaction which varies from site to site, with the local field having an isotropic distribution of orientations and a Gaussian distribution of amplitudes. Given these assumptions, their result for the zero-field signal is

$$S(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2) \exp(-\Delta^2 t^2/2) , \quad (7-6)$$

$$\text{where } (\Delta/\gamma)^2 = \overline{B_X^2} = \overline{B_Y^2} = \overline{B_Z^2} ;$$

thus Δ is a measure of the local field strength. The 1/3 of the signal which does not evolve here arises from the assumed symmetry of the local field at each site; the component of magnetization parallel to the local field vector does not evolve.

The basic assumptions of the Kubo-Toyabe theory are difficult to justify. That is, they do not accurately represent dipole-dipole couplings. Nevertheless, Equation (7-6) is at least roughly confirmed by experiments in zero-field muon spin resonance¹⁴ and in zero-field proton NMR in some cases where there are no well-defined clusters¹⁵.

7.6 Simulations of zero- and high-field NMR for model systems

Figure 7.12 shows calculated high-field and zero-field powder spectra for systems of up to $N=6$ coupled, static, and equivalent protons in various geometries. For small N , the zero-field spectra are better resolved than their high-field counterparts, primarily because the frequency spreading is eliminated. At about $N=6$ spins, the zero-field spectra become sufficiently complex that even they may be of little use in structure determination.

Each of the high-field powder spectra is calculated by summing the simulated spectra for a large number of different orientations of the spin system relative to an externally applied magnetic field (varying from 14400 orientations for the three-spin systems to 400 for the six-spin systems). The sum (essentially a discrete average) is then convoluted with a Gaussian function. The zero-field spectra are calculated by the procedure presented in Section 4.3 (and with the program DBZINT), and then convoluted with the same Gaussian broadening function. In most of the odd-spin simulations, the intense zero-frequency line has been truncated in the unbroadened spectra, and in some of the broadened spectra where indicated by broken lines.

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Figure 7.12 Calculated high-field and zero-field NMR spectra for systems of up to six coupled, static protons with various geometries

Figure 7.12

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Appendix: Fortran program for dipolar zero-field simulations

The program DBZINT, which calculates zero-field powder spectra for homonuclear (proton) systems up to $N=6$, follows:

```

      program dbzint
c
c      computes intensities for the dz/tb field-cycling experiment on
c      coupled proton systems
c      this one is set up to generate spectra to dbz's specifications
c
      dimension numb(2,64),lst(2,64),isp(6),coors(6,3),dd(15),theta(15)
      dimension phi(15),vv(4096),pp(4096),e(64),ss(1024),vr(1024),iflip(2)
      complex h(4096),u(4096),xx(4096),yy(4096),zz(4096),wvec(64)
      character*64 title
      common/et/ title,e
      common n,nst,lst
      equivalence (h(1),xx(1))
c
      indx(i,j)= (j-1) * nst + i
c
      kfunk(i1,i2)=(2*n - i1)*(i1 - 1)/2 - i1 + i2
c
c
      dconst=120.067
      pi=4.0 * atan(1.0)
      rad57=180. / pi
c
      np=1024
c
10      type 501
501      format('1',/,/, ' enter the type of system :',/,5x,'0 = general',
1      /,5x,'1 = two flipping water molecules',/,5x,
2      '2 = a planar polygon of spins',/,5x,
      accept *,isys
c
      if(isys .eq. 1) go to 30
c
c
c      questions for the general and planar-polygon cases .....
c
c
      type 502
502      format(//, ' how many spins ? (.lt. 7) ',/$)
      accept *,n
c
      if(isys .eq. 2) go to 15
c
      type 503
503      format(//, ' enter the x, y, and z coordinates of each nucleus ',
1      '(in Angstroms) :',/,)
c
      do 12 i=1,n
      type 504,i
504      format(5x,'nucleus ',i1,' : ',/$)
      accept *,(coors(i,j), j=1,3)
12      continue
c
      go to 18
c
c
15      type 505
505      format(//, ' enter the nearest-neighbor separation in Angs. : ',/$)

```



```

type 512
format(//,' enter the intramolecular H-H distance in Angs. : ', $)
accept *,rhh

c
type 513
format(//,' enter the inter-water separation in Angs. : ', $)

accept *,rwv

c
type 514
format(//,' enter polar angles theta and phi (in degs.) describing'.
1 /,' the position of water-2 relative to water-1 : ', $)
accept *,thetaw,phiw

c
type 515
format(//,' enter polar angles theta and phi (in degs.) describing'.
1 /,' the orientation of the H-H vector in water-2 : ', $)
accept *, theta2,phi2

c
n=4

c
dd(1)=dconst / rhh**3
dd(2)=dconst / rwv**3
dd(3)=dd(2)
dd(4)=dd(2)
dd(5)=dd(2)
dd(6)=dd(1)

c
theta(1)=0.0
theta(2)=thetaw / rad57
theta(3)=theta(2)
theta(4)=theta(2)
theta(5)=theta(2)
theta(6)=theta2 / rad57

c
phi(1)=0.0
phi(2)=phiw / rad57
phi(3)=phi(2)
phi(4)=phi(2)
phi(5)=phi(2)
phi(6)=phi2 / rad57

c
print 501
print 602, lags
print 511
print 512
print 518, rhh
518 format(f10.3)
print 513
print 518, rwv
print 514
print 519, thetaw,phiw
519 format(2f10.3)
print 515
print 519, theta2,phi2

```

```

c
c
c
35  type 555
555  format(//,' is there rapid motion around the z axis ?',/,
      1  ' (0=no,1=yes) ', $)
      accept *,imot

      type 573
573  format(' for no visual output of matrices, enter -1 here ')
      accept *,mview


c
c
c
type 520
520  format(//,' in which "spec" file should data be stashed ?',
      1  ' /.' (for no spectrum storage, enter -1) ', $)
      accept *,ifl

c
      if(imot .ne. 0) print 556
556  format(//,' THERE BE RAPID MOTION AROUND THE Z AXIS, MATEY')
      print 520
      print 602, ifl

c
      nst=2**n
      nml=n-1
      np1=n+1
      ncp=n * nml / 2
      do 38 k=1,ncp
38  dd(k)=dd(k) / 4

c
c
c
      generate and arrange the spin-product states .....
c
      call numsort(numb,n,nst)
c
      k=0
      do 45 js=1,np1
      is=np1 - js
      do 40 j=1,nst
      if(numb(2,j) .ne. is) go to 40
      k=k+1
      lst(1,k)=numb(1,j)
      lst(2,k)=is
40  continue
45  continue

c
c
c
      set up the untruncated dipolar Hamiltonian .....
c
      do 100 m=1,nst
      do 100 l=1,m
      lm=indx(1,m)
      h(lm)=0.0

```

```

c      if(1 .ne. n) go to 60
c
c      diagonal "A" terms ....
c
      msk=1
      do 50 k=1,n
        isp(k)=1
        if((1st(1,1) .and. msk) .ne. 0) isp(k)=1
50      msk=msk + msk
c
      kk=
      do . 1=1,nml
        dr . j=i+1,n
        v . n+1
          s i=cos(theta(kk))
          z=3*costh*costh - 1
          /lm=h(lm) - dd(kk) * p2 * isp(j) * isp(i)

55      continue
      go to 100
c
c
c      off-diagonal terms ....
c
60      jw=1
      jsp=0
      msk=1
      do 75 k=1,n
        if((1st(1,1) .and. msk) - (1st(1,m) .and. msk)) 70,75,70
70      jsp=jsp + 1
        iflip(jw)=k
      jw=2
75      msk=msk + msk
c
      if(jsp .gt. 2) go to 95
      if(jsp .eq. 1) go to 80
c
      kd=kfunk(iflip(1),iflip(2))
      if(1st(2,1) .ne. 1st(2,m)) go to 78
c
c      "B" flip-flop terms ....
c
      costh=cos(theta(kd))
      h(lm)=dd(kd) * (3*costh*costh - 1)
      go to 95
c
c      "E" terms ....
c
78      if(1mot .ne. 0) go to 95
      sinh2=sin(theta(kd)) ** 2
      h(lm)= -dd(kd) * 3 * sinh2 * cexp(cmplx(0.0,-2*phi(kd)))
      go to 95
c
c      "C" terms ....

```



```

c
80  if(imot .ne. 0) go to 95
    kfl=iflip(1)
    msk=1
    do 85 k=1,n
      if(k-kfl) 81,85,82
81  kd=kfunk(k,kfl)
      go to 84
82  kd=kfunk(kfl,k)
84  sincos=3 * sin(theta(kd)) * cos(theta(kd))
      kspin=-1
      if((1st(1,1) .and. msk) .ne. 0) kspin=1
      h(lm)=h(lm) - dd(kd) * kspin * sincos * cexp(cmplx(0.0,-phi(kd)))
85  msk=msk + msk
c
c
95  ml=indx(m,1)
    h(ml)=conjg(h(lm))
c
100 continue
c
c
    if(n .gt. 4 .or. mview .lt. 0) go to 105
    title=' THE HAMILTONIAN ..... '

    call hardball(h,0)
c
c
c    now diagonalize the sucker .....
c
105  call heigen(h,u,nst)
c
    do 110 i=1,nst
      ii=indx(i,i)
110  e(i)=real(h(ii))
c
    print 521
521  format('1',//,' ENERGIES IN KHZ .....',//)
    prin. 522, (e(i), i=1,nst)
522  format(f15.4)
c
    if(n .gt. 4 .or. mview .lt. 0) go to 120
    title=' EIGENVECTORS ..... '
    call hardball(u,1)
c
c
c    generate Ix, Iy, and Iz in the spin-product basis .....
c
120  do 150 i=1,nst
      do 150 j=1,nst
        ij=indx(i,j)
        xx(ij)=0.0
        yy(ij)=0.0
        zz(ij)=0.0
        if(i .ne. j) go to 130

```

```

c      zz(ij)=1st(2,i) - n/2.0
      go to 150
c
130    if(iabs(1st(2,i) - 1st(2,j)) .ne. 1) go to 150
      ksp=0
      msk=1
      do 140 k=1,n
        if((1st(1,i) .and. msk) .eq. (1st(1,j) .and. msk)) go to 140
        ksp=ksp + 1
140    msk=msk + msk
c
      if(ksp .ne. 1) go to 150
      xx(ij)=0.5
      if(j .gt. i) yy(ij)=cmplx(0.0,-0.5)
      if(i .gt. j) yy(ij)=cmplx(0.0,0.5)
c
150    continue
c
c      convert lx, ly, and lz to the basis set of the full dipolar Hamiltonian
c
      call uamu(u,xx,nst,wvec)
      call uamu(u,yy,nst,wvec)
      call uamu(u,zz,nst,wvec)
c
      if(n .gt. 4 .or. mvview .lt. 0) go to 160
      title='lx in the dipolar basis .....'
      call hardball(xx,1)
      title='ly in the dipolar basis .....'

      call hardball(yy,1)
      title='lz in the dipolar basis .....'
      call hardball(zz,1)
c
c      calculate frequencies and intensities .....
c
160    dink=0.0001
      p0=n * 2.** (n-2)
c
      k=0
      do 180 i=1,nst
        do 180 j=1,nst
          ij=indx(i,j)
          ji=indx(j,i)
          vvv=s(j) - s(i)
          ppp=real( xx(ij)*xx(ji) + yy(ij)*yy(ji) + zz(ij)*zz(ji) ) / 3
          if(ppp .lt. dink) go to 180
          k=k+1
          if(k .eq. 4097) go to 190
          vv(k)=vvv
          pp(k)=ppp/p0
180    continue
c

```

```

c      sort frequencies and intensities .....
c
190  iover=0
      if(k .gt. 4096) iover=1
      kmax=min0(k,4096)
      do 200 i=1,kmax-1
      do 200 j=i+1,kmax
      if(vv(j) .ge. vv(i)) go to 200
      call switch(vv(i),vv(j))
      call switch(pp(i),pp(j))
200  continue

      vwide = 2.0*(abs(vv(1)))
      type 534, vwide
534  format(' Full scale width of spectrum is ',f10.4,' kHz')
      type 532
532  format(' How big should the spectrum we dump into be ?')
      accept *, v2max
      if (vwide .ge. v2max) v2max = 1.2*vwide

c
c
c      generate a spectrum .....
c
      dv=1024. / v2max
      hzppt=1000./dv
      vmax=v2max/2.0

c
      do 210 i=1,np
210  ss(i)=0.0
c
      do 220 k=1,kmax
      iv=513 + nint(vv(k)*dv)
      if (iv .eq. 1025) go to 220
      ss(iv)=ss(iv) + pp(k)

      vr(iv)=vv(k)
220  continue
c
c
c      output results .....
c
      print 530
530  format('l',/,/,10x,'frequency (kHz)',6x,'intensity',6x,
1    'point #',/,/,10x,15('-'),6x,9('-'),6x,7(' '),/)
c
      k=0
      do 230 iv=1,np
      if(ss(iv) .lt. dink) go to 230
      k=k+1
      print 531, k,vr(iv),ss(iv),iv
531  format(i4,f18.4,f18.6,i11)
230  continue
c

```

```

      if(iover .eq. 1) print 533
533   format(///,' NOTE : there are over 4096 allowed transitions -- ',
1     'lines missing in the table and in the plot')
c
c
      if(if1 .lt. 0) go to 240
c
c
      vmin=-vmax
      print 535, vmin,vmax,hzppt
535   format(///,3x,'spectral range : ',f10.4,' kHz to ',f10.4,' kHz',
1     5x,'(',f9.4,' Hz per point)')
c
      call defile('spec',if1,0)
      write(1,602) np
      write(1,603) hzppt
      write(1,603) (ss(i), i=1,np)
      close(unit=01)
c
c
240   type 539
539   format(///,' another system ?? (0=no,1=yes) ',%)
      accept *,ian
      if(ian .ne. 0) go to 10
c
      print 540
540   format('1',/)
c
c
602   format(16)
603   format(e14.6)
c
      end
c
c
c
c
c
      subroutine switch(a,b)
      c=a
      a=b
      b=c
c
c
      return
      end
c
c
c
c
      subroutine hardball(p,ibasis)
c
c   displays complex matrices (up to 16x16) on one page
c
c       ibasis=0 : spin-product basis

```

```

c      ibasis=1 : other
c      ibasis=-1 : half and half
c
c      complex p(256)
c      dimension mag(16),iph(16),lst(2,16),idp(4,16),e(16)
c      character*64 title
c      common/et/ title,e
c      common n,nst,lst
c
c      indx(i,j)=(j-1)*nst + i
c
c      pi=4.0*atan(1.0)
c      rad57=180 / pi
c
c      do 10 k=1,4
c      do 10 j=1,16
10      idp(k,j)=' '
c
c      print 101, title
101      format('1',///,5x,64a)
c      print 102
102      format(///)
c
c      if(ibasis .eq. 1) go to 20
c
c      set up +'s and -'s to describe direct product states.....
c
c      msk=nst / 2
c      do 15 k=1,n
c      do 14 j=1,nst
12      if(lst(1,j) .and. msk) 12,13,12
c      idp(k,j)=lh+
c      go to 14
13      idp(k,j)=lh-
14      continue
c      msk=msk / 2
15      continue
c      if(ibasis .eq. 0) print 105, ((idp(k,j), k=1,4), j=1,nst)
105      format(11x,16(' ',4a1,'>'))
c
c      if(ibasis .ne. 0) print 106, (e(j), j=1,nst)
106      format(11x,16f7.2)
c
c
c      calculate phase and magnitude for each matrix element, then print....
c
c
c
c
30      print 112
112      format(1x,130(1h-))
c
c      do 50 i=1,nst
c      do 40 j=1,nst
c      ij=indx(i,j)

```

```

      xx=real(p(ij))
      yy=aimag(p(ij))
      zz=cabs(p(ij))
      if(zz .lt. 0.0001) go to 35
      if(xx) 34,31,34
      if(yy) 33,32,32
31      iph(j)=90
32      go to 40
33      iph(j)=-90
      go to 40
34      ph=atan2(yy,xx) * rad57
      iph(j)=ph + sign(0.5,ph)
      go to 40
35      iph(j)=0
40      mag(j)=1000. * zz + sign(0.5,zz)
      if(ibasis .le. 0) print 114, (ldp(k,i), k=1,4),(mag(j), j=1,nst)
114      format(1h0,' <',4a1,'|',1617)
      if(ibasis .eq. 1) print 115, e(i),(mag(j), j=1,nst)
115      format(1h0,f7.2,'|',1617)
      print 116, (iph(j), j=1,nst)
116      format(10x,1617)
50      continue
c
      return
      end

      subroutine defile(name, kk, io)
c
c      opens a file on the disk
c          io=1 for input
c          io=0 for output
c
      dimension m(3)
      m(1)=name
      m(2)=4h0.da
      m(3)=0
c
      m2l=4hl.da
      inc=m2l - m(2)
      m(2)=m(2) + kk*inc
c
      if(io .eq. 0) open(unit=01, name=m, type='new', err=900)
      if(io .eq. 1) open(unit=01, name=m, type='old', err=900)
      return
c
c
900      type 901, kk
901      format(/, ' open error for file ', i1, /)
      return
      end

      subroutine haigen(h,u,nm)
c
c      this subroutine diagonalizes an nm by nm hermitian matrix h by

```

```

c      the Jacobi method and outputs h and the unitary transformation
c      matrix u. the procedure is adapted from subroutine "eigen"
c      in the IBM system/360 scientific subroutine package.
c
      complex h(nm,nm),u(nm,nm),u11,u1m,u1l,umm,th,tu
      nm=n-1
      qn=nm
      range=5.0e-7
      do 20 i=1,nm
      do 10 j=1,nm
10      u(i,j)=0.0
20      u(i,i)=1.0
c
      anorm=0.0
      do 30 i=1,nm
      ii=i+1
      do 30 j=ii,nm
30      anorm=anorm + real(h(i,j)*conjg(h(i,j)))
      if(anorm .le. range) return
      anorm=sqrt(2.0 * anorm)
      anormx=anorm * range / qn
      ind=0
      thr=anorm
c
40      thr=thr/qn
c
50      do 80 l=1,nm
      ll=l+1
      do 80 m=ll,nm
      if( cabs(h(l,m)) .lt. thr ) go to 80
c
      ind=l
      diff=real( h(m,m) - h(l,l) )
      if(diff .eq. 0.0) diff=1.0e-15
      ar=0.5 * atan( 2.0 * real(h(l,m)) / diff )
      ai=0.5 * atan( 2.0 * aimag(h(l,m)) / diff )
      sini=sin(ai)
      cosi=cos(ai)
      sinr=sin(ar)
      cosr=cos(ar)
      u11=cplx( cosr*cosi, sinr*sini )
      u1m=cplx( -sinr*cosi, -cosr*sini )
      u1l=cplx( sinr*cosi, -cosr*sini )
      umm=cplx( cosr*cosi, -sinr*sini )
c
      do 60 j=1,nm
      th= u11*h(l,j) + u1m*h(m,j)
      h(m,j)=u1l*h(l,j) + umm*h(m,j)
      h(l,j)=th
      continue
60
c
      do 70 i=1,nm
      th= umm*h(i,1) - u1l*h(i,m)
      h(i,m)=u1m*h(i,1) + u11*h(i,m)
      h(i,1)=th
      tu= umm*u(i,1) - u1l*u(i,m)
      u(i,m)=u1m*u(i,1) + u11*u(i,m)
      u(i,1)=tu
70      continue
c

```

```

80      continue
c
      if(ind .eq. 0) go to 100
      ind=0
      go to 50
c
100     if(thr .gt. snormx) go to 40
      return
      end
      subroutine numsort(numb,n,nn)
c
c      tabulates the number of 'ones' in the binary representation
c      of integers
c
      dimension numb(2,nn)
      do 20 j=1,nn
      jj=j-1
      numb(1,j)=jj
      kk=1
      ll=0
      do 10 k=1,n
      if((jj .and. kk) .ne. 0) ll=ll+1
      kk=kk+kk
10      continue
      numb(2,j)=ll
20      continue
      return
      end
      subroutine uamu(u,b,n,v)
c
c      performs unitary transformations:      b = u-adjoint * b * u
c
      complex u(n,n),b(n,n),v(n)
c
      call matraml(u,b,n,v)
      call matml(b,u,n,v)
      return
      end
c
c
c
c
c
c      subroutine matml(a,b,n,rv)
c
c      a matrix multiplier:      a = a * b
c
      complex a(n,n),b(n,n),rv(n),s
      do 14 i=1,n
      do 12 j=1,n
      s=0.0
      do 11 k=1,n
11      s=s + a(i,k)*b(k,j)
12      rv(j)=s

```



```

13      do 13 j=1,n
14      a(i,j)=rv(j)
      continue
      return
      end
c

```

```

c
c
c
c

```

```

      subroutine matram1(a,b,n,cv)
c
c      a matrix multiplier:      b = a-adjoint * b
c
      complex a(n,n),b(n,n),cv(n),s
      do 14 j=1,n
      do 12 i=1,n
      s=0.0
      do 11 k=1,n
11      s=s + conjg(a(k,i))*b(k,j)
12      cv(i)=s
      do 13 i=1,n
13      b(i,j)=cv(i)
14      continue
      return
      end

```

Chapter 8: Time-Domain Nuclear Quadrupole Resonance

Nuclei possessing electric quadrupole moments serve as tiny probes of the electric field gradients within molecules and crystals. In general, this electric field gradient has to do with the distribution of electronic and nuclear charges around a given point. The electric quadrupole moment, which interacts specifically with the electric field gradient, is closely associated with the magnetic dipole moment and angular momentum of the nucleus. Thus magnetic resonance experiments are sensitive to the electrical environment at certain nuclear sites. High-field NMR is often used to get at this information, but for polycrystalline or powdered samples it suffers from frequency spreading as discussed in Chapters 1 and 3. In zero field, the quadrupolar spectrum appears without this complication¹. Incidentally, zero-field NMR when applied to quadrupolar nuclei is conventionally called nuclear quadrupole resonance, NQR, or pure NQR.

In covalently bonded systems, NQR can provide information about the bond strength, including inductive or substituent effects, and coordination symmetry. In ionic crystalline systems, NQR can be informative about coordination symmetry and crystal symmetry, and can also probe very sensitively the breaking of the nominal crystal symmetry near dislocations, impurity sites, and other lattice defects.

The quadrupolar interaction is a single-spin interaction. Thus the number of lines in the spectrum increases linearly with the number of inequivalent sites. In this sense it is like the chemical shift in high-field NMR. This is in contrast to the dipolar spectrum, where the number of lines in zero field is nearly an exponential function of

the number of coupled spins. Because of this relative simplicity of the spectrum, combined with sensitivity to molecular structure, zero-field NQR is the area of field-cycling NMR most readily applicable to chemical problems.

The first Section of this Chapter deals with deuterium NQR experiments on isotopically-enriched organic compounds. There we review the theory of a spin-1 nucleus, which applies to ^{14}N as well as to deuterium. The middle Section covers our results for ^7Li and ^{27}Al which, as half-integer spins, require a separate treatment. The final Section describes NQR experiments involving demagnetized spin states.

8.1 NQR of deuterium

To solve the problem of a single spin-1 nucleus in zero field, we first express the Hamiltonian [Equation (2-27)] as a matrix in the basis set of eigenstates of I_z :

$$H_q = A_q \begin{bmatrix} +1 & 0 & -1 \\ 1 & 0 & \eta \\ 0 & -2 & 0 \\ \eta & 0 & 1 \end{bmatrix} \begin{matrix} +1 \\ 0 \\ 0 \\ -1 \end{matrix}, \quad \text{with } A_q = \frac{e^2 q Q}{4}. \quad (8-1)$$

$|0\rangle_z$ is evidently an eigenstate. The other eigenstates and energies are obtained by diagonalizing the 2×2 submatrix involving the $m = \pm 1$ states. Hence:

$$\begin{aligned}
|X\rangle &= (1/\sqrt{2}) [|-1\rangle_Z - |+1\rangle_Z], & E_X &= (1-\eta)A_q, \\
|Y\rangle &= (1/\sqrt{2}) [|-1\rangle_Z + |+1\rangle_Z], & E_Y &= (1+\eta)A_q, \\
\text{and } |Z\rangle &= |0\rangle_Z, & E_Z &= -2A_q.
\end{aligned} \tag{8-2}$$

Using Equation (4-25), and going through some algebraic work, we obtain I_z in this basis set of eigenstates:

$$I_z = \hbar \begin{bmatrix} X & Y & Z \\ 0 & -i \cos \theta & i \sin \theta \sin \phi \\ i \cos \theta & 0 & -i \sin \theta \cos \phi \\ -i \sin \theta \sin \phi & i \sin \theta \cos \phi & 0 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}. \tag{8-3}$$

The spin-1 problem closely resembles the problem of a dipolar-coupled spin-1/2 pair (Sections 6.2 and 6.4). The three energy levels of the spin-1 nucleus are similar to the triplet manifold of the spin-1/2 pair. The spin-1 signal, calculated from Equations (8-3) and (4-24), and then powder averaged, is also similar to that of the spin-1/2 pair [as in Equation (6-20)]:

$$S(t)_{\text{powder}} = \frac{1}{3} \left\{ \cos[2\eta A_q t/\hbar] + \cos[(3+\eta)A_q t/\hbar] + \cos[(3-\eta)A_q t/\hbar] \right\}. \tag{8-4}$$

For static, covalently-bonded deuterium sites, η tends to be small (typically less than 0.1). Therefore, in the zero-field spectrum of three lines, one line is found at a relatively low frequency (conventionally called ν_0). The other two lines (at frequencies ν_- and ν_+) appear as a pair split by the frequency of the low frequency line.

As an experimental example of this pattern, Figure 8.1 shows the zero-field deuterium spectrum of perdeuterated α -glycine ($\text{ND}_3\text{CD}_2\text{CO}_2^-$). The T_1 of the ammonium group is very short, so we detect signal only from the methylene group. From each distinguishable site, we expect three lines of equal intensity. In fact we see seven lines; the lowest frequency line is an impurity, and the six remaining lines are assignable to two distinct sites. If the molecule were in a symmetrical conformation, the two methylene sites would be equivalent; in this solid phase, each molecule is slightly twisted about the methylene-carboxylate bond, so that the two methylene sites are inequivalent.

α -glycine will now serve as a simple example of spin-1 zero-field spectral analysis. The measured line frequencies, in kHz are:

(1) 0.8	(2) 3.38	(3) 7.68	
(4) 118.40	(5) 121.73	(6) 122.89	(7) 130.62.

All lines are 0.60 to 0.90 kHz wide (FWHM). We expect the lines to occur in sets of three, such that $\nu_0 + \nu_- = \nu_+$. The observed frequencies (2), (4), and (5) make up one such set, while (3), (6), and (7) constitute a second. No other combination fits the summation rule within experimental error. From this assignment, we calculate the following quadrupolar parameters for α -glycine:

Site A:	$e^2qQ/h = 160.09 \text{ kHz}$	$\eta = 0.042$
Site B:	$e^2qQ/h = 169.01 \text{ kHz}$	$\eta = 0.091$

Assuming the experimental frequencies are accurate to ± 0.1 kHz, the corresponding uncertainties for e^2qQ/h and η are about ± 0.1 kHz and ± 0.002 respectively. These measurements are in good agreement with the results of single-crystal deuterium NMR studies².

XBL 857-8922

Figure 8.1 Zero-field deuterium spectrum of polycrystalline perdeuterated α -glycine. Each methylene site yields three lines of equal intensity, as predicted by Equation (8-4). The lowest-frequency line is probably due to a sample impurity. The ammonium signal is not observed here because the T_1 of those sites is much shorter than the time required for shuttling the sample between high and low field.

Deuterium nuclei occurring in methyl groups must be treated as a special case. There the rapid rotational motions bring about an averaging of the quadrupolar interactions³. This has three commonly observed effects: (1) All deuterium nuclei in the methyl group are rendered equivalent, with the result: (2) Dipole-dipole couplings within the methyl group (which, incidentally, are motionally averaged) yield resolvable splittings. (3) The largest effect is that the quadrupolar interactions are scaled by about a factor of $-1/3$, that is, $(3\cos^2\theta - 1)/2$ with θ , the bond angle, approximately equal to the tetrahedral angle of -109.5° . Thus methyl NQR signals are to be found at much lower frequency than the ν_- and ν_+ lines of static hydrocarbon sites.

The zero-field ^2D spectrum of polycrystalline perdeuterated dimethylterephthalate, shown in Figure 8.2, illustrates the special behavior of methyl groups. The intense band at 39 kHz is associated with the methyl groups. Near 130 kHz, four relatively weak lines are observed; this indicates that there are two distinct aromatic ring sites, corresponding to those near to and far from the methyl groups. (In the solid state, the molecule is fixed in the *trans* conformation approximately as shown in the Figure.) The low intensity of the aromatic signal is primarily due to the long aromatic T_1 , i.e., long compared to the interval allowed for polarization before the zero-field interval. The peaks near zero frequency are ν_0 transitions from both the aromatic and methyl sites. The maximum of intensity at zero frequency suggests that each methyl group is in a nearly symmetric environment. The ν_0 peaks of the aromatic sites are of low intensity and are obscured by the relatively large methyl ν_0 peak. Thus, on the

XBL 847-3143

Figure 8.2 Zero-field ^2D spectrum of perdeuterated polycrystalline dimethylterephthalate. Four lines are observed around 130 kHz; these correspond to a pair of lines from each of two aromatic ring sites which are inequivalent because of the *trans* molecular conformation in the solid state. The signal near 39 kHz arises from the methyl sites, where the rapid rotational motions cause a decrease in the effective quadrupolar interaction. The disparity in the line intensities is due to the high-field relaxation characteristics; the methyl T_1 is ~ 10 s, and the aromatic T_1 is ≥ 10 minutes, while the high-field polarization interval was 2 minutes.

basis of these data alone, we cannot make a reliable determination of e^2qQ and η for the aromatic sites.

An expanded view of the 39 kHz methyl band appears in Figure 8.3. The first moment (center of gravity) of this band is 39.1 kHz, corresponding to $e^2qQ/h = 52.1$ kHz. Splittings within the methyl spectrum could arise either from a small asymmetry of the averaged electric field gradient, or from dipole-dipole couplings. In this case, the electric field gradient is nearly symmetric; the splittings are mainly due to $^2D-^2D$ dipolar couplings within the $-CD_3$ group. The seven-line stick spectrum in Figure 8.3 is a computer simulation of the dipolar splitting pattern for a $-CD_3$ group in a symmetric environment with $\omega_d/2\pi = 490$ Hz. From the dipolar coupling strength, we calculate a $^2D-^2D$ distance of 1.79Å within the methyl group.

The zero-field spectrum of deuterium in polycrystalline perdeuterated 1,4-dimethoxybenzene is shown in Figure 8.4. This spectrum is roughly similar to that of dimethylterephthalate. Four lines about 134 kHz indicate that there are two inequivalent aromatic sites, as is known from single-crystal x-ray diffraction studies⁴. The pattern around 36 kHz arises from the methyl sites. In this case, peaks near zero frequency are well resolved; two lines are identified as the ν_0 lines of the aromatic sites, and a broad cluster of lines is assigned to the methyl group. The appearance of methyl ν_0 lines displaced from zero frequency indicated that the average electric field gradient is slightly asymmetric. This asymmetry is also evident in the methyl $\nu_{\pm}$ band; dipolar couplings alone cannot explain the pattern of splittings there. From the measured centers of gravity of

Figure 8.3 Methyl region of the NQR spectrum of perdeuterated dimethylterephthalate, expanded to show the structure arising from dipole-dipole couplings within the methyl group. The seven-line stick spectrum is a simulation assuming $\omega_d = 2\pi \times 490$ Hz for each coupling and $\eta = 0$ for the averaged quadrupolar interaction.

XBL 8310-12106

Figure 8.4 Zero-field deuterium NQR spectrum of polycrystalline 1,4-dimethoxybenzene- d_{10} . The upper plot shows the full spectrum. The lower plots show expanded views of the three regions of interest, assignable to ν_Q lines, methyl sites, and aromatic sites, respectively. Peaks correspond to two inequivalent aromatic sites are labeled A and B; these sites differ because of the *trans* molecular conformation, and correspond to positions "near to" and "far from" the methyl groups. The methyl signal here is more complicated than that appearing in Figure 8.3 because the averaged quadrupolar interaction is not symmetric.

the methyl ν_0 and $\nu_{\pm}$ bands, we calculate:

$$\text{Methyl: } e^2qQ/h = 47.9 \text{ kHz} \quad \eta = 0.096 .$$

For the aromatic sites, the experimental line frequencies yield the following quadrupolar parameters:

$$\text{Site A: } e^2qQ/h = 178.5 \text{ kHz} \quad \eta = 0.045 ,$$

$$\text{Site B: } e^2qQ/h = 179.1 \text{ kHz} \quad \eta = 0.067 .$$

The zero-field ^2D spectrum of polycrystalline perdeuterated 1,8-dimethylnaphthalene is shown in Figure 8.5. Components of the signal appear in three distinct bands, just as in the preceding cases of dimethoxybenzene and dimethylterephthalate. The pattern appearing near 35 kHz is similar to that shown in Figure 8.3, and characteristic of methyl groups in symmetric local environments. Aromatic ν_0 , ν_{-} , and ν_{+} lines are observed, although here they overlap in such a way that we have so far been unable to sort the lines out according to the sum rule to get individual values of e^2qQ and η .

There is a similar but worse problem in the case of perdeuterated lauric acid, the spectrum of which is shown in Figure 8.6. The peaks from about 95 to 120 kHz arise from the methylene sites. In view of the chemical similarity of all the methylene sites, one may be surprised to observe such a large range of frequencies; the frequency spreading suggests that different methylene sites along the chain are undergoing different degrees of motion. The linewidths in the methylene band are relatively large also, and this is probably the result of ^2D - ^2D dipolar couplings within each methylene group⁵.

XBL 844-1458

Figure 8.5 Zero-field deuterium spectrum of polycrystalline 1,8-dimethylnaphthalene- d_{12} . The group of peaks around 130 kHz represents signal from the aromatic ring sites. The signal near 35 kHz is associated with the methyl sites.

XBL 844-1459

Figure 8.6 Zero-field ^2D spectrum of polycrystalline perdeuterated lauric acid [$\text{CD}_3(\text{CD}_2)_{10}\text{CO}_2\text{D}$]. The signal from the methyl groups appears around 35 kHz. The methylene signal appears in the range of 95 to 120 kHz; this broad distribution of frequencies probably reflects a range of quadrupolar frequencies along the chain, and this may be related to differences in molecular motions along the chain.

8.2

NQR of nuclei with half-integer spin

From Kramer's theorem⁶, each energy level of an isolated half-integer spin in zero field is doubly degenerate; such a nucleus has $2I+1$ eigenstates, but only $(2I+1)/2$ distinct energy levels.

This may be seen plainly by writing the quadrupolar Hamiltonian [Equation (2-27)] as a matrix in terms of eigenstates of I_z . If the rows and columns are arranged in the order $m = I, I-2, I-4, \dots, -I+1, -I, -I+2, \dots, I-1$, the matrix is clearly block diagonal, with two identical blocks of dimension $(2I+1)/2$. For spin $I = 5/2$, for example, we get

$$H_q = \frac{e^2 q Q}{40} \begin{bmatrix} 5/2 & 1/2 & -3/2 & -5/2 & -1/2 & 3/2 \\ 10 & \eta\sqrt{10} & 0 & & & \\ \eta\sqrt{10} & -8 & \eta\sqrt{18} & & & \\ 0 & \eta\sqrt{18} & -2 & & & \\ & & & 10 & \eta\sqrt{10} & 0 \\ & & & \eta\sqrt{10} & -8 & \eta\sqrt{18} \\ & & & 0 & \eta\sqrt{18} & -2 \end{bmatrix} \begin{matrix} 5/2 \\ 1/2 \\ -3/2 \\ -5/2 \\ -1/2 \\ 3/2 \end{matrix} \quad (8-5)$$

The two blocks have the same eigenvalues, and hence we have a double degeneracy for all energy levels.

For $\eta = 0$, the quadrupolar eigenstates are the same as the eigenstates of I_z . Each state then has a characteristic quantum number m , and only transitions with $\Delta m = \pm 1$ are observable as oscillating magnetizations. Thus only $I - 1/2$ frequencies (positive and excluding zero frequency) are observable for each distinct site.

For $\eta \neq 0$, the off-diagonal terms in $\mathcal{H}_q$ complicate things. The quadrupolar eigenstates are then mixtures of various eigenstates of I_z . Thus transitions are observable between all pairs of energy levels, giving us $(4I^2 - 1)/8$ positive nonzero frequencies. Note however, that the transitions which are allowed only for nonzero η are generally low in amplitude; one cannot expect to see all such transitions in practical circumstances.

For $I = 3/2$, $\mathcal{H}_q$ can be solved without difficulty to get energies and eigenstates; this amounts to diagonalizing a 2×2 matrix. Then the powder-averaged signal obtained by Equation (4-28) is

$$S(\tau) = [3 + 2\cos(\omega_q \tau)] / 5, \quad \text{with } \omega_q = \frac{e^2 q Q}{2\hbar} \left(1 + \frac{\eta^2}{3}\right)^{1/2}. \quad (8-6)$$

Since the eigenstates change as a function of η , it is surprising (at least to the author) that the line intensities are independent of η . This special property does not hold for $I > 3/2$.

The existence of a single nonzero frequency in this signal function means that $e^2 q Q$ and η cannot be uniquely determined from the zero-field NQR spectrum of a spin-3/2 nucleus. Even so, the observed frequency is useful for site identification; one line is observed for each chemically distinct site. This is illustrated in Figure 8.7, which shows the zero-field ^7Li spectra of lithium carbonate, Li_2CO_3 , and lithium sulfate hydrate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. For lithium carbonate, one line is observed; this is consistent with the results of single-crystal x-ray diffraction studies⁷, which indicate one type of lithium site in the unit cell. For lithium sulfate hydrate, two lines are

Figure 8.7 Zero-field NQR spectra of ^7Li in lithium carbonate (above) and lithium sulfate hydrate (below). In the zero-field spectrum of a spin-3/2 species, one line (other than at zero frequency) is observed for each distinct site. The spectrum of Li_2CO_3 indicates one type of site; for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, two sites are indicated. These findings are consistent with those of single-crystal x-ray diffraction studies.

observed, indicating that there are two inequivalent lithium sites in the crystal lattice. This is consistent with the structure known from x-ray diffraction⁸, and consistent also with the results of single-crystal ⁷Li NMR studies⁹.

For $I=5/2$ and $\eta=0$, the powder-averaged signal from Equation (4-28) is

$$S(\tau) = [53 + 32\cos(\omega_q \tau) + 20\cos(2\omega_q \tau)] / 105, \quad (8-7)$$

$$\text{with } \omega_q = 3e^2qQ/20\hbar.$$

For $\eta \neq 0$, the secular equation (a cubic equation for $I=5/2$) would have to be solved to get the energies and then frequencies¹⁰. For small η and $I=5/2$, the following approximations apply:

$$\begin{aligned} \omega_q^{3/2,1/2} &= \langle A_q/\hbar \rangle [6 + (59\eta^2/9)] + O(\eta^4), \\ \text{and } \omega_q^{5/2,3/2} &= \langle A_q/\hbar \rangle [12 - (22\eta^2/9)] + O(\eta^4), \end{aligned} \quad (8-8)$$

for the transitions which derive continuously from the $\pm 3/2 \leftrightarrow \pm 1/2$ and $\pm 5/2 \leftrightarrow \pm 3/2$ transitions, respectively, for $\eta=0$. For nonzero η , a third line of low intensity appears at the sum of the first two frequencies; this corresponds to the $\pm 5/2 \leftrightarrow \pm 1/2$ transition for $\eta=0$. From a measurement of any two of these frequencies (in practice, usually the first two), e^2qQ and η can be determined.

Figure 8.8 shows two experimental examples; at top and center are the zero-field ²⁷Al spectra of potassium alum, $KAl(SO_4)_2 \cdot 12H_2O$, and ammonium alum, $NH_4Al(SO_4)_2 \cdot 12H_2O$. Two of the three transitions

Figure 8.8 Zero-field NQR spectra of ^{27}Al in $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (at top), $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (at center), and a physical mixture of the two (at bottom). The mixture contains 56 mol % potassium alum and 44 mol % ammonium alum. Each distinct site contributes two lines to the zero-field spectrum. The first two spectra indicate the presence of one site in each of the pure samples.

are observed in each case. From the line frequencies and Equation (8-8), we obtain:

$$\text{K alum : } e^2qQ/h = 391 \text{ kHz and } \eta = 0.17 ;$$

$$\text{NH}_4 \text{ alum : } e^2qQ/h = 438 \text{ kHz and } \eta = 0.17 .$$

The spectrum at the bottom of Figure 8.8, obtained with a physical mixture of the two compounds, is intended to show that zero-field NQR could resolve signals arising from inequivalent sites.

At the aluminum sites in this compound, x-ray diffraction studies indicate a cubic symmetry, and the aluminum atoms are octahedrally coordinated by six water molecules. Our measurement of a nonzero quadrupolar interaction rules out the possibility of an exact cubic symmetry about the aluminum atoms, but the relatively low frequency does indicate a near symmetry. High-field aluminum NMR studies of these compounds have been published¹¹.

An interesting minor detail of these aluminum spectra is that the linewidths are unequal. The line broadening here is probably the result of ^{27}Al - ^1H dipolar couplings, which are partially truncated by the quadrupolar interaction¹². Consider the $\eta = 0$ case, using the quadrupolar eigenstates $|m\rangle_2$ for the ^{27}Al spin (and any basis set for the protons). For $\|H_q\| \gg \|H_d\|$, the off-diagonal elements of the dipolar Hamiltonian have no effect to first order, except for those connecting the (degenerate) $m = \pm 1/2$ states. If this implies that the $m = \pm 1/2$ states are spread over a larger range of energies, this would explain the linewidth pattern observed in these experiments.

When dealing with half-integer spins occurring in hydrated compounds, it may often be desirable to deuterate the compound, e.g., by crystallizing it from D_2O . We expect this to greatly reduce the

dipolar broadening¹³, which of course would enable a more accurate determination of the quadrupolar interaction.

8.4 NQR with pulsed magnetic fields

8.4.1 Homonuclear spin systems

Consider the application of a magnetic field pulse to a quadrupolar spin system otherwise in zero field:

$$\begin{aligned} B &= 0 \quad \text{for } t < 0, \\ \vec{B} &= \hat{z}B_1 \quad \text{for } 0 \leq t \leq \tau, \\ B &= 0 \quad \text{for } \tau < t. \end{aligned} \tag{8-9}$$

We shall assume that the pulse amplitude B_1 is sufficiently large that the Zeeman interaction is dominant during the pulse:

$$\|\gamma B_1 I_z\| \gg \|H_q\|, \tag{8-10}$$

and that the pulse length τ is sufficiently short that no local-field evolution can take place during the pulse:

$$\tau \ll 1/\omega_{\max}, \tag{8-11}$$

where $\omega_{\max}$ is the largest natural frequency of the spin system in zero field. Then, for a homonuclear spin system, the effect of the z pulse is simply to rotate the spin state about the z axis by an angle α :

$$\rho(r) = \exp(-i\alpha I_z/\hbar) \rho(0) \exp(+i\alpha I_z/\hbar), \quad \text{where } \alpha = \gamma B_1 r. \quad (8-12)$$

Consider now the case where the initial density operator $\rho(0)$ is stationary, i.e., diagonal in the basis set of zero-field eigenstates. In general, this means

$$[\rho(0), \mathcal{H}_q] = 0. \quad (8-13)$$

In specific cases, $\rho(0)$ may be proportional to $\mathcal{H}_q$ or otherwise functionally dependent on $\mathcal{H}_q$. For a general rotation, the rotated density operator has off-diagonal elements, which evolve after the pulse. Many schemes are possible for detecting this evolving spin order. In the following discussion, we present two simple examples in the context of the practical field cycles shown schematically in Figure 8.9.

Detection of the zero-field evolution may be accomplished by the sudden application of a field in the same direction as the first pulse (along $\hat{z}$). A field cycle for this scheme is illustrated in Figure 8.9(a). We shall call this the "one-pulse" field cycle. The sample starts in high field with $\rho \propto I_z$ (or some other stationary high-field order). Then the field is adiabatically reduced to zero. With well-behaved systems, the zero-field populations are then simply equal to the initial high-field populations. In zero field, the system is pulsed, causing evolution to occur for an interval t_1 . Then an intermediate field is suddenly switched on to lock the z component of magnetization. An adiabatic field shift is made to high-field, and finally the magnetization is measured by high-field NMR methods. By

Figure 8.9 Schematic diagrams of field cycles for pulsed zero-field NQR. The sample is demagnetized by adiabatically shifting the field to zero. The spin system after demagnetization is in eigenstates of the zero-field Hamiltonian. Evolution may be initiated by applying a dc field pulse. After the variable evolution interval the result may be stored by a field step, as in (a), or by a second pulse, as in (b). Then the high field is restored and the NMR signal is recorded.

Equation (4-8), the high-field signal is

$$\begin{aligned} \langle I_z \rangle &= \text{Tr} [I_z \exp(-iH_q t_1/\hbar) \exp(-i\alpha I_z/\hbar) \rho(0) \exp(i\alpha I_z/\hbar) \exp(iH_q t_1/\hbar)] \\ &= \sum_i \sum_j \exp(i\omega_{ij} t_1) \langle i | \exp(-i\alpha I_z/\hbar) \rho(0) \exp(i\alpha I_z/\hbar) | j \rangle \langle j | I_z | i \rangle. \end{aligned} \quad (8-14)$$

For a spin-1 nucleus, all matrix elements of I_z are imaginary [as shown in Equation (8-3)]. The matrix elements of $\rho(0)$ are populations and must be real. From these points, it can be shown that the signal given by Equation (8-14) reduces to

$$\langle I_z \rangle(t_1) = \quad (8-15)$$

$$\sum_i \sum_j i \sin(\omega_{ij} t_1) \langle i | \exp(-i\alpha I_z/\hbar) \rho(0) \exp(i\alpha I_z/\hbar) | j \rangle \langle j | I_z | i \rangle$$

Thus in the sine Fourier transform, all lines should be in phase.

Experimental results obtained by this one-pulse scheme are shown in Figure 8.10 for the deuterium nuclei in perdeuterated polycrystalline 1,4-dimethoxybenzene. For these experiments, the auxiliary coil pulser was modified, by changing the current-limiting resistor to 6 Ω , to increase the available electrical power to about 4000 W; with this, we were able to get a pulse amplitude of 280 G with transition times of 0.7 μs . The sine Fourier transform spectra are plotted here. For small pulse angles, all lines appear in phase as predicted. For larger pulse angles, the lines tend to go out of phase. One might explain this as being due to an experimental inadequacy, e.g., an intermediate field too small or too slowly

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Figure 8.10 Experimental spectra (sine Fourier transforms) of 1,4-dimethoxybenzene- d_{10} with the one-pulse field cycling scheme of Figure 8.9(a). The pulse angles are: a) $\alpha = 40^\circ$; b) $\alpha = 60^\circ$; c) $\alpha = 90^\circ$; d) $\alpha = 120^\circ$; e) $\alpha = 135^\circ$; f) $\alpha = 180^\circ$. For small pulse angles, all lines appear in phase, as predicted by Equation (8-15).

switched. However this goes against the observation that the methyl signal is farther out of phase than the aromatic signal; the intermediate field should be more effective for the methyl sites, which are more weakly coupled.

An alternative explanation is that we may be detecting some spin order other than I_z back in high field. The intermediate field can store spin order as high-field quadrupolar order, $3I_z^2 - I(I+1)\hbar^2$. The matrix elements $\langle i | 3I_z^2 - I(I+1)\hbar^2 | j \rangle$ are real, so the signal detected by high-field quadrupolar order will appear as cosines rather than sines,

$$\langle 3I_z^2 - I(I+1)\hbar^2 \rangle(t_1) = \quad (8-16)$$

$$\sum_i \sum_j \cos(\omega_{ij}t_1) \langle i | \exp(-i\alpha I_z/\hbar) \rho(0) \exp(i\alpha I_z/\hbar) | j \rangle \langle j | 3I_z^2 - I(I+1)\hbar^2 | i \rangle.$$

i.e., 90° out of phase with the signal we would ordinarily expect [by Equation (8-15)]. The pulsed spin-locking detection sequence used for these experiments may well be detecting high-field quadrupolar order in addition to Zeeman (I_z) order; to the extent that it is, we expect to see components of the signal with somewhat arbitrary phases.

An alternative idea for detection of pulsed NQR is to apply a second pulse after the evolution interval, as Figure 8.9(b) shows. We shall refer to this as the "two-pulse" experiment. Just as the first pulse transforms some of the population spin order into coherences, the second pulse should transform some portion of the coherences back into populations. After adiabatic remagnetization, the population

differences are measurable by high-field NMR techniques. Assuming that the detected spin order is proportional to the order with which we started, the high-field signal is now given by

$$\begin{aligned} \langle W \rangle \propto \text{Tr} [& \rho(0) \exp(-i\alpha' I_z/\hbar) \exp(-i\tilde{H}t_1/\hbar) \exp(-i\alpha I_z/\hbar) \\ & \times \rho(0) \exp(i\alpha I_z/\hbar) \exp(i\tilde{H}t_1/\hbar) \exp(i\alpha' I_z/\hbar)] . \end{aligned} \quad (8-17)$$

If $\alpha' = -\alpha$, then the signal takes on a particularly simple form:

$$\langle W \rangle \propto \sum_i \sum_j \cos(\omega_{ij} t_1) | \langle i | \exp(-i\alpha I_z/\hbar) \rho(0) \exp(i\alpha I_z/\hbar) | j \rangle |^2. \quad (8-18)$$

In the cosine Fourier transform, all lines should be in phase.

Experimental spectra obtained by this scheme are displayed in Figure 8.11 for polycrystalline perdeuterated 1,4-dimethoxybenzene. For the $-\alpha$ pulses, we actually used $2\pi - \alpha$ pulses. The lines appear in phase for small pulse angles, but they deviate from "correct" phase for larger pulse angles. This suggests that the second pulse is storing some kind of spin order other than $\rho(0)$, which in the adiabatic remagnetization would be transformed into high-field quadrupolar order and subsequently detected.

As this discussion of unexpected line phases suggests, a general problem with either of the pulsed NQR schemes of Figure 8.9 is that we may not know or be able to calculate the spin order which is prepared and detected by adiabatic field shifts. In fact, in practice we have found it difficult to predict or analyze the observed line phases and intensities. However the frequency information is still accurate and interpretable, since the observed frequencies depend only on the local

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Figure 8.11 Experimental spectra (cosine Fourier transforms) of 1,4-dimethoxybenzene- d_{10} with the two-pulse field cycling scheme of Figure 8.9(b). For each of these, we set $\alpha' = 2\pi - \alpha$ to approximate $\alpha' = -\alpha$. The pulse angles are: a) $\alpha = 30^\circ$; b) $\alpha = 45^\circ$; c) $\alpha = 75^\circ$; d) $\alpha = 90^\circ$.

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Figure 8.11 Experimental spectra of 1,4-dimethoxybenzene- d_{10} in the $(\alpha, -\alpha)$ two-pulse experiment. The pulse angles are:
e) $\alpha = 120^\circ$; f) $\alpha = 135^\circ$; g) $\alpha = 150^\circ$; h) $\alpha = 180^\circ$.

interactions.

Some articles describing similar or related field cycling experiments with pulsed fields have recently been published¹⁴.

8.4.2 Heteronuclear spin systems

With heteronuclear spin systems, the pulsed NQR schemes shown in Figure 8.9 have two new and useful properties:

(1) The field pulses rotate the spin species by different amounts, according to their gyromagnetic ratios. For a two-spin (I-S) system, we have

$$\alpha_I = \gamma_I B_1 \tau \quad \text{and} \quad \alpha_S = \gamma_S B_1 \tau . \quad (8-19)$$

In practical terms, this means that we can manipulate the two spin species independently.

(2) The adiabatic field shifts allow the spin species to communicate, i.e., to exchange spin order, at or near zero field. This allows transfer of polarization from one nuclear species to another prior to the evolution interval. Also, after the evolution interval, it allows the transfer of signal from one species to another for subsequent detection. This is particularly important where protons are involved, since the initial polarization of the protons is relatively large, and since the proton high-field NMR signal can be obtained with relatively good sensitivity.

One way to view the polarization transfer is illustrated in Figure 8.12, which is a simplified graph of natural frequencies vs.

Figure 8.12 Transition frequencies as a function of field strength for a system of protons and deuterons. Where the proton and deuteron frequencies match, as indicated by the circled regions, a transfer of polarization from one species to the other can take place. In field cycling experiments involving demagnetized spin systems, this polarization transfer allows, for example, the deuterium NQR spectrum to be detected indirectly through the protons. This can bring about a substantial enhancement in sensitivity.

magnetic field, for a system made up of deuterons and protons. For protons, the transition frequencies are determined primarily by the Zeeman interaction, and hence they occur near the proton Larmor frequency (or integer multiples thereof). The deuteron transition frequencies are determined in a more complicated manner by the combined Zeeman and quadrupolar interaction. At certain fields, there is a frequency match (*i.e.*, spin-spin resonance, also termed "level crossing") between the two species, where the two can exchange polarization without violating energy conservation laws. Some interaction is required to make such an exchange, and that is the dipole-dipole coupling between the two spin species. As we attempt an adiabatic field shift with this system, level crossings occur; at each one, polarization is transferred. Assuming the protons initially have a high polarization, after demagnetization, the quadrupolar spins will have gained a comparable polarization. The two-pulse field cycle stores the NQR signal as quadrupolar-spin polarization. In that experiment, level crossings during the adiabatic remagnetization transfer this spin polarization to the protons. Thus the high-field signal of the protons is modulated according to the zero-field evolution of the quadrupolar spin species. Polarization transfer in field cycling is well known in frequency-domain NQR¹⁵. The same idea is also used in cross-relaxation studies¹⁶.

Figure 8.13 shows a spectrum obtained by the two-pulse experiment with proton detection on a polycrystalline sample of 1,4-dimethoxybenzene, deuterated to the extent of 60 to 70% at the ring sites only. The sharp lines are deuterium NQR lines from the aromatic ring sites, detected indirectly by their effect on the

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Figure 8.13 Zero-field deuterium spectrum of 1,4-dimethoxybenzene, obtained by pulsed field cycling with indirect detection through the protons. The sample was ~65% deuterated at the ring sites only. The proton signal, which would normally appear below ~40 kHz, has been reduced by using $\sim 2\pi$ pulses for the protons. (This spectrum was provided by J. M. Millar and A. M. Thayer.)

protons. With arbitrary pulse lengths, the protons would ordinarily make their own contribution to the zero-field spectrum, usually as a broad line from zero to ~ 40 kHz. For this experiment, however, the pulse lengths were adjusted to minimize the proton response, i.e., α and α' for the protons were nearly integer multiples of 2π . Thus only a trace of the proton signal is found at the lower frequencies. This selectivity may prove particularly important for deuterium NQR studies, where the ν_0 lines would usually be obscured by a large proton response.

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Chapter 9: NMR in Low Fields

Nuclear magnetic resonance (NMR) spectroscopy is usually done in large magnetic fields, so that the Zeeman interaction is by far the strongest spin interaction. Hence the NMR signals are observed only around the Larmor frequency ω_0 , corresponding to transitions of $\Delta m = \pm 1$ between the stationary states $|m\rangle$ of the Zeeman interaction. When internuclear dipole-dipole interactions or nuclear quadrupolar interactions are present, the usual result is merely a splitting or spreading of the resonance at ω_0 .

When the static applied field is low, such that the Zeeman interaction is only a few times larger than the local dipolar and quadrupolar interactions, the situation is more complicated. The local interactions are then a major perturbation on the Zeeman interaction, and the stationary spin states are mixtures of the various states $|m\rangle$. This allows transitions to be observed at several integer multiples of ω_0 .¹ As the applied field approaches zero, resonances at multiples of ω_0 merge, ultimately resulting in a "pure" dipolar or quadrupolar NMR spectrum.

This Chapter presents experimental data which illustrate this transition from high-field to zero-field behavior, for systems of dipolar-coupled protons, with applied fields in the range of 0 to 18 G.

9.1 Experimental technique and apparatus

With liquid samples in uniform fields, low-field NMR experiments can be conducted entirely in low field with moderate sensitivity².

For solids, this approach is impractical; the sensitivity is far worse because of the much larger signal bandwidth. However low-field NMR in solids can be accomplished by field cycling; most such work has been done by frequency-domain techniques³.

In this work, we take the time-domain field cycling approach to low-field NMR, using the technique outlined in Figure 9.1. In each field cycle, the sample is initially magnetized in a large field (about 43 kG), assumed parallel to $\hat{z}$. Then the sample is brought adiabatically to an intermediate field, B_1 (100 G), still along $\hat{z}$ and large enough that there is no significant demagnetization. The intermediate field is suddenly switched to a low field level, B_2 (0 to 18 G), oriented along $\hat{z}$, whereupon the spins begin to evolve under the combined Zeeman and dipolar interactions. After a set interval at the low field level, the intermediate field is suddenly restored, thus fixing the x-magnetization amplitude. After adiabatically restoring the high field, the magnetization can be measured by pulsed NMR methods. We use the multiple echo sequence illustrated in Figure 5.5(c), with phase cycling to compensate for baseline artifacts. The field cycle is repeated with a variable low-field interval to measure the magnetization as a function of time. Finally the data are Fourier transformed to get the low-field spectrum.

Figure 9.1 shows what is termed a transverse experiment, where the initial magnetization is perpendicular to the applied field. When the experiment is modified so that $\vec{B}_1$ and $\vec{B}_2$ are both parallel to $\hat{z}$, it is referred to as longitudinal.

The apparatus is essentially like that described in Chapter 5 for

Figure 9.1 Field cycle for low-field NMR. The sample is removed from the high field magnet B_0 to an intermediate field B_1 which is suddenly replaced by a low field B_2 . The magnetization evolves according to the combined local and Zeeman interactions for a time t_1 . Then the evolved magnetization is stored by reapplying the intermediate field. After restoring the high field, the magnetization is measured by pulsed NMR methods.

zero-field NMR, but with the addition of an extra magnet coil to provide a spatially uniform, low-amplitude static field (B_z in the above description). This coil is of a square Helmholtz design⁴, with two 27 cm $\times$ 27 cm square windings, each of 27 turns of 16 AWG (0.137 cm diameter) copper wire, set 14 cm apart on a box-shaped frame. The low-field coil is thus designed to fit around the other coils and field-cycling apparatus in either of two orientations, to produce a field either parallel or perpendicular to the other applied fields. During the experiments, the low-field coil was powered continuously by a current-regulated supply providing 0 to 10.0 amps.

9.2 Theory of transverse NMR at an arbitrary field level

Before the low-field interval, the Zeeman interaction is dominant. Thus the reduced density operator at that point is approximately

$$\rho = I_x, \quad (9-1)$$

to within a constant of proportionality, using the high-temperature approximation, and assuming there is only a single spin species. The field is suddenly switched to the low level at $t=0$, so for $t \geq 0$,

$$\rho(t) = \exp(-i\mathcal{H}t/\hbar) I_x \exp(i\mathcal{H}t/\hbar), \quad (9-2)$$

where $\mathcal{H}$ is the total low-field Hamiltonian, in this case the sum of $\mathcal{H}_z$ and $\mathcal{H}_2$, the Zeeman and local Hamiltonians. After an evolution

interval of t_1 , we observe the magnetization μ_x , proportional to I_x :

$$\langle \mu_x \rangle(t_1) \propto \text{Tr} \left[\exp(-i\mathcal{H}t_1/\hbar) I_x \exp(i\mathcal{H}t_1/\hbar) I_x \right]. \quad (9-3)$$

We denote the energies and eigenstates of $\mathcal{H}$ as E_i and $|i\rangle$ respectively. Then Equation (9-3) can be written as

$$\langle \mu_x \rangle(t_1) \propto \sum_i \sum_j \cos(\omega_{ij}t_1) |\langle i|I_x|j \rangle|^2, \quad (9-4)$$

with $\omega_{ij} = (E_j - E_i)/\hbar$.

This is similar to the zero-field signal function, Equation (4-23). In this case, however, the energies and eigenstates of the total Hamiltonian are orientation dependent and not easily obtained. In the high-field limit, perturbation theory can be used to get a simple result. For two identical spin-1/2 nuclei, there is an analytic solution for the energies and eigenstates at any field level⁵. In any other case, the energies and eigenstates must be found numerically or by approximate methods. For example, for spin systems of moderate complexity, this can be done by numerically diagonalizing the total low-field Hamiltonian matrix.

To analyze the orientation dependence of the signal, we first define the molecular frame: $\hat{X}$, $\hat{Y}$, and $\hat{Z}$ are selected so that the local Hamiltonian, when expressed in that frame, is independent of the orientation of the molecule. A rotation $R(\alpha, \beta, \gamma)$ would rotate the molecular frame to the lab frame. Thus, in the molecular frame, the direction of the external field ($\vec{B}_0$, along $\hat{z}$) is given by the polar

angles α and β (specifying azimuth and declination, respectively). The Hamiltonian, energies, and eigenstates are functions of α and β . In the transverse experiment, the signal for a particular orientation depends also on the third angle, γ , which specifies the direction of the detector axis $\hat{k}$ in the molecular frame: this is unusual since only two of the Euler angles are needed in ordinary zero-field or high-field NMR.

In the high-field limit, each state $|i\rangle$ has a definite value of m , and only transitions with $\Delta m = \pm 1$ are observed in the transverse experiment. In finite (but large) fields, however, the Zeeman eigenstates are slightly mixed, so that each state $|i\rangle$ looks like

$$|i\rangle = |m\rangle + \sum_{m' \neq m} \epsilon_{m'} |m'\rangle, \quad (9-5)$$

with $\epsilon_m \ll 1$. Thus transitions are weakly allowed at integer multiples of the Larmor frequency. The problem can be treated by a perturbation approach to get the eigenstates $|i\rangle$ and then the line intensities. It has been shown^{3d} that the relative line intensities I , in the high-field limit, are approximately:

$$I \approx \langle \|H_x\| / \|H_z\| \rangle^2, \quad 1, \quad \langle \|H_x\| / \|H_z\| \rangle^2, \quad \langle \|H_x\| / \|H_z\| \rangle^4, \quad \text{etc.},$$

for $\omega \approx \quad 0, \quad \omega_0, \quad 2\omega_0, \quad 3\omega_0, \quad \text{etc.}$

9.3 Experimental results for proton spin systems

Figure 9.2 presents transverse proton NMR spectra of polycrystalline barium chlorate hydrate, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, in zero field

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Figure 9.2 Powder patterns for barium chlorate hydrate (observing protons) at different magnetic fields, obtained using the sequence shown in Figure 9.1. In zero field, lines at zero frequency and $3\omega_d/2$ are observed. As the field is increased, a Pake pattern emerges together with the $\Delta m = 2$ overtone transition.

and various static applied fields up to 18.0 G. The H_2O molecules in this compound are relatively far apart in the crystal lattice, so they behave nearly like isolated spin-1/2 pairs. As the field increases, the simple zero-field spectrum splits and then spreads out. At 18 G, the spectrum includes a recognizable "Pake pattern"⁶ near the Larmor frequency, and a relatively narrow pattern just above twice the Larmor frequency. This is consistent with our expectations; in high field, the $\Delta m = \pm 1$ transitions are split to first order by the dipolar perturbation; for spin-1/2 pairs (or isolated spin-1 nuclei) in high field, the $\Delta m = \pm 2$ transition is weakly allowed and shifted to second order, so a relatively narrow powder pattern appears near $2\omega_0$. For ^{14}N nuclei in solids, the $2\omega_0$ transition can be observed by overtone NMR spectroscopy⁷; for deuterium in solids, that transition is accessible by double-quantum NMR⁸. The ordinary high-field NMR spectrum of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ (at ~ 43 kG) may be found in Figure 1.2 for purposes of comparison.

Low-field proton NMR spectra of silver acetate are shown in Figure 9.3. The protons here are influenced most strongly by the dipolar couplings within each methyl group. For isolated methyl groups in the high-field limit, we expect the powder spectrum to appear as a Pake pattern with a relatively narrow peak at its center⁹. At ~ 18 G (Figure 9.3 at bottom) we see broad and narrow components, but the broad pattern is not recognizable as a Pake pattern. This is probably due to dipolar broadening. It would be interesting to repeat these experiments with an isotopically diluted sample, as in the zero-field experiments discussed in Section 7.2, to get better resolution.

Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, is an example of a "crowded" multi-

Figure 9.3 Proton spectra of silver acetate in zero and low fields. For the methyl group, some of the transitions are not split or shifted by the intramolecular dipolar interactions, so the spectrum includes a narrow component at all applied fields.

spin system, where the dipolar couplings result in a broadening of the proton NMR line, but no resolvable structure in high field or zero field. In Figure 9.4, we present transverse proton spectra of ammonium sulfate in zero field and low fields up to 18 G. The prominent peak, which is at ω_0 , appears to change little in shape or intensity as a function of field strength. In the high-field limit, the intensities of the peaks at $2\omega_0$ and $3\omega_0$ are expected to fall off approximately as B_2^{-2} and B_2^{-4} , respectively^{3d}. However, we observe no significant difference in intensity between 9.5 and 18.0 G.

The low-field experiment can be performed with the low field $\vec{B}_2$ parallel to the intermediate field $\vec{B}_1$. In that case, we observe oscillations of the longitudinal magnetization, given by

$$\langle \mu_z \rangle(t_1) = \sum_i \sum_j \cos(\omega_{ij} t_1) |\langle i | I_z | j \rangle|^2. \quad (9-6)$$

At higher fields, the oscillations become smaller, and in the high-field limit the magnetization is locked (*i.e.*, static) along the field. Figure 9.5 presents longitudinal low-field proton spectra of barium chlorate hydrate. A broad pattern about ω_0 , and a narrow pattern near $2\omega_0$, are observed with comparable intensities. Note that the signal-to-noise ratio becomes drastically worse at higher fields, as the magnetization becomes more nearly stationary. In overtone NMR spectroscopy⁷ there is an analogous longitudinal experiment.

Figure 9.4 Proton spectra of ammonium sulfate in zero and low fields. The spectrum here is broad and unresolved at any field, owing to the complexity of the multi-spin dipolar interaction. Lines at harmonics of the Larmor frequency are observable at low fields; in these experiments, the second and third harmonics are observed.

Figure 9.5 Longitudinal proton spectra of barium chlorate hydrate in zero and low fields. As the applied field is increased, it tends to lock the observed magnetization so that little evolution occurs, and thus the sensitivity is diminished.

9.4 Low-field experiments involving demagnetized spin states

In all of the experiments discussed so far in this Chapter, the initial condition and the detected observable have been magnetization operators such as I_x or I_z . Low-field experiments with other initial and detected conditions are possible with the field cycling apparatus. Of course, different initial or detected conditions will not change the observed frequencies, but they do give us some control over the line intensities. The possibility of enhancing the sensitivity when measuring overtone transitions is of particular interest.

Consider, as an example, the experiment shown schematically in Figure 9.6(a); this is the field cycle used by Strombotne and Hahn for studies of low-field NMR¹⁰. In their scheme, the spins are first polarized in a large field, and then adiabatically demagnetized to zero field so that in general $[\rho(0), \hat{H}_d] \neq 0$; for the present, assume that $\rho(0) \propto \hat{H}_d$. The low field is then suddenly applied to start a period of evolution in which a transient, oscillatory magnetization develops. At the end of the evolution interval, the magnetization is locked by suddenly applying a relatively large intermediate field. After return to the high field, the magnetization is detected. The measured signal as a function of low-field evolution time is thus (for a single molecular orientation)

$$\langle \mu_z \rangle(\tau) \propto \sum_i \sum_j \exp(i\omega_{ij}\tau_1) \langle i | \hat{H}_d | j \rangle \langle j | I_z | i \rangle. \quad (9-7)$$

A related experiment is depicted in Figure 9.6(b). Here the initial condition $\rho(0)$ and detected operator $\hat{W}$ both commute with the local

Figure 9.6 Schematic diagrams of field cycles designed for low-field NMR of demagnetized spin systems. In experiment (a), the initially demagnetized state evolves in low field for a time t_1 . The magnetization which develops as a result of this evolution is locked by the intermediate field and subsequently detected in high field. Experiment (b) serves to detect the demagnetized spin order remaining after the low-field interval.

interaction, i.e., $[\rho(0), \mathcal{H}_d] = 0$ and $[W, \mathcal{H}_d] = 0$. The signal in general may be obtained by Equation (4-29). If $W \propto \rho(0) \propto \mathcal{H}_d$, then the signal (for a single orientation) is

$$\langle W \rangle(t) \propto \sum_i \sum_j \cos(\omega_{ij} t_1) |\langle i | \mathcal{H}_d | j \rangle|^2. \quad (9-8)$$

In high field, where the eigenstates have definite values of m , the matrix elements of $\mathcal{H}_d$ are large for pairs of states with $\Delta m = 0, \pm 1$, and ± 2 . Thus we expect the signal function of Equation (9-8) to have components of large intensity at $\omega \approx 0$, ω_0 , and $2\omega_0$, and we expect the intensities to be independent of field strength (in the high-field limit, that is).

As an demonstration of this, we present in Figure 9.7 the proton spectrum of polycrystalline barium chlorate hydrate in a field of about 260 G, obtained by the field cycle of Figure 9.6(b). Note that the lines at ω_0 and $2\omega_0$ are of comparable intensity. We expect a line of comparable intensity to appear also around zero frequency, but here the resolution was insufficient to register it accurately. This kind of low-field experiment is practical for fields up to ~ 1000 G, and may prove useful for investigations requiring sensitive detection of zero-frequency and overtone transitions^{3e}.

Figure 9.7 Proton NMR spectrum of barium chlorate hydrate in a field of 260 G, obtained by the field cycle shown in Figure 9.6(b). In most low-field schemes, the overtone line intensities fall off rapidly as the field is increased. In this experiment, however, the reverse of that situation holds; the $2\omega_0$ overtone transition remains intense as long as the Zeeman interaction is much larger than the local interactions. (These data were provided by J. M. Millar and A. M. Thayer.)

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