An Outline of Quantum Mechanics for Nuclear Magnetic Resonance

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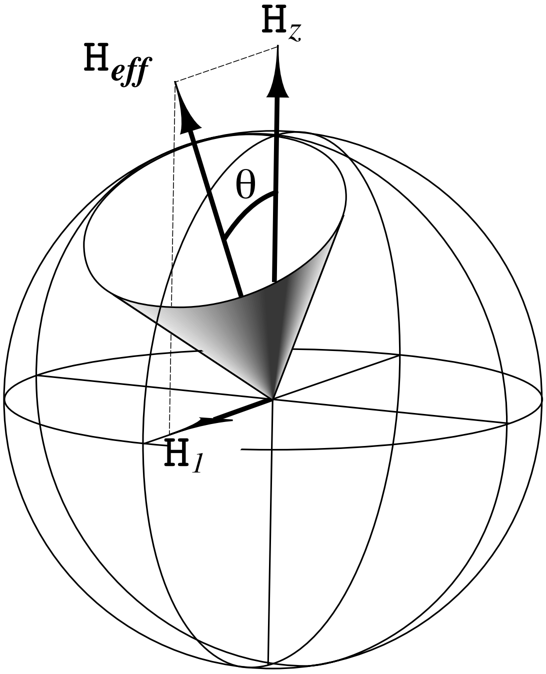


March 1999

Adapted from:
L. Emsley, D.D. Laws and A. Pines,"Lectures on Pulsed NMR (3rd Edition),"

International School of Physics Enrico Fermi, World Scientific, Amsterdam (1999).

1.0. Introduction

This chapter provides a rapid sketch of the quantum mechanics required to perform calculations in nuclear magnetic resonance (NMR). We will not provide too many details, no derivations, and will not answer any philosophical questions. The approach is designed to be *simple* and *pratical*.

1.1. Nuclear Magnetic Resonance

We are going to build a spectrum from first priciples. Figure 1.1 shows the spectrum recorded in the absence of any NMR interactions. (Note that the spectrum is not a flat line because there is "noise" in the signal that can arise from various sources). The first interaction we will consider is the Zeeman effect.

NMR is concerned soley with the motion of nuclear magnetic moments: that is what is detected in the experiment. The nucleus possesses an intrinsic magnetic moment of classical energy

$$E = -\vec{\mu} \cdot \vec{B}, \tag{1.1}$$

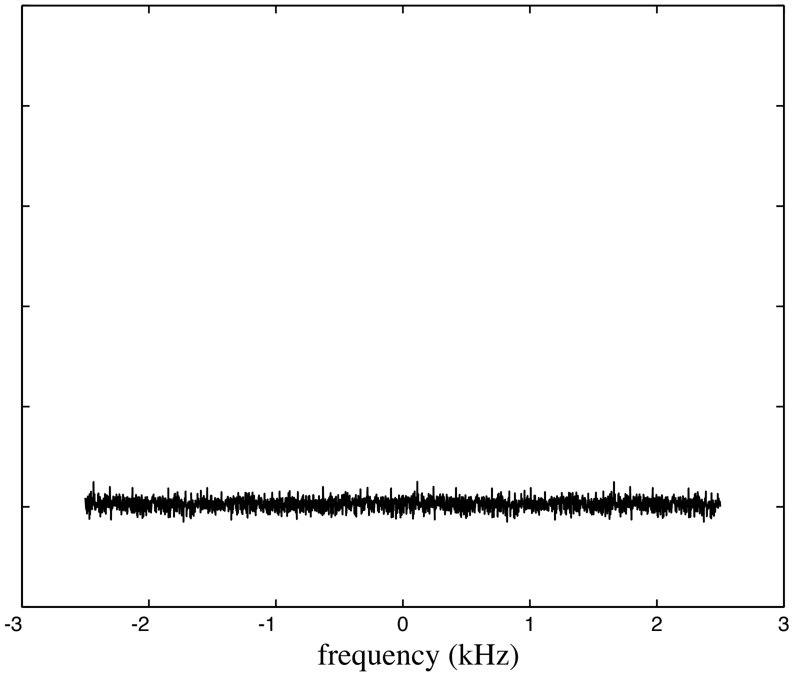


Figure 1.1. An uninteresting NMR spectrum.

where $\vec{\mu}$ is the magnetic moment and $\vec{B}$ an external magnetic field. The corresponding Hamiltonian in quantum mechanics is the Zeeman Hamiltonian

$$\hbar\mathcal{H} = -\vec{\mu}\cdot\vec{B}. \tag{1.2}$$

This Zeeman Hamiltonian is added to the purely nuclear Hamiltonian and it turns out that

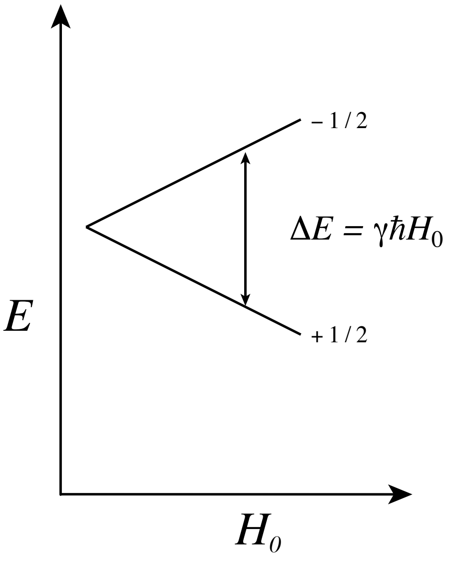
$$\vec{\mu} = \gamma\hbar I, \tag{1.3}$$

where γ is the magnetogyric ratio and where $\vec{I}$ is the operator corresponding to spin. Thus we obtain in a static external magnetic field: $\vec{B} = \left(0,0,B_0\right)$

$$\mathcal{H}_Z = -\gamma B_0 I_z. \tag{1.4}$$

Thus, to understand NMR we need to understand the properties and dynamics of spin operators. For a more detailed methodic treatment see, for example, Goldman.[3] We will stick to the essentials necessary for the story.

Besides a possible orbital angular momentum associated with their wave function in 3D space, some particles posses an intrinsic angular momentum which is called spin. This is the case for the electron, the muon, the quark... (and hence ESR and μSR, but not QSR!). The nuclei are complex aggregates of elementary particles and they have a total angular momentum resulting from the coupling of the orbital and spin momenta of their constituents. From the NMR point of view the nucleus is a point particle, and by extension of the language the total angular



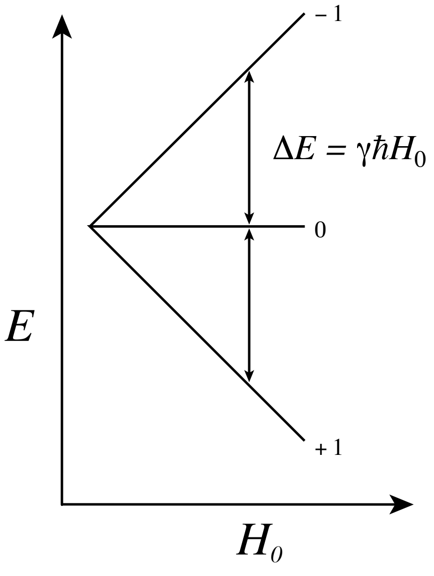


Figure 1.2. Zeeman energy levels as a function of magnetic field strength for a spin I = 1/2 (left), and a spin I= 1 (right).

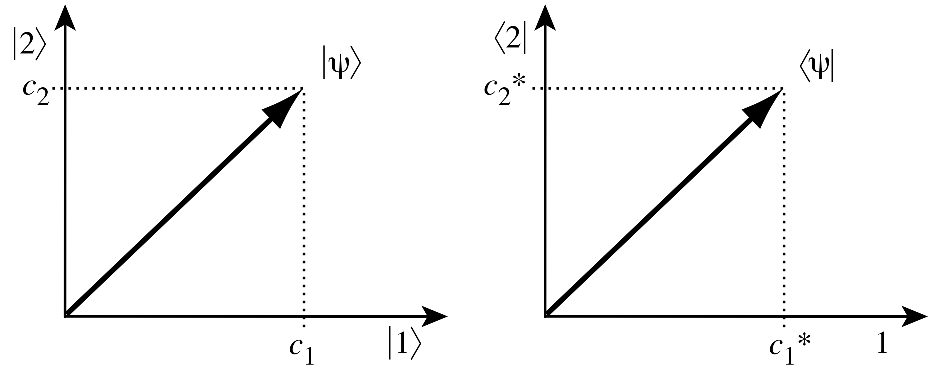


Figure 1.3. Vector representation of the state of a quantum mechanical spin system.

momentum of the nucleus is given the name spin. For example, ^{1}H has a spin $I = \frac{1}{2}$ and can occupy states $m = +\frac{1}{2}, -\frac{1}{2}$. These states are of equal energy in the absence of an external magnetic field. This degeneracy is lifted by the field, as illustrated in figure 1.2a. The nuclei carbon-13, nitrogen-15, phosphorus-31, silicon-29, and others, all have $I = \frac{1}{2}$. Deuterium has a spin $I = 1$ and can occupy states $m = -1, 0, +1$ as illustrated in figure 1.2b. Sodium-23 has a spin $I = \frac{3}{2}$ and can occupy states $m = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$; etc.,

In classical mechanics the angular momentum characterises the instantaneous rotation of the particle with respect to the origin. In fact, the angular momentum operator l_z is a generator of rotations about O_z. The simplest way of characterising the components of a vectorial spin operator is to consider them as generators of rotations in a *spin space* intrinsic to each spin and without any relation to the physical (Kirk) space. This is justified by its consequences which have been verified by many experiments.

1.2. Vectors and Operators in Spin Space

In the vectorial formulation of quantum theory, illustrated in figure 3, the *state* of the system is labelled by a *vector* in a vector space called Hilbert space. A *physical variable* (such as an external magnetic field) is labelled by an *operator* acting in this space. It transforms any vector into another vector.

The Dirac notation was introduced in 1930. In this notation we define a vector called a vector ket (or simply ket), written $|\phi\rangle$. For each ket there is a conjugate vector called a bra, $\langle\phi|$. The scalar product of two vectors $|\psi\rangle$ and $|\phi\rangle$, in this order, is written as a braket, $\langle\psi|\phi\rangle$. *The scalar product in Hilbert space is not commutative*, but it is defined such that $\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*$.

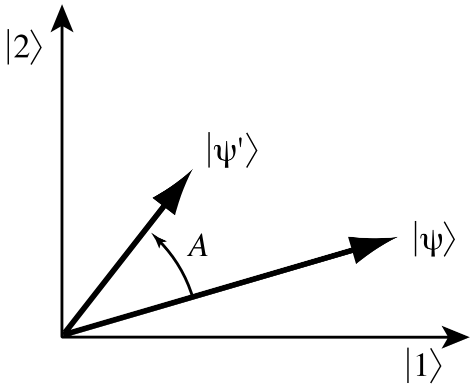


Figure 1.4. The action of an operator A on a state vector is to transform it into another state vector.

Operators acting in Hilbert space.

As we see pictorially in figure 1.4, an operator A acts on a ket or a bra to produce a transformation:

$$\begin{aligned} A|\psi\rangle &= |\psi'\rangle \\ \langle\phi|A &= \langle\phi'| \end{aligned} \tag{1.5}$$

Bases

If the vector space has a finite number of dimensions it is possible to find a complete set of kets which are of unit norm and which have are mutually orthogonal,

$$\langle i|j\rangle = \delta_{ij} \tag{1.6}$$

which constitute an *orthonormal basis*. The basis is complete if is possible to write any ket as

$$|\psi\rangle = \sum_i a_i|i\rangle = \sum_i |i\rangle\langle i|\psi\rangle. \tag{1.7}$$

where the symbol $|i\rangle\langle i|$ is an operator acting on $|\psi\rangle$ and transforming it into its *projection* on $|i\rangle$.

Matrix of an operator.

We find that the set of numbers

$$A_{ij} = \langle i|A|j\rangle. \tag{1.8}$$

constitutes the matrix representation of an operator.

Commutation relations between spin operators.

We consider the spin $I = \frac{1}{2}$. The operator **I** is a vectorial operator and one can choose three mutually orthogonal components I_x, I_y and I_z. Using the fact that they must transform as normal vectors, and also as operators, we can derive commutation relations for the components

$$\begin{aligned} \left[I_z, I_x\right] &= iI_y \\ \left[I_y, I_z\right] &= iI_x \, . \\ \left[I_x, I_y\right] &= iI_z \end{aligned} \tag{1.9}$$

where the commutator $[A, B] = AB - BA$ and reflects the fact that rotations do not normally commute. These relations are characteristic of angular momentum. In fact they define angular momentum as a generator of rotations.

Matrix representation of the operators I_x, I_y and I_z for spin $I = \frac{1}{2}$.

The particular matrix representation, which we need for many calculations, depends on the choice of basis set. Two examples follow for a two-level, one spin $I = \frac{1}{2}$ system. Using the identity

$$1 = |1\rangle\langle 1| + |2\rangle\langle 2| \, . \tag{1.10}$$

to the left and right of an operator A, we obtain

$$A = A_{11}|1\rangle\langle 1| + A_{12}|1\rangle\langle 2| + A_{21}|2\rangle\langle 1| + A_{22}|2\rangle\langle 2| \, . \tag{1.11}$$

where $A_{rs} = \langle r|A|s\rangle$, from which we obtain the complete set of four orthogonal basis operators. That is, with $1 = \alpha$ and $2 = \beta$,

$$
\begin{aligned}
|\alpha\rangle\langle\alpha| &= I^{a} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \\
|\beta\rangle\langle\beta| &= I^{\beta} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \\
|\alpha\rangle\langle\beta| &= I^{+} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\
|\beta\rangle\langle\alpha| &= I^{-} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}
\end{aligned}
\quad . \qquad (1.12)
$$

The operators I^{α} and I^{β} are referred to as polarisation operators and I^{+} and I^{-} are referred to as shift operators. Basis sets are chosen for mathematical convenience (the outcome of the calculation of a physical observable cannot depend on the choice of basis), and a more often used basis set is obtained by taking the linear combinations:

$$
\begin{aligned}
\tfrac{1}{2}\left(|1\rangle\langle 2| + |2\rangle\langle 1|\right) &= I_x = \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
-\tfrac{i}{2}\left(|1\rangle\langle 2| - |2\rangle\langle 1|\right) &= I_y = \tfrac{i}{2}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \\
\tfrac{1}{2}\left(|1\rangle\langle 1| - |2\rangle\langle 2|\right) &= I_z = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\
\tfrac{1}{2}\left(|1\rangle\langle 1| + |2\rangle\langle 2|\right) &= \tfrac{1}{2}1 = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\end{aligned}
\quad . \qquad (1.13)
$$

These matrices are the Pauli matrices, and the operators satisfy the commutation relations of equation (1.9) and have eigenvalues of $\pm\frac{1}{2}$, so they must be I_x, I_y and I_z! Note that the fourth component is invariant under unitary transformation and thus the space is completely defined by I_x, I_y and I_z, which correspond to the components of angular momentum along I_z (polarisation) in the direction of the field and to the transverse components I_x and I_y. The three-dimensional space defined by the basis operators is called Liouville space (the space of operators) as opposed to the complex two-dimensional Hilbert space (the state space).

1.3. The Density Matrix

The commutation relations between the components of angular momentum are a direct consequence of the impossibility of measuring more than one component simultaneously. Consider the double Stern-Gerlach experiment shown in figure 1.5. Once the beam is separated into the basis states $\left|M_z = +\frac{1}{2}\right\rangle$ and $\left|M_z = -\frac{1}{2}\right\rangle$, eigenstates of I_z, of which one is selected and passed through a second magnetic field to separate into the eigenstates

$\left|M_x = \pm\frac{1}{2}\right\rangle$ the spots are

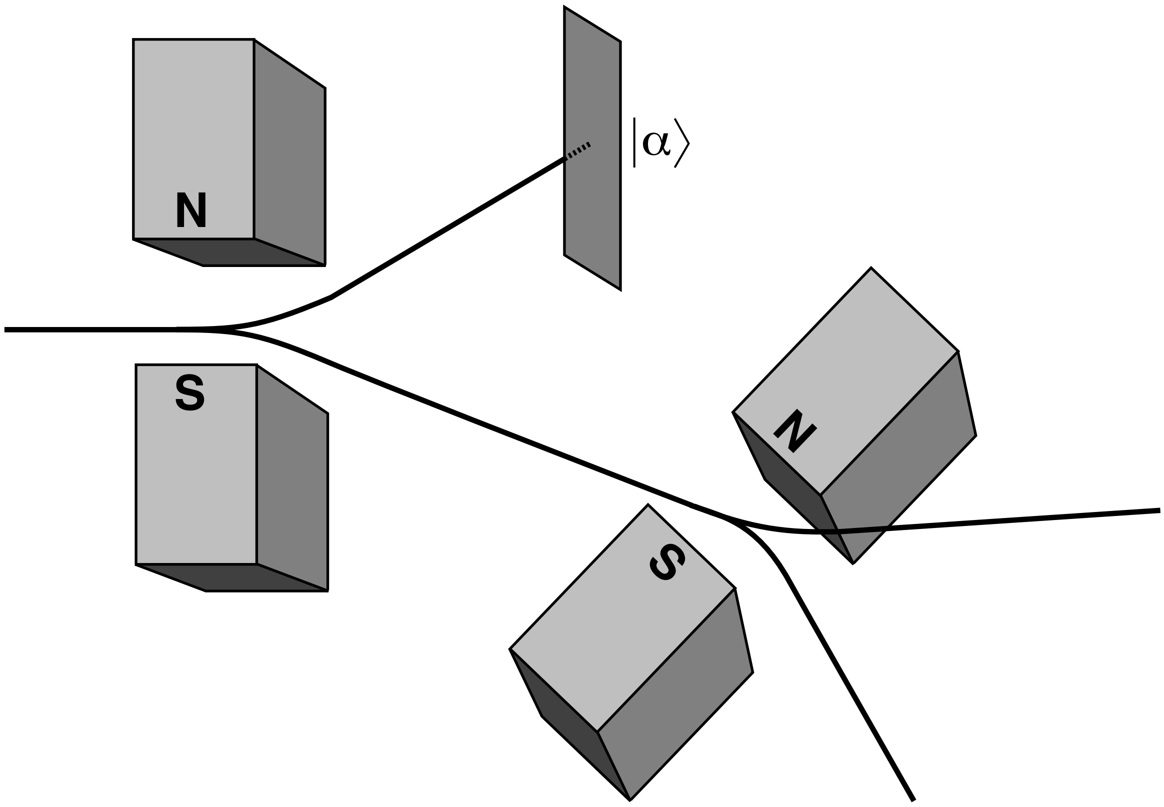


Figure 1.5. A double Stern-Gerlach experiment. See text for details.

always equal. Measurement of M_z renders the angular momentum along any other axis completely uncertain. *However, this doesn't feel like an NMR experiment.*

The problem is that so far we have only treated the behavior of a single isolated spin. We cannot hope to describe the whole ensemble represented by the sample using a ket in a 2^N dimensional Hilbert space of $N \sim 10^{21}$ identical isolated spins $I = \frac{1}{2}$. Even if we could, how would we interpret it? Thus, we adopt a statistical description of the ensemble of subsystems in terms of a representative ket.

We consider an ensemble of identical Hilbert spaces and define a distribution of probabilities

$$P(\psi)\,d\tau\,.$$

for the system to be located in the hypervolume $d\tau$. In a state of ket $|\psi\rangle$ the expectation value of a variable corresponding to an operator A is equal to $\langle\psi|A|\psi\rangle$. For a statistical distribution of kets with the probability law $P(\psi)$, the average value of this variable is equal to

$$\langle A\rangle = \int P(\psi)\langle\psi|A|\psi\rangle d\tau\,. \tag{1.14}$$

So far this is identical to the classical analogue. We now introduce an orthonormal basis. According to the closure theorem $\langle A\rangle$ can be written

$$\begin{aligned}\langle A\rangle &= \sum_{ij}\int P(\psi)\langle\psi|i\rangle\langle i|A|j\rangle\langle j|\psi\rangle d\tau \\ &= \sum_{ij}\langle i|A|j\rangle\int P(\psi)\langle j|\psi\rangle\langle\psi|i\rangle d\tau\end{aligned}\,. \tag{1.15}$$

We now *define* an operator

$$\sigma = \int P(\psi)|\psi\rangle\langle\psi|d\tau\,. \tag{1.16}$$

and equation (1.15) becomes

$$\langle A\rangle = \sum_{ij}\langle i|A|j\rangle\langle j|\sigma|i\rangle\,. \tag{1.17}$$

or else

$$\langle A\rangle = Tr(A\sigma)\,. \tag{1.18}$$

where the trace of a matrix is defined as

$$Tr(A) = \sum_{i}\langle i|A|i\rangle. \tag{1.19}$$

Note that the trace is an essential element in quantum mechanics since the expectation value of an operator is obtained through the trace. The trace has all sorts of useful properties. Most importantly, despite the fact that the diagonal elements of a matrix depend on the basis set used, *their sum is independent of the basis*. Thus the trace may be calculated in the basis in which the calculation is easiest.

All the statistical information on the spectrum is contained in the operator σ. It is called the density matrix.

Note that the density matrix is a Hermitian operator, and therefore its diagonal elements are real numbers, as befits probabilities. In a given basis set a matrix element of σ is

$$\langle i|\sigma|j\rangle = \int P(\psi)\langle i|\psi\rangle\langle\psi|j\rangle d\tau . \tag{1.20}$$

expanding $|\psi\rangle$ in this basis $|\psi\rangle = \sum_i a_i|i\rangle$ yields

$$\langle i|\psi\rangle\langle\psi|j\rangle = a_i a_j^* . \tag{1.21}$$

and we obtain

$$\langle i|\sigma|j\rangle = \overline{a_i a_j^*} . \tag{1.22}$$

where the bar denotes an ensemble average, that is, the elements of the density matrix are *averages* of coeficients.

Physical Significance of the elements of σ.

For a *pure state* written in a given basis

$$|\psi\rangle = \sum_i p_i \exp(i\phi_i)|i\rangle . \tag{1.23}$$

which, when the p_i are positive real numbers, yields a density matrix with elements of the form

$$\begin{aligned} \langle i|\sigma|i\rangle &= p_i^2 \\ \langle j|\sigma|j\rangle &= p_j^2 \qquad . \\ \langle i|\sigma|j\rangle &= p_i p_j \exp\{i(\phi_i - \phi_j)\} \end{aligned} \tag{1.24}$$

If niether $\langle i|\sigma|i\rangle$ nor $\langle j|\sigma|j\rangle$ vanish, *nor does* $\langle i|\sigma|j\rangle$. This is a consequence of the fact that the ket $|\psi\rangle$ is a *superposition* of basis states. For a statistical mixture of kets that could be found in an ensemble the off-diagonal element $\langle i|\sigma|j\rangle$ may vanish even if $\langle i|\sigma|i\rangle$ and $\langle j|\sigma|j\rangle$ are both non-zero, for example if the phases ϕ_i and ϕ_j are distributed at random. The existence of a non-zero off-diagonal matrix element means therefore that the phases ϕ_i and ϕ_j are not at random, but retain some *coherence* on the average.

The statistical state of the system described by this density matrix is said to exhibit a coherence between the quantum states $|i\rangle$ and $|j\rangle$ or else that it contains a coherent superposition of these quantum states. *The concept of quantum coherence plays a fundamental and absolutely central role in modern NMR spectroscopy.*

Evolution equation of the density matrix

From the Schrodinger equation

$$\frac{d}{dt}|\psi\rangle = |\dot{\psi}\rangle = -i\mathrm{H}\,|\psi\rangle \tag{1.25}$$

and

$$\frac{d}{dt}\langle\psi| = \langle\dot{\psi}| = -i\langle\psi|\mathrm{H} \tag{1.26}$$

we obtain for the time-derivative of the projection operator on $|\psi\rangle$

$$\begin{aligned}\frac{d}{dt}|\psi\rangle\langle\psi| &= |\dot{\psi}\rangle\langle\psi| + |\psi\rangle\langle\dot{\psi}| \\ &= -i\mathrm{H}|\psi\rangle\langle\psi| + i|\psi\rangle\langle\psi|\,. \\ &= -i[\mathrm{H}\,,|\psi\rangle\langle\psi|]\end{aligned} \tag{1.27}$$

Since this relation is true for any projection operator, it is also true for any linear combination of projection operators, such as the combination that corresponds to the density matrix. We thus obtain *the Liouville-von Neumann equation*

$$\frac{d}{dt}\sigma = -i[\mathcal{H},\sigma]\,. \tag{1.28}$$

Time evolution of the Hamiltonian.

For a time independent Hamiltonian, in a basis of eigenkets of the Hamiltonian,

$$\mathrm{H}|i\rangle = \Omega_i|i\rangle \tag{1.29}$$

we find that the diagonal elelments of σ are constant as a function of time and that the off-diagonal elements of σ oscillate without decaying at a frequency $\Omega_i - \Omega_j$.

For the time-independent Hamiltonain the solution to the Liouville-von Neumann equation is

$$\sigma(t) = \exp\left(-i\mathcal{H}t\right)\sigma(0)\exp\left(+i\mathcal{H}t\right). \tag{1.30}$$

In general, even when the Hamiltonian is time dependent we have

$$\sigma(t) = U(t)\sigma(0)U^{\dagger}(t) \tag{1.31}$$

with

$$U(t) = T\exp\left\{-i\int_{0}^{t}\mathcal{H}(t')dt'\right\}. \tag{1.32}$$

Both of these results are very important.

Equation (1.30) will form the basis of the following calculations. Since the Hamiltonian is Hermitian, $U = \exp\{-i\mathrm{H}\, t\}$ is a *unitary transformation* (i.e., the norm is conserved) which corresponds to a rotation in spin space around an axis defined by the Hamiltonian (we will return to this idea shortly).

Now that we have a way of describing the time evolution of the ensemble, and of calculating observables, we just need to know what σ is.

The density matrix at thermal equilibrium.

The density matrix at thermal equilibrium must be *time-independent*. Therefore it is not surprising that by general arguments we say that the phases are random and that the off-diagonal elements are zero. (The mechanism by which the phases are randomised is T_2 relaxation. The mechanism for relaxation (that is, contact with the lattice) and the validity of the division between "system" and "lattice" is beyond the scope of this work.)

The diagonal elements characterise probabilities of finding the system in any of its possible eigenstates. It can be shown that the probability of finding the system in a state of energy E_i is

$$p_i = A\exp\left(\frac{E_i}{kT}\right). \tag{1.33}$$

The density matrix satisfying these conditions is

$$\sigma = A\exp(-\beta \mathsf{H}) \tag{1.34}$$

with $\beta = \hbar/kT$ which is the inverse spin temperature. In the high-temperature domain, so that $|\beta\Omega_i| << 1$ we obtain by expansion to first order

$$\sigma \approx A(1-\beta \mathsf{H}). \tag{1.35}$$

The validity of keeping first order terms is usually very good. However, to explain certain experiments it is necessary to keep also higher order terms. So far, these experiments only seem relevant to liquid, so for the purposes of solid state NMR it is a good asumption.

We will always be interested in relative quantities, rather than absolutes, so we drop the normalisation factor to obtain

$$\sigma = 1-\beta \mathsf{H} \tag{1.36}$$

and since the unity matrix has no effect (it commutes with everything), we finally obtain with $\beta = -1$

$$\sigma = \mathsf{H} \tag{1.37}$$

1.4. The Zeeman interaction.

We had left the NMR experiment with the Zeeman Hamiltonian of equation (1.4). Now we can write the evolution of the system according to equation (1.31) with

$$U = \exp\{-i\mathsf{H}\, t\} = \exp\{i\gamma H t I_z\} \tag{1.38}$$

which is an operator of rotation around z by an angle $\phi = -\gamma H t$ proportional to time. The evolution is therefore a precession around z with a frequency

$$\omega = -\gamma H \tag{1.39}$$

which is the same result as obtained by the so-called classical approach.[3-6]

Let us now proceed to some detailed calculations. Normally we write the Zeeman Hamiltonian as

$$\mathsf{H}_z = \omega I_z . \tag{1.39}$$

The density matrix at time t is now

$$\sigma(t) = \exp\{-i\omega I_z t\}\sigma(0)\exp\{+i\omega I_z t\} . \tag{1.40}$$

We are interested in the time evolution of the magnetization, or equivalently the spin operators proportional to it. We can obtain an expression for the expectation value of an operator

$$\langle Q\rangle(t) = Tr\left\{U^{\dagger}(t)QU(t)\sigma(0)\right\} \tag{1.41}$$

and when H is independent of time

$$\langle Q\rangle(t) = Tr\{\exp\{i\mathsf{H}\,t\}Q\exp\{-i\mathsf{H}\,t\}\sigma(0)\} \tag{1.42}$$

Thus, we find that the z-component is independent of time

$$\begin{aligned}\langle I_z\rangle(t) &= Tr\{\exp(i\omega I_z t)I_z\exp(-i\omega I_z t)\sigma(0)\} \\ &= Tr\{I_z\sigma(0)\} = \langle I_z\rangle(0)\end{aligned} . \tag{1.43}$$

Why are we doing this?! Why are we so interested in time evolution? NMR is all about time evolution. Most importantly what we detect is the oscillation of magnetization. Oscillating components of magnetization will induce an oscillating voltage in a coil of suitable geometry: This is what we observe. *Thus the time-independent z component does not look very useful.*

We can calculate the evolution of the two transverse components simultaneously if we look at the (non-Hermitian) operator $I_+ = I_x + iI_y$. Thus

$$\langle I_+\rangle(t) = Tr\{\exp(i\omega I_z t)I_+\exp(-i\omega I_z t)\sigma(0)\} . \tag{1.44}$$

simpifies to

$$\langle I_+\rangle(t) = \exp(i\omega t)\langle I_+\rangle(0) . \tag{1.45}$$

using the relation $\exp(i\phi I_z) I_+ \exp(-i\phi I_z) = \exp(i\phi) I_+$.)). We now separate the real and imaginary parts which correspond to the expectation values of I_x and I_y respectively.

$$\begin{aligned} \langle I_x \rangle(t) &= \langle I_x \rangle(0)\cos\omega t - \langle I_y \rangle(0)\sin\omega t \\ \langle I_y \rangle(t) &= \langle I_y \rangle(0)\cos\omega t + \langle I_x \rangle(0)\sin\omega t \end{aligned} . \tag{1.46}$$

This is the case for H along *z*. Note that we have calculated the evolution equations for the expectation values *which do not depend on* $\sigma(0)$.

Our choice of H along *z* was arbitrary and we may generalise to say that evolution is always precession about the Hamiltonian, e.g.,

$$\mathsf{H} = -\gamma\left(H_x I_x + H_y I_y + H_z I_z\right). \tag{1.47}$$

This is true for *any* H at a given instant *t*, whether it is time dependent or not and whether it contains only single spin operators or whether it contains more than three components. Thus, much of NMR calculation is concerned with calculating H, or an "effective H "). Evolution *always* corresponds to precession about a field defined by its components in a $N = 2^n$ dimensional space of operators, as illustrated for one spin $I = \frac{1}{2}$ in figure 1.6. Thus for the spin $I = \frac{1}{2}$ we may generalise

$$\frac{d}{dt}\vec{I} = -\gamma\vec{H} \times \vec{I} = \vec{\omega} \times \vec{I} . \tag{1.48}$$

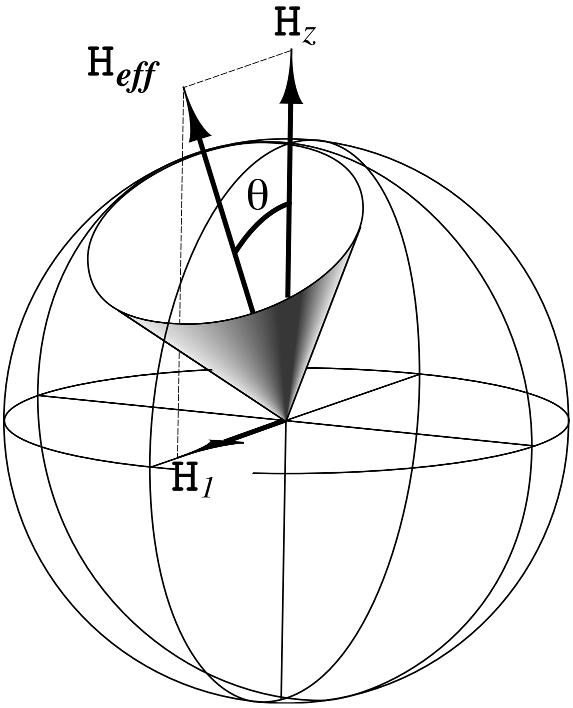


Figure 1.6. The effective Hamiltonian is simply the sum of its orthogonal components. The evolution of the system can always be represented as a rotation around an axis defined by an effective Hamiltonian in a suitably dimensioned space.

This is identical to the "classical" Bloch Equations

$$\frac{d}{dt}\vec{M} = -\gamma\vec{H}\times\vec{M}\,. \tag{1.49}$$

So, *why bother with the quantum treatment?* The quantum treatment is easily adapted to treat multi-spin systems in a larger dimensional space. The Bloch equations treat a single spin in a three-dimensional space.

The spectrum we now observe is shown in figure 1.1. We have found that, even though there is a difference in energy levels induced by the magnetic field, there is no oscillating transverse component. To obtain a detectable signal we must create a *transverse coherence*. (This is not surprising since we have to irradiate the sample one way or another in all forms of spectroscopy). In modern NMR we create the coherence with a *radio-frequency pulse* applied at a frequency close to the Larmor frequency.

Although it is not a very useful example (since in the following it will be assumed by default), we will outline the effect of an rf pulse and the transformation to the rotating frame, since it is a good pratical example of a *change of representation* which renders the Hamiltonian time independent. (Once again it is representative of many NMR calculations). In addition to H_0 we now apply a second field H_1, much smaller in magnitude than H_0 and perpendicular to it, and rotating at a frequency ω.

The *laboratory frame* Hamiltonian is

$$\mathcal{H} = \omega_0 I_z + \omega_1\left(I_x \cos\omega t + I_y \sin\omega t\right). \tag{1.50}$$

where $\omega_1 = \gamma B_1$. In order to render $\mathcal{H}$ time independent we use a change of representation. Starting with

$$\frac{d}{dt}\sigma = i\left[\mathcal{H},\sigma\right].$$

a change of representation goes as follows: given an operator Q we can associate it to another operator $\tilde{Q}$ where

$$\tilde{Q} = U(t)QU^{\dagger}(t) \tag{1.51}$$

where $U(t)$ is defined by the equation

$$\frac{d}{dt}U(t) = iAU(t) \tag{1.52}$$

with A a Hermitian operator which could be time dependent. Thus for $\tilde{\sigma}$ we have

$$\begin{aligned}\frac{d}{dt}\tilde{\sigma} &= \frac{d}{dt}U\sigma U^{\dagger} \\ &= \dot{U}\sigma U^{\dagger} + U\dot{\sigma}U^{\dagger} + U\sigma\dot{U}^{\dagger}\end{aligned} \tag{1.53}$$

and by substitution of $\dot{U},\dot{\sigma},\dot{U}^{\dagger}$

$$\frac{d}{dt}\tilde{\sigma} = iAU\sigma U^{\dagger} - U\left[H,\sigma\right]U^{\dagger} - iU\sigma U^{\dagger}A. \tag{1.54}$$

Since U is unitary it follows that

$$U\left[\mathcal{H},\sigma\right]U^{\dagger} = \left[U\mathcal{H}U^{\dagger},U\sigma U^{\dagger}\right] = \left[\tilde{\mathcal{H}},\tilde{\sigma}\right] \tag{1.55}$$

and we obtain

$$\frac{d}{dt}\tilde{\sigma} = -i\left[\left(\tilde{\mathcal{H}} - A\right),\tilde{\sigma}\right]. \tag{1.56}$$

In the new representation, defined by equation (1.51), the evolution of $\tilde{\sigma}$ is the same as if the system were subjected to an *effective Hamiltonian*

$$\mathcal{H}_{eff} = \tilde{\mathcal{H}} - A. \tag{1.57}$$

Returning to the problem we chose

$$A = \omega I_z \tag{1.58}$$

in equation (1.52) and we have

$$U = \exp(-iAt) = \exp\left(i\omega I_z t\right). \tag{1.59}$$

This change of representation corresponds to a rotation around z at a frequency $-\omega$, hence the name "rotating frame."

The time-dependent term in $\mathcal{H}$ can be written

$$\begin{aligned} I_x \cos\omega t + I_y \sin\omega t &= \exp\left(-i\omega I_z t\right) I_x \exp\left(i\omega I_z t\right) \\ &= U^\dagger(t) I_x U(t) \end{aligned} \tag{1.60}$$

The effective Hamiltonian in the rotating frame is therefore

$$\begin{aligned} \mathcal{H}_{eff} &= \left(\omega_0 - \omega\right) I_z + \omega_1 U U^\dagger I_x U U^\dagger \\ &= \left(\omega_0 - \omega\right) I_z + \omega_1 I_x \end{aligned}. \tag{1.61}$$

This Hamiltonian is time-independent. It is of the form of the Zeeman interaction with a effective field B_{eff} with components

$$\begin{aligned} B_z &= -\left(\omega_0 - \omega\right)/\gamma \\ B_x &= B_1 \end{aligned}. \tag{1.62}$$

When $\omega_0 = \omega$ the effective field is purely transverse and the magnetization precesses around the x axis with a frequency ω_1 corresponding to the magnitude of the applied magnetic field. If the irradiation is applied for a time τ, such that $\omega_1\tau = \pi/2$, I_z *will be converted into pure* I_y, as illustrated in figure 1.7

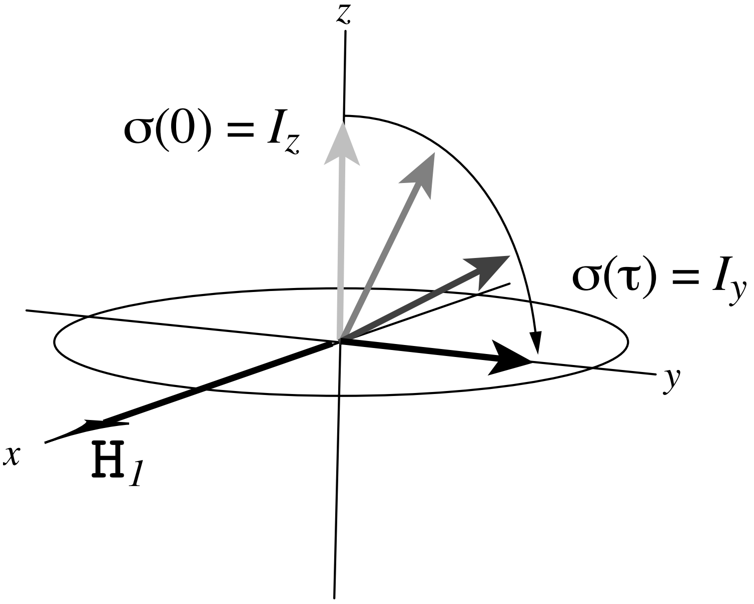


Figure 1.7. In the rotating frame the effect of a radio-frequency pulse applied at the resonance frequency is to rotate the magnetization around the field. If the field is applied for a duration such that $\omega_1\tau = \pi/2$ then the effect is to transform longitudinal magnetisation into a pure transverse coherence.

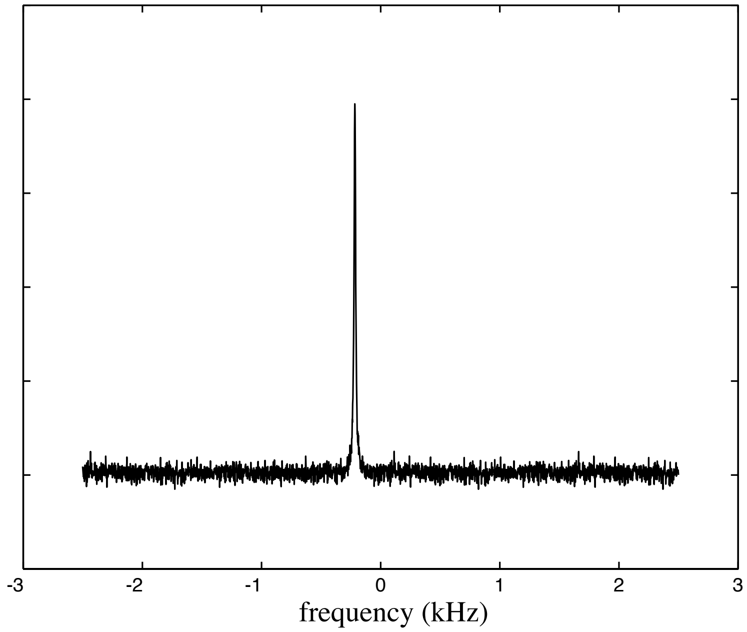


Figure 1.8. A simulated NMR spectrum containing one resonance line. This would be the spectrum obtained for a given nucleus in the presence of only the Zeeman interaction.

If the applied transverse field is then removed, the magnetization will precess purely around I_z in the laboratory frame *at the Larmor frequency*. (In the rotating frame representation it will be *stationary* because the frame is rotating itself at the Larmor frequency), and an oscillating transverse coherence will induce a voltage in a coil with suitable geometry. This time-domain signal is digitized and Fourier transformed to yield a frequency-domain spectrum. (The advantages of time-domain over frequency-domain spectroscopy are so significant that we will not even try to compare the two; many of the experiments discussed in the following pages could not be done with cw spectroscopy).

So we now have a "spectrum", as shown in figure 1.8, containing *one resonance line per nucleus*, with an intensity roughly proportional to γ, and a width which is related to the duration of the time domain signal (the "transverse relaxation time", a mysterious quantity which will not be discussed in more detail here). This is still not a very useful spectroscopy.

1.5. The chemical shift.

Luckily, there is at least one interaction that makes NMR useful. The chemical shift (first observed in 1949-50 for ^{14}N by Procter and Yu, for ^{19}F by Dickinson and for ^{1}H independently by Lindstrom and Thomas. In 1951 Packard and coworkers first published a single spectrum in which three separate ^{1}H resonance peaks were observed in a single compound, ethanol, due to three different types of proton. This is what launched NMR into the world of chemistry.

The external field induces local fields in the electronic structure of a molecule and these currents (both diamagnetic and partially paramagnetic) will tend to add or subtract to the field at the nucleus, thereby modifying the resonance frequency. since the perturbation depends on local electronic structure (especially on inner shell electrons) the frequency shift is likely to be different for nuclei in different electronic environments.

Calculating these chemical shifts is outside the scope of this work (although it is a very dynamic area of research), for the moment we just want to find out what they do to the spectrum, and how to measure them. The chemical shift is expressed as follows:

$$\mathcal{H}_{cs} = \gamma I \cdot \sigma \cdot B . \tag{1.63}$$

where I is the spin vector, H is the external magnetic field vector, and σ represents the coupling between them. It is a 3 x 3 matrix, with a special name, a tensor (in this case the chemical shift tensor). Thus we obtain for H along z,

$$\mathcal{H}_{cs} = \gamma\left(I_x\sigma_{xz}^{lab} + I_y\sigma_{yz}^{lab} + I_z\sigma_{zz}^{lab}\right)B_0. \tag{1.64}$$

where the $\sigma_{\alpha z}^{lab}$ are the elements of the laboratory frame representation of the chemical shift tensor. We will discuss the tensorial nature of the chemical shift shortly in more detail, and see some of its consequences, but for now we will just accept it, as is.

Note that the local fields of most nuclei are very small compared to H_0. In fact, chemical shifts are usually measured in ppm (^{1}H has a chemical shift range for diamagnetic solids of about 10 ppm, ^{13}C about 200 ppm, etc..). Thus the shifts of the energy levels of the local interactions can be treated in first order perturbation theory with respect to $\mathrm{H}_z = \omega_0 I_z$. In this way we truncate the Hamiltonian. In a general way (and one that will be used often elsewhere) we approach truncation by considering an interaction representation that transforms away the effect of the big Hamiltonian $\mathcal{H}_0$ in the time evolution of the density matrix.

$$\sigma'(t) = \exp\left(i\mathcal{H}_0 t\right)\sigma(t)\exp\left(-i\mathcal{H}_0 t\right) \tag{1.65}$$

and

$$\mathcal{H}_1'(t) = \exp\left(i\mathcal{H}_0 t\right)\mathcal{H}_1\exp\left(-i\mathcal{H}_0 t\right) \tag{1.66}$$

and

$$\dot{\sigma}'(t) = -i\left[\mathcal{H}_1(t), \sigma'(t)\right]. \tag{1.67}$$

In this interaction frame (i.e. the rotating frame rotating at $\omega = \omega_0$ the Hamiltonian $\mathcal{H}_0$ does not appear directly, and *the components of $\mathcal{H}_1$ that do not commute with $\mathcal{H}_0$ appear time-dependent*. Since $\mathcal{H}_0 >> \mathcal{H}_1$, the harmonic oscillations imposed on $\mathcal{H}_1$ by $\mathcal{H}_0$ will lead to a *zero average*. Thus, for the chemical shift we obtain a truncated chemical shift Hamiltonian

$$\mathcal{H}_{\mathrm{cs}} = -\gamma B_0 \sigma_{zz}^{lab} I_z \tag{1.68}$$

and a total Hamiltonian

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{\mathrm{cs}} = \omega_0\left(1 - \sigma_{zz}^{lab}\right)I_z. \tag{1.69}$$

Note that "truncation" was a form of averaging. It represents the first example of replacing the full (complicated) Hamiltonian by an *average Hamiltonian*. Average Hamiltonians will be discussed further in practically all the later chapters. Thus the spectrum now looks like that in Figure 1.9. Indeed we are approaching reality, and spectra that resemble this can be recorded.

We will now come back to the consequences of the tensorial nature of the solid-state NMR Hamiltonian. First, though, we will discuss the other interactions which are important in solid-state NMR and show that all the interactions have the same mathematical form.

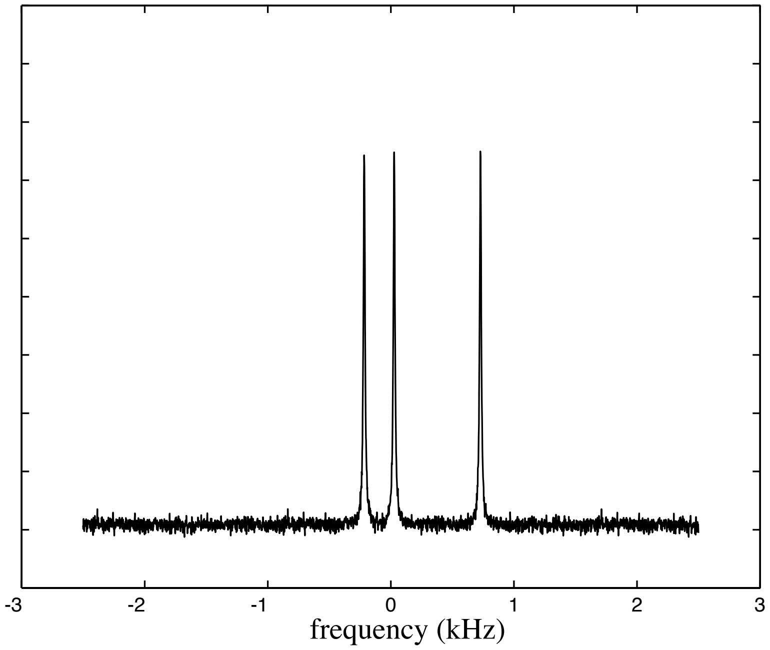


Figure 1.9. A simulated NMR spectrum containing three peaks. this is the kind of spectrum that results from the presence of Zeeman and isotropic chemical shift interactions only.

1.6. Other Interactions.

The full Hamiltonian can have up to 13 interactions. Fortunately most are usually zero or are unobservable. For solid-state NMR the relevant terms are usually

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_Q + \mathcal{H}_D + \mathcal{H}_{cs} + \mathcal{H}_J. \tag{1.70}$$

where $\mathcal{H}_Q$ is the quadrupolar Hamiltonian, $\mathcal{H}_D$ is the dipolar Hamiltonian, and $\mathcal{H}_J$ is the scalar coupling Hamiltonian.

The dipolar interaction.

As an example let us take the dipolar interaction. The classical interaction energy E between two magnetic moments μ_1 and μ_2 is

$$E = \left(\frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3(\mu_1 \cdot \vec{r})(\mu_2 \cdot \vec{r})}{r^5} \right) \frac{\mu_0}{4\pi} \tag{1.71}$$

and the corresponding spin Hamiltonian is therefore

$$\mathcal{H}_D = \frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r_{12}^3} \left(I_1 \cdot I_2 - \frac{3(I_1 \cdot r_{12})(I_2 \cdot r_{12})}{r_{12}^2} \right). \tag{1.72}$$

We will now do something strange, because we know that subsequently the dipolar interaction, like the chemical shift, will be truncated by $\mathcal{H}_0$. We expand $\mathcal{H}_D$ into a series of *orientationally dependent* terms, called the dipolar alphabet:

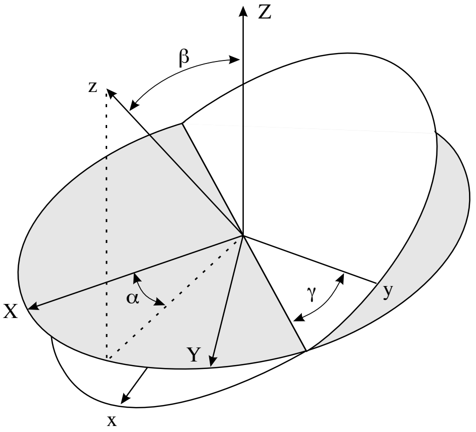


Figure 1.10. Definition of the coordinate system for Wigner rotations.

$$\mathcal{H}_D = \frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} (A + B + C + D + E + F)$$

where

$$\begin{aligned}
A &= I_{1z} I_{2z} \left(1 - 3\cos^2\theta\right) \\
B &= -\tfrac{1}{4}\left(I_1^+ I_2^- + I_1^- I_2^+\right)\left(1 - 3\cos^2\theta\right) \\
C &= -\tfrac{3}{2}\left(I_1^+ I_{2z} + I_{1z} I_2^+\right)\sin\theta\cos\theta\exp(-i\phi) \\
D &= -\tfrac{3}{2}\left(I_1^- I_{2z} + I_{1z} I_2^-\right)\sin\theta\cos\theta\exp(+i\phi) \\
E &= -\tfrac{3}{4} I_1^+ I_2^+ \sin^2\theta\exp(-2i\phi) \\
F &= -\tfrac{3}{4} I_1^- I_2^- \sin^2\theta\exp(+2i\phi)
\end{aligned}. \tag{1.73}$$

where the coordinate system is defined in figure 1.10.

This notation appears useful when we note that $\mathcal{H}_z$ and $\mathcal{H}_D$ do not commute. Since $\mathcal{H}_D$ is about 20 kHz and $\mathcal{H}_z$ about 100 MHz, $\mathcal{H}_D$ is a perturbation on $\mathcal{H}_z$, or, in other words, $\mathcal{H}_z$ will truncate $\mathcal{H}_D$ and we retain only those parts of $\mathcal{H}_D$ that commute with H_z. Thus the *high-field truncated dipolar Hamiltonian* is

$$\mathcal{H}_D = \frac{1}{2}\frac{\mu_0\hbar^2\gamma_1\gamma_2}{4\pi r^3}\left(1-3\cos^2\theta\right)\left(3I_{1z}I_{2z} - I_1\cdot I_2\right) \tag{1.74}$$

and $\left[\mathcal{H}_z,\mathcal{H}_D\right]=0$, which amounts to dropping the terms C, D, E, F. This is the *homonuclear dipolar Hamiltonian*. Furthermore, if I_1 and I_2 are different nuclei, such that $|\omega_1-\omega_2| >> |\mathcal{H}_D|$, there is a further truncation, since now the term B is also non-secular, and we obtain

$$\mathcal{H} = \omega_1 I_{1z} + \omega_2 I_{2z} + dI_{1z}I_{2z} \tag{1.75}$$

where $d = \frac{\mu_0\hbar^2\gamma_1\gamma_2}{4\pi r^3}\left(1-3\cos^2\theta\right)$.

Effect on the spectrum (heteronuclear interaction)

To calculate the effect on the spectrum we must first of all find a suitable basis set for the *coupled two spin system*. The Hilbert space is now sixteen dimensional and we obtain a product basis spanned by 16 basis operators of the two spins *I* and *S*

$$\begin{gathered}\mathbf{1}, I_x, I_y, I_z, S_x, S_y, S_z,\\ I_xS_x, I_yS_x, I_zS_x, I_xS_y, I_yS_y, I_zS_y, I_xS_z, I_yS_z, I_zS_z\end{gathered} \tag{1.76}$$

The matrix representation of these operators is in terms of 4 x 4 matrices obtained from the Pauli matrices for spin $I = \frac{1}{2}$ with the direct product as follows:

$$I_x = I_x \otimes \mathbf{1} = \frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\otimes\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} = \frac{1}{2}\begin{pmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{pmatrix}$$

$$S_x = \mathbf{1}\otimes S_x = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\otimes\frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = \frac{1}{2}\begin{pmatrix}0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 1 & 0\end{pmatrix}$$

$$I_zS_z = I_z \otimes S_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

etc....

Afterwards the calculation proceeds as before. For the homonuclear dipolar coupling we can calculate the free precession signal analytically. After a 90° pulse along y

$$\sigma_+(0) = I_x(+S_x). \tag{1.77}$$

Typically in NMR calculations we only follow the fate of one component at a time. Thus, for the moment we neglect the presence of transverse magnetization of S. We have for the transverse magnetization of I at time t

$$\langle I_+ \rangle(t) = Tr\{\exp(+i\mathcal{H}\,t)I_+\exp(-i\mathcal{H}\,t)I_x\}. \tag{1.78}$$

Using the fact that the Hamiltonian is the sum of three commuting parts and that $\left[I_+, S_z\right] = 0$, we obtain

$$\begin{aligned} \exp(+i\mathcal{H}\,t)I_+\exp(-i\mathcal{H}\,t) &= \exp\left(i(\omega_I + DS_z)I_z t\right)I_+\exp\left(-i(\omega_I + DS_z)I_z t\right) \\ &= \exp\left(i(\omega_I + DS_z)t\right)I_+ \\ &= \exp(i\omega_I t)\left\{\cos\frac{D}{2}t + 2iS_z\sin\frac{D}{2}t\right\}I_+ \end{aligned} \tag{1.79}$$

which we obtained by using the operator relation $\exp(i\phi I_z)I_+\exp(-i\phi I_z) = \exp(i\phi)I_+$.)) and from the relation

$$R_z(\phi) = \cos\frac{\phi}{2} - 2iI_z\sin\frac{\phi}{2}. \tag{1.80}$$

Inserting this into the expression for I_+ we obtain

$$\langle I_+ \rangle(t) = I_0\exp(i\omega_I t)\cos\frac{D}{2}t. \tag{1.81}$$

Thus the dipolar spectrum consists of a doublet at ±D/2 centered at ω_I (and similarly for ω_S, as shown schematically in figure 1.11a

It is very important to note that (i) the splitting contains information about the internucler distance, and (ii) it is orientation dependent.

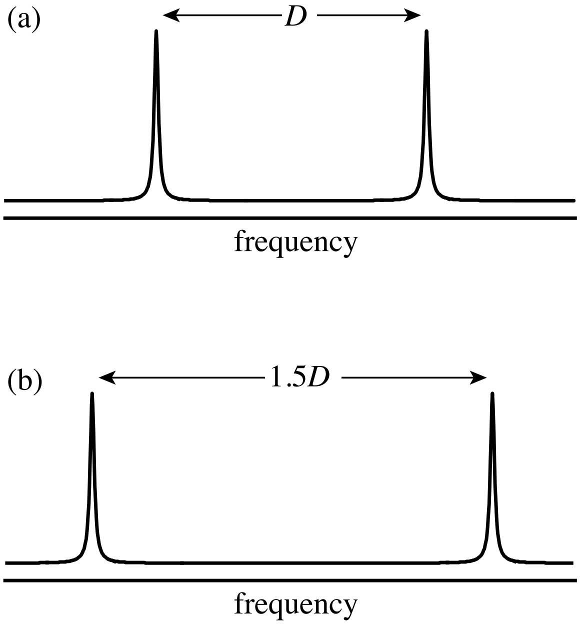


Figure 1.11. Schematic doublet splittings obtained at high field under the heteronuclear (a) and homonuclear (b) dipolar interaction.

The splitting depends on the orientation of the internuclear vector with respect to the magnetic field. The orientation dependence or *anisotropy* was introduced by truncation. It is an all important feature of NMR in solids as well as liquids. Note that for $\theta = 54.74°$, $P_2(\cos\theta) = 0$, $\mathcal{H}_D = 0$.

Homonuclear dipolar spectrum.

In the limit of $|\omega_1 - \omega_2| = 0$, we obtain a single doublet splitting, with a modified value of the splitting with respect to the heteronuclear case, figure 1.11b. All our other remarks for the heteronuclear case about anisotropy are also valid for the homonuclear case.

Quadrupolar Hamiltonian.

The quadrupolar interaction arises from the presence of an electric field gradient at the nucleus interacting with a non-spherical charge distribution. We will not go into more detail. We will just note that $\mathcal{H}_Q = 0$ for spin $I = \frac{1}{2}$, but that it is normally not zero for $I > \frac{1}{2}$. The Hamiltonian is expressed as

$$\mathcal{H}_Q = \frac{eQ}{6I(2I-1)\hbar}\sum_{\alpha,\beta=x,y,z} V_{\alpha\beta}\left[\tfrac{3}{2}\left(I_\alpha I_\beta + I_\beta I_\alpha\right) - \delta_{\alpha\beta} I(I+1)\right] \tag{1.82}$$

$$\mathcal{H}_Q = \frac{eQ}{6I(2I-1)\hbar} I \cdot V \cdot I \tag{1.83}$$

where *eQ* is the *nuclear quadrupole moment* and *V* is the electric field gradient tensor. We define a quadrupolar coupling constant

$$\omega_Q = \frac{3e^2qQ}{4I(2I-1)\hbar} \tag{1.84}$$

where *eq* represents the field gradient component V_{zz}, and with an asymmetry parameter given by $\eta = \left(V_{xx} - V_{yy}\right)/V_{zz}$, and the secular Hamiltonian becomes

$$\mathcal{H}_Q = \frac{\omega_Q}{3}\left(3I_z^2 - I^2 + \eta\left(I_x^2 - I_y^2\right)\right)\left(\tfrac{1}{2}\left(3\cos^2\theta - 1\right) + \tfrac{1}{2}\eta\sin^2\theta\cos 2\phi\right) \tag{1.85}$$

This is very similar to the homonuclear dipolar Hamiltonian for $I_1 = I_2$, and indeed for spin $I = 1$, e.g. ^{2}H, we obtain a doublet with an orientation dependent splitting. For higher spins we see more lines, e.g. for spin $I = \frac{3}{2}$ (^{23}Na) we see an orientation independent central transition and two orientation dependent outer lines, as shown in figure 1.12. In general there are $2I$ non-degenerate transitions.

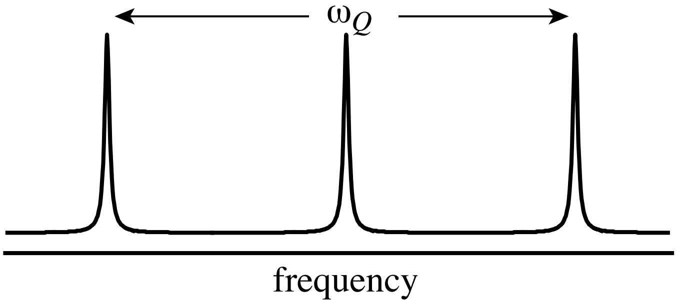


Figure 1.12. Schematic splitting obtained at high field under the first order quadrupolar interaction for a spin I = 3/2. The center line is at zero frequency, and is flanked by an orientation dependent doublet splitting.

In conclusion, we have clearly seen that the secular parts of $\mathcal{H}_{cs}$,$\mathcal{H}_D$ and $\mathcal{H}_Q$ are all orientation dependent with respect to $\mathcal{H}_z$. They all have a tensorial nature.

Tensor notation.

What does the "tensorial character" mean? It means that since we measure only the "z-component" of the interaction that the observables depend on the direction in which we look at them. This is perhaps easiest to explain intuitively for the chemical shift in phenomenological terms. If we take the example of figure 1.13, where the chemical shift of each carbon atom is shown as an ellipsoid. This means that, for example, if the aromatic ring is oriented parallel to the field the resonance frequency of an aromatic carbon is relatively high, since there is relatively little electronic shielding in this direction compared to when the aromatic ring is perpendicular to the field. In the perpendicular orientation there is more electronic shielding along the direction of the field, and so the resonance frequency is lower in this orientation. The chemical shift is therefore naturally seen to be orientation dependent.

We can also think of the dipolar interaction - if the dipolar interaction is "aligned" with the field, its projection onto the field will be large. If it is "orthogonal" to the field its projection will be zero. For example, if the effect of an interaction were simply to add a small dc field, its transverse component would be truncated and we are left with the projection $\mathcal{H}_z^{\text{int}} = \mathcal{H}^{\text{int}} \cos\theta$. The resultant field depends on the orientation of the dc field. Such an interaction transforms as a rank 1 tensor ($\cos\theta$). We shall see that the spatial part of the NMR Hamiltonians transform as

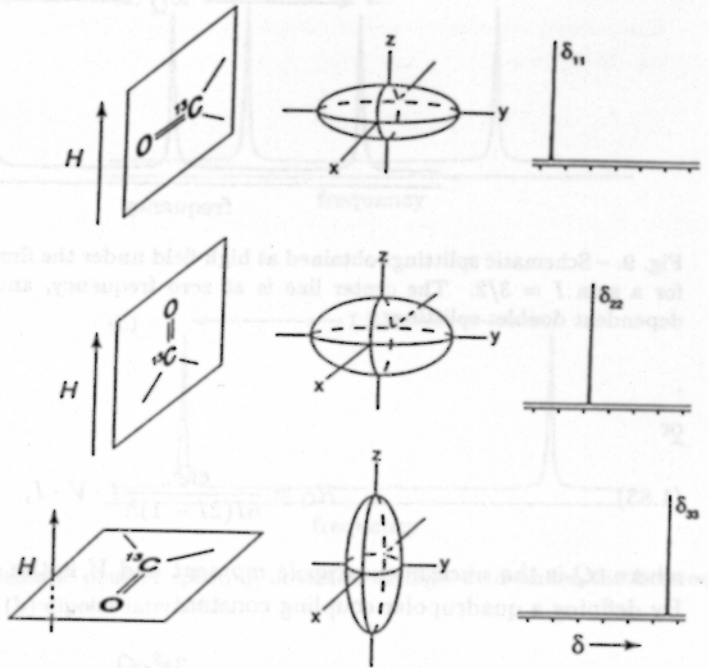


Figure 1.13. Schematic representation of the effect of chemical shift anisotropy on the spectrum of a single orientation. The position of each peak depends on the relative orientation of the magnetic field with respect to the principle axis of the chemical shift tensor.

rank 2 tensors, so they have a slightly non-intuitive ($3\cos^2\theta - 1$) dependence, i.e., "orthogonal" = 54.74°. (Note that some of the spin parts of the Hamiltonian often transform as rank 1 tensors).

All of the Hamiltonians we have seen up to now have a common structure

$$\mathcal{H}_\lambda = C^\lambda \sum_{\alpha\beta = xyz} I_\alpha R^\lambda_{\alpha\beta} A^\lambda_{\alpha\beta} = C^\lambda \sum_{\alpha\beta = xyz} R^\lambda_{\alpha\beta} T^\lambda_{\beta\alpha} \tag{1.86}$$

The C^λ depends only on fundamental constants and properties of the nuclear ground state. They are in particular constants with respect to rotation in *either* spin space or space (Kirk) space (the final frontier).

The $T^\lambda_{\beta\alpha}$ are tensors constructed from two vectors, one of which is always a nuclear spin vector, whereas the other can be the same nuclear spin vector ($\lambda = Q$), another nuclear spin vector ($\lambda = D$), or the external magnetic field ($\lambda = cs$).

The R are spin state independent coupling tensors. *All R^λ are rank 2 tensors*. For example

$$\mathcal{H}_D = C^D \sum_{\alpha\beta = xyz} I_{1\alpha} \cdot D_{\alpha\beta} \cdot I_{2\beta} \tag{1.87}$$

where $D_{\alpha\beta}$ consists simply of the coefficients going with $I_{1\alpha} I_{2\beta}$

$$\mathcal{H}_D \propto D_{xx} I_x S_x + D_{yy} I_y S_y + D_{zz} I_z S_Z + D_{xy} I_x S_y \ldots \tag{1.88}$$

where, for the untruncated Hamiltonian, the coefficients are found in the dipolar alphabet and where, for the truncated heteronuclear dipolar Hamiltonian, only D_{zz} is non-zero.

The R^λ can be decomposed into their irreducible representations with respect to the full three-dimensional rotation group O3:

$$\begin{aligned}
R &= R^{(0)} + R^{(1)} + R^{(2)} \\
R^{(0)} &= \tfrac{1}{3} Tr\{R1\} = R_{iso} \\
R^{(1)}_{\alpha\beta} &= \tfrac{1}{2}\left(R_{\alpha\beta} - R_{\beta\alpha}\right) \\
R^{(2)}_{\alpha\beta} &= \tfrac{1}{2}\left(R_{\alpha\beta} + R_{\beta\alpha}\right) - R\delta_{\alpha\beta}
\end{aligned} \tag{1.89}$$

R_{iso} the orientation independent, *isotropic*, component, $R^{(1)}_{\alpha\beta}$ is the traceless anti-symmetric part, and $R^{(2)}_{\alpha\beta}$ is the traceless symmetric part of the interaction. Note that the chemical shift contains all three parts, in principle, but that the $R^{(1)}_{\alpha\beta}$ component is generally not secular and thus inobservable. The dipolar and first order quadrupolar interactions are traceless symmetric by their very nature. We therefore ignore $R^{(1)}_{\alpha\beta}$ in the following.

For all R^{λ} there are *principle axis systems* in which the tensors are diagonal. The diagonal components are called the principle components R_{xx}, R_{yy} and R_{zz}. By convention

$$|R_{zz} - R| \geq |R_{xx} - R| \geq |R_{yy} - R| \tag{1.89}$$

(the $R_{\alpha\alpha} - R$ are the principle components of $R^{(2)}$. We often define three other parameters:

$$\begin{aligned} R_{iso} &= \tfrac{1}{3} Tr\{R\} \\ \delta &= R_{zz} - \tfrac{1}{3} Tr\{R\} = R_{zz} - R \\ \eta &= \frac{R_{yy} - R_{xx}}{R_{zz} - \tfrac{1}{3} Tr\{R\}} = \frac{R_{yy} - R_{xx}}{\delta} \end{aligned} \tag{1.90}$$

δ, the *anisotropy*, is a measure of how sensitive the interaction is to orientation. η, the *asymetry parameter*, quantifies the deviation from axial symmetry. The dipolar interaction is axially symmetric about the line connecting the two nuclei, thus for R^{D}, $\eta = 0$, and the principle axis system is easy to define. For σ and Q the PAS can be harder to find.

1.7. Lineshapes in Solids.

To calculate the resonance frequency we need to calculate for a given orientation of the molecule in the magnet (i.e., for a given orientation of the PAS in the *laboratory frame*) the "projection" onto the secular component of the Hamiltonian. To do this we must *rotate* the PAS into the laboratory frame. Note that, additionally, all the techniques of *coherent averaging* which will be discussed later, rely on rotations. Thus rotations are crucial, and that is why we introduced tensor notation, for which the algebra of rotations is highly developed. Thus in strict tensor notation we write

$$\mathcal{H}^{\lambda} = C^{\lambda} \sum_{l} \sum_{m=-l}^{l} (-1)^m R^{\lambda}_{l,-m} T^{\lambda}_{l,m} \tag{1.91}$$

where the $R^{\lambda}_{l,m}$ derive from the $R^{\lambda}_{\alpha,\beta}$, and the $T^{\lambda}_{l,m}$ derive from the $T^{\lambda}_{\alpha,\beta}$. We are now dealing with *spherical tensors*, as opposed to cartesian tensors. At first sight this may seem complicated, but we shall see that in the end it yields simple recipies and tables to calculate spectra.

We can already make some simplifications. (i) For second rank symmetric Cartesian tensors $R^{\lambda}_{\alpha,\beta}$, only $R^{\lambda}_{l,m}$ with l = 0,2 will be non-zero. (ii) For the R^{λ} in their PAS, only components with m = 0,±2 are non-zero. Thus we find that the $\rho_{l,m}$, the components of $R_{l,m}$ in their PAS, are

$$\begin{aligned}
&\rho_{0,0} = R_{iso} \\
&\rho_{2,0} = \sqrt{\tfrac{3}{2}}\left(R_{zz} - \tfrac{1}{3}Tr\{R\}\right) = \sqrt{\tfrac{3}{2}}\delta \qquad (1.92) \\
&\rho_{2,\pm 2} = \tfrac{1}{2}\eta\delta
\end{aligned}$$

Since we observe the time-evolution of the spin operators in the laboratory, we express the $T_{l,m}$ in the laboratory frame. As a result we must also express the $R^{\lambda}_{l,m}$ in the laboratory frame. Since they are irreducible tensor oerators they may be expressed in terms of the $\rho_{l,m}$ and of the *Wigner rotation matrices*, $D^{l}_{m',m}\left(\alpha^{\lambda},\beta^{\lambda},\gamma^{\lambda}\right)$, so that

$$R^{\lambda}_{l,m} = \sum_{m'} D^{l}_{m',m}\left(\alpha^{\lambda},\beta^{\lambda},\gamma^{\lambda}\right)\rho^{\lambda}_{l,m'} \qquad (1.93)$$

where $\alpha^{\lambda},\beta^{\lambda},\gamma^{\lambda}$ (denoted by Ω^{λ}) are the *Euler angles* by which the laboratory frame can be brought into coincidence with the λth PAS system, using the sign convention shown in figure 1.10. The transformation correponds to a rotation by α around z, by β around the *new y* axis, and by γ around the *new z* axis. $D^{0}_{0,0}$ is a constant (unity), and reflects the isotropic component. Thus the only Wigner matrix we actually need is the $D^{2}_{m',m}$ matrix which is given in table 1.1. Similarly, the irreducible spin operators $T^{\lambda}_{l,m}$ are obtained from the Cartesian $T^{\lambda}_{\alpha,\beta}$, are also given in table 1.1.

We can now express the Hamiltonian in terms of rotational invariants, irreducible tensor operators, and elements of the Wigner matrix $D^{2}_{m',m}$.

For example, for the dipolar coupling,

$$\begin{aligned}
&C^{D} = 2\gamma^{I}\gamma^{S}\hbar^{2}\mu_{0}/4\pi \\
&\rho^{D}_{2,0} = \sqrt{\tfrac{3}{2}}\delta^{D} = \sqrt{\tfrac{3}{2}}r^{-3} \qquad (1.94) \\
&\rho^{D}_{2,m'} = 0 \; for \; m' \neq 0
\end{aligned}$$

which yields

$$R^D_{2,m} = D^2_{0,m}\left(\Omega^D\right)\sqrt{\tfrac{3}{2}}r^{-3} \tag{1.95}$$

which in turn yields

$$\mathcal{H}^D = -\sqrt{6}\,\frac{\gamma^I\gamma^S\hbar^2\mu_0}{4\pi}\sum_m (-1)^m D^2_{0,-m}\left(\Omega^D\right)T^D_{2,m} \tag{1.96}$$

(Note that the $D^2_{0,m}$ are identical to the spherical harmonics $Y_{2,m}$ which behave under rotation exactly as the $R_{l,m}$.) For the truncated Hamiltonian we find that only $T^D_{2,0}$ contributes, so

$$\mathcal{H}^D = -\sqrt{6}\,\frac{\gamma^I\gamma^S\hbar^2\mu_0}{4\pi}D^2_{0,0}\left(\Omega^D\right)T^D_{2,0} \tag{1.97}$$

and we recover

$$\mathcal{H}^D = \frac{1}{2}\frac{\gamma^I\gamma^S\hbar^2\mu_0}{4\pi}\left(1-3\cos^2\beta\right)\left(3I_{1z}I_{2z} - I_1\cdot I_2\right) \tag{1.98}$$

For the chemical shift we find by a similar calculation

$$\mathcal{H}_{cs} = \omega_0 I_Z\left(\sigma + \delta\left[\frac{3\cos^2\beta - 1}{2} + \frac{1}{2}\eta\sin^2\beta\cos 2\gamma\right]\right) \tag{1.99}$$

This notation/formalism will be useful everywhere.

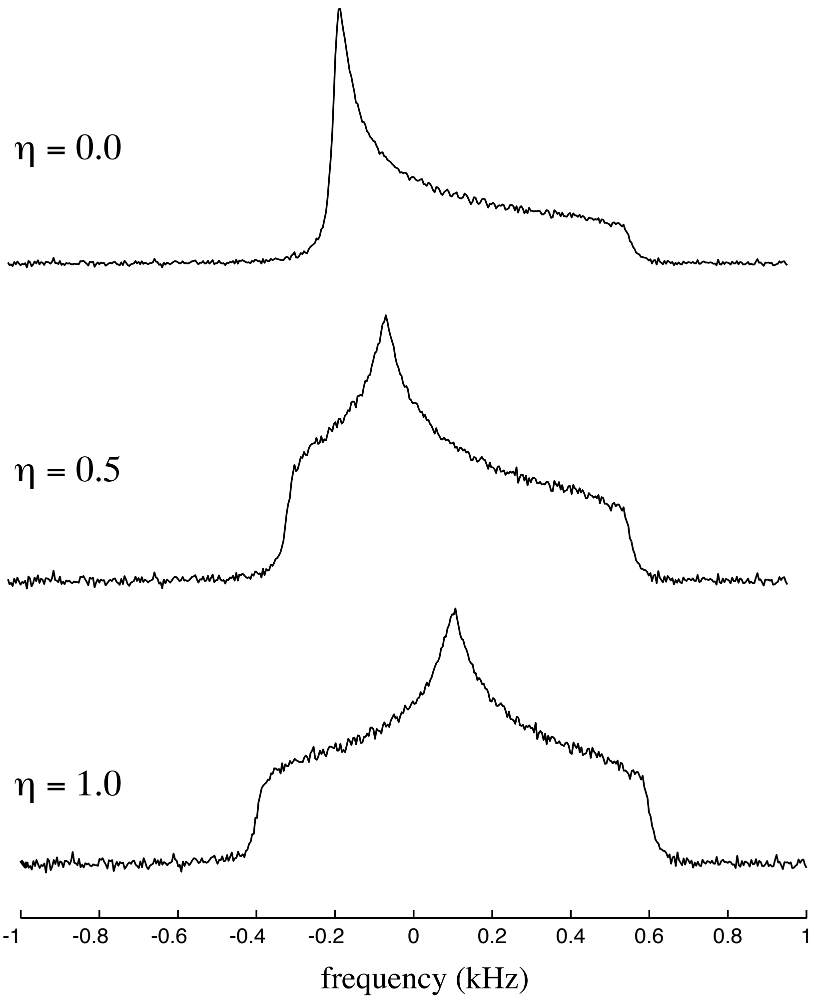


Figure 1.14. Simulated spectra showing the lineshape due to the anisotropic chemical shift interaction in the high-field NMR spectrum of a single spin I = 1/2 in a static powder sample for three different values of the anisotropy parameter.

Consequences of anisotropy on the spectroscopy of solids

In general the calculation of a solid-state NMR spectrum involves the following transformations:

$$PAS \xrightarrow{\Omega_{PAS-CRYS}} CRYSTAL \xrightarrow{\Omega_{MOL-LAB}} LAB$$

1. Single Crystal Spectra. This is what we have been calculating so far. In principle a spectrum of a single crystal will be different for different orientations of the crystal. By recording the spectra as a function of orientation with respect to the field we can determine all the principle values and the orientation of the CSA tensors in a crystal fixed frame.

2. Powder Spectra. These are more interesting samples (since they are not suitable for X-ray studies). A powder is a superposition of all possible crystallite orientations. Therefore we

expect to see a spectrum which contains all the frequencies seen in rotation plots, suitably weighted by their populations. Thus the lineshape is given by

$$I(\omega) = \int_0^{2\pi}\int_0^{\pi} \delta(\omega - \omega_{zz}) p(\Omega) d\alpha \sin\beta d\beta \tag{1.100}$$

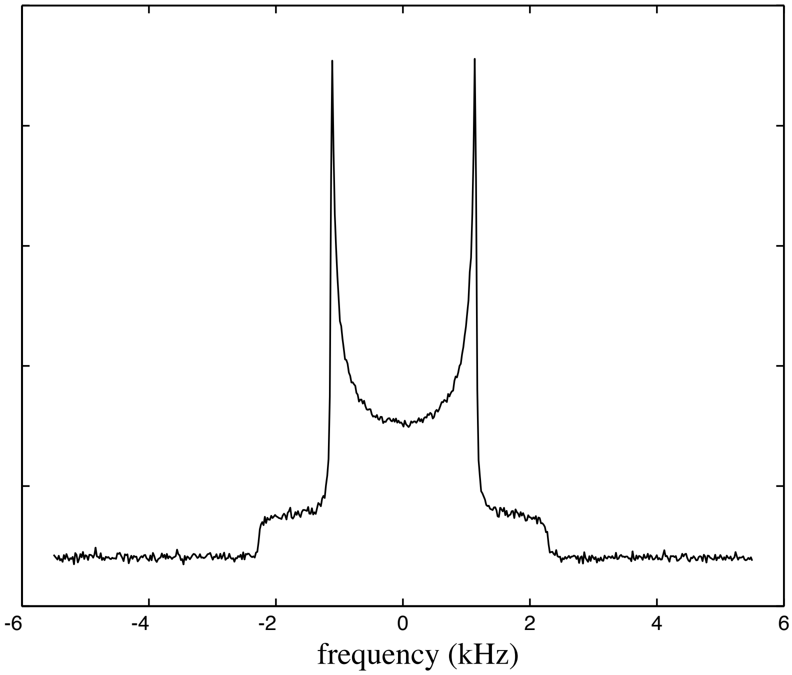


Figure 1.15. Simulated spectrum showing the lineshape due to the dipolar interaction in the high-field NMR spectrum of a pair of identical spins $I = 1/2$ in a static powder sample. (An identical lineshape is observed for the quadrupolar interaction for a single spin $I = 1$).

where $p(\Omega)$ is the probability of finding a particular orientation. ω_{zz} is the observed frequency for that orientation, and is calculated as described above. This form for the lineshape leads to a *powder pattern*. (Note that this is valid for all of CSA, dipolar or quadrupolar interactions.), as shown in figure 1.14 and figure 1.15. Note that the princicple values of the CSA tensor are available by simple inspection, but that *no* information is now available with respect to the orientation of the PAS. The powder pattern is, of course, invariant to the orientation of the sample. Note also that powder spectra are inherently low resolution. The width of the pattern is

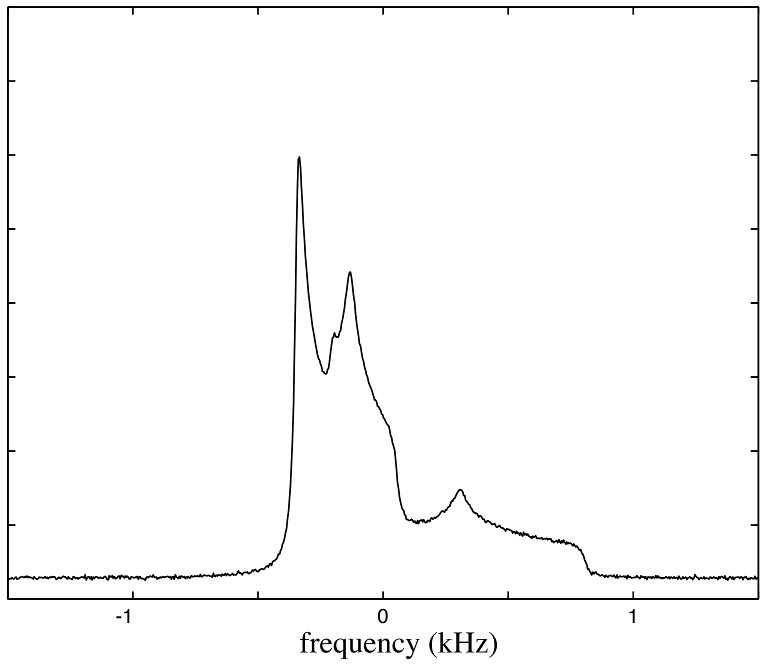


Figure 1.16. Simulated spectrum for three chemically different spin $I = 1/2$ sites in a static powder sampleEach site has a different value of the isotropic chemical shift and different anisotropy parameters. This is typical of "real" samples, and demonstrates how the spectrum becomes intractable in the absence of simplification.

often comparable to the difference in chemical shift, leading to spectra such as that shown in figure 1.16. One way to improve resolution is to orient the sample.

1.8. Spin Echoes.

The objective of this section is to show how to approach the calculation of the effect of a series of rf pulses and delays.

Spin echoes for isolated spin I = 1/2

The spin echo pulse sequence is shown in 1.17a. We can see from a very simple classical analysis shown in figure 1.17b that we expect the sequence to "refocus" the chemical shift interaction. Let's see if we can obtain this result analytically.

For a spin whose resonance frequency in the rotating frame is ω_{cs},

$$\mathcal{H} = \omega_{cs} I_z \tag{1.101}$$

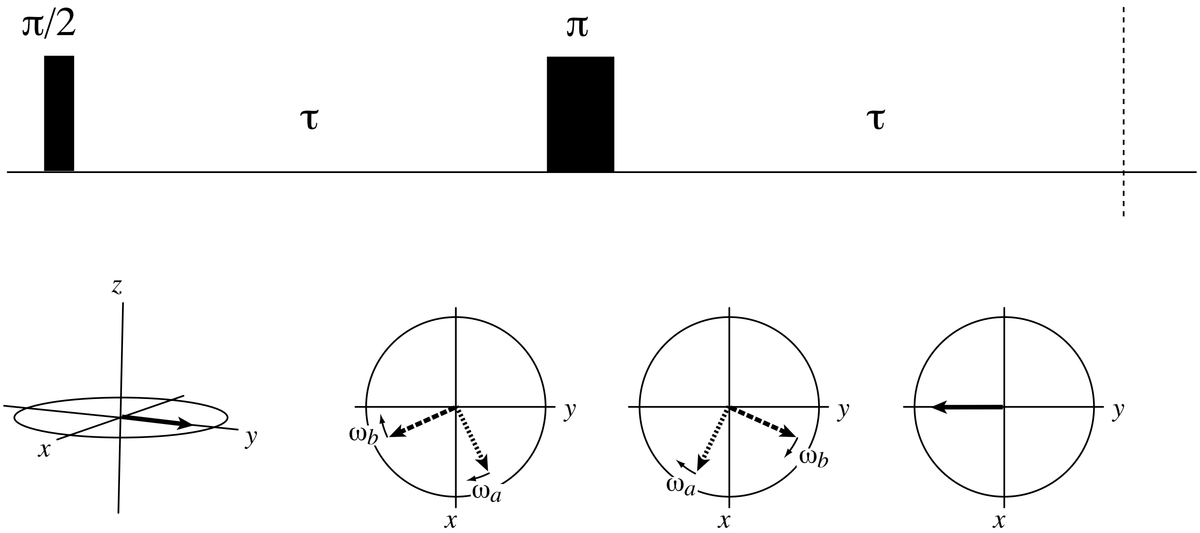


Figure 1.17. The sequence suitable to produce a spin echo, and the vectorial representation of the evolution of two chemically different species *a* and *b* evolving at frequencies ω_a and ω_b during the sequence. Note that at the end of the second τ period the two spins have been refocused.

at time τ we have the operator for evolution

$$U = \exp\left(-i\omega_{cs}\tau I_z\right) \tag{1.102}$$

Immediately after the second pulse we have

$$U\left(\tau_+\right) = \exp\left(-i\pi I_x\right)\exp\left(-i\omega_{cs}\tau I_z\right), \tag{1.103}$$

and at a time *t* later this becomes

$$U\left(t+\tau\right) = \exp\left(-i\omega_{cs}tI_z\right)\exp\left(-i\pi I_x\right)\exp\left(-i\,\omega_{cs}\tau I_z\right) \tag{1.104}$$

which can be written under the form

$$U\left(t+\tau\right) = \exp\left(-i\omega_{cs}\left(t-\tau\right)I_z\right)\exp\left(-i\omega_{cs}\tau I_z\right)\exp\left(-i\pi I_x\right)\exp\left(-i\omega_{cs}\tau I_z\right). \tag{1.105}$$

Considering the last three operators on the right hand side of eq. (1.105)

$$R = \exp\left(-i\,\omega_{cs}\tau I_z\right)\exp\left(-i\pi I_x\right)\exp\left(-i\omega_{cs}\tau I_z\right). \tag{1.106}$$

It can be shown that if *U* is a unitary operator

$$U\exp(A)U^{-1} = \exp\left(UAU^{-1}\right), \tag{1.107}$$

and going back to equation (1.106) we can write

$$R = \exp\left(-i\,\omega_{cs}\tau I_z\right)\exp\left(-i\pi I_x\right)\exp\left(-i\omega_{cs}\tau I_z\right)\exp\left(i\pi I_x\right)\exp\left(-i\pi I_x\right) \tag{1.108}$$

where the product of the three central operators is of the form of equation (1.107) with

$$U = \exp\left(-i\pi I_x\right), A = -i\,\omega_{cs}\tau I_z, f(A) = \exp\left(-i\omega_{cs}\tau A\right) \tag{1.109}$$

so that

$$\exp\left(-i\pi I_x\right)\exp\left(-i\,\omega_{cs}\tau I_z\right)\exp\left(i\pi I_x\right) = \exp\left(i\omega_{cs}\tau I_z\right) \tag{1.110}$$

and equation (1.106) yields

$$R = \exp\left(-i\,\omega_{cs}\tau I_z\right)\exp\left(i\omega_{cs}\tau I_z\right)\exp\left(-i\pi I_x\right) = \exp\left(-i\pi I_x\right). \tag{1.111}$$

Thus, equation (1.105) becomes

$$U\left(t+\tau\right) = \exp\left(-i\omega_{cs}\left(t-\tau\right)I_z\right)\exp\left(-i\pi I_x\right). \tag{1.112}$$

Note that we have manipulated the evolution operator, which is a very common trick in NMR, and not the density matrix. Thus the result is valid for any initial state of the system represented by σ. We note that the total evolution operator consists of (i) an initial pulse of angle π about x, (ii) precession about z by an angle $\phi = \omega_{cs}\left(t-\tau\right)$. Note especially that for $\tau = t$,

$$U(2\tau) = \exp\left(-i\pi I_x\right). \tag{1.113}$$

and the evolution is independent of chemical shift. This corresponds to the formation of a *spin echo*, as was predicted in figure 1.17.

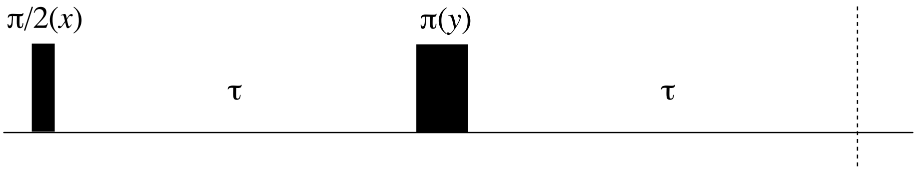


Figure 1.18. The qudrupolar echo pulse sequence.

Quadrupolar Echoes.

The quadrupolar echo (or "solid echo") serves to refocus the evolution of spins under Hamiltonians which are bilinear in the same type of spins, such as homonuclear dipolar or quadrupolar couplings of the form

$$\mathsf{H} = 3I_{1z}I_{2z} - I_1 \cdot I_2. \tag{1.114}$$

which are not refocused by the sequence above (the Hahn echo). The quadrupolar echo is generated using the sequence shown in figure 1.18, which leads to the following propagator

$$U(t+\tau) = \exp\left(-i\omega_\theta \tau\left(3I_{1z}I_{2z} - I_1 \cdot I_2\right)\right)\exp\left(+i\tfrac{\pi}{2}I_y\right)\exp\left(-i\omega_\theta t\left(3I_{1z}I_{2z} - I_1 \cdot I_2\right)\right). \tag{1.115}$$

Analogously to the previous example, this can be written

$$\begin{aligned} U(t+\tau) = \exp\left(-i\omega_\theta \tau\left(3I_{1z}I_{2z} - I_1 \cdot I_2\right)\right)\exp\left(+i\tfrac{\pi}{2}I_y\right)\exp\left(-i\omega_\theta t\left(3I_{1z}I_{2z} - I_1 \cdot I_2\right)\right) \\ \times\exp\left(-i\tfrac{\pi}{2}I_y\right)\exp\left(+i\tfrac{\pi}{2}I_y\right) \end{aligned} \tag{1.116}$$

and using equation (1.107) again we obtain

$$U(t+\tau) = \exp\left(-i\omega_\theta \tau\left(3I_{1z}I_{2z} - I_1 \cdot I_2\right)\right)\exp\left(-i\omega_\theta t\left(3I_{1x}I_{2x} - I_1 \cdot I_2\right)\right)\exp\left(+i\tfrac{\pi}{2}I_y\right). \tag{1.117}$$

The two leftmost exponentials can be combined, since $I_{1z}I_{2z}$ commutes with $I_{1x}I_{2x}$, so that for $\tau = t$, by using the relation

$$3I_{1z}I_{2z} - I_1 \cdot I_2 + 3I_{1x}I_{2x} - I_1 \cdot I_2 + 3I_{1y}I_{2y} - I_1 \cdot I_2 = 0\,, \tag{1.118}$$

(which is of great relevance elsewhere) and by expanding the scalar product $I_1 \cdot I_2$ we obtain

$$U(2\tau) = \exp\left(-i\omega_\theta \tau\left(3I_{1y}I_{2y} - I_1 \cdot I_2\right)\right)\exp\left(+i\tfrac{\pi}{2}I_y\right). \tag{1.119}$$

For $\sigma(0) = I_y$, created by an *x* pulse from z magnetization, we thus find an echo condition

$$\sigma(2\tau) = U(2\tau)I_yU^\dagger(2\tau) = I_y\,. \tag{1.120}$$

since $\left[3I_{1y}I_{2y} - I_1 \cdot I_2, I_y\right] = 0$ (analogously to Zeeman truncation). Note that this only works for a single dipolar interaction. For a many spin dipolar coulping, with the sum over all pairs, it does not work. It always works for the first order quadrupolar interaction, and is widely used to avoid "deadtime effects," and to study molecular dynamics (since dynamics can interfere with the echo formation).[7]

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