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DOUBLE QUANTUM NMR IN SOLIDS

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Double Quantum NMR in Solids

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Lectures presented at the Ampere Summer School, Pula, Yugoslavia,
September, 1976
INTRODUCTION

One of the recent interesting areas of magnetic resonance is the development of high resolution techniques for nmr in solids.\textsuperscript{1,2} A survey of the literature indicates that all of the work on high resolution nmr has been done on spin-$\frac{1}{2}$ nuclei. These include protons, carbon-13, nitrogen-15, fluorine-19, silicon-29, phosphorus-31, and more. It would be extremely useful to extend these techniques and to be able to observe high resolution nmr of spin-1 nuclei. Particularly attractive candidates would be deuterium and nitrogen-14. Clearly, we could expand the whole area of the analytical applications of nmr if we could incorporate deuterium selectively into certain positions in a large molecule. Decoupling the protons while observing the deuterium nmr spectrum would yield a high resolution nmr spectrum of the local environment of the deuterium.

Now, why hasn't the high resolution nmr of spin-1 nuclei developed, in fact? In order to understand this, let us remember that spin-1 nuclei have a non-zero quadrupole moment and look at Figure 1. In the absence of a quadrupole moment we would have a Zeeman splitting which would give two allowed transitions $\Delta m = 1$ at the same frequency $\omega_0$. In the presence of the quadrupole moment there is a shift of the energy levels due to the interaction of the quadrupole moment with local field gradients, causing...
a splitting of the two allowed transitions by an amount $2\omega_Q$. The quadrupole Hamiltonian is given by:

$$\mathcal{H}_Q = \frac{1}{3} \omega_Q (3I_z^2 - I^2)$$  \hspace{1cm} (1)

where

$$2\omega_Q = \frac{e^2 qQ}{2I(2I-1)} \left[ \frac{1}{2} (3 \cos^2 \theta - 1) + \eta \sin^2 \theta \cos 2\phi \right]$$  \hspace{1cm} (2)

and $\theta, \phi$ are the angles of the field gradient axes in the laboratory frame.

Now for the case of deuterium, the quadrupole moment is of such a magnitude that typical splittings $2\omega_Q$ range up to 200 KHz. If we recall that the kind of resolution we require in order to obtain chemical shift and dipole-dipole coupling information is of the order of 100 Hz or so, you see that the quadrupole splitting dominates by many orders of magnitude the required resolution. In fact, in the case of a powder we get a continuous distribution of values of $\omega_Q$ leading to a smearing out of the spectrum and leaving a broad resonance of up to 200 KHz in width. An example of this is shown in Figure 2 where we see the central portion of the deuterium nmr spectrum of perdeuterated solid dimethylsulfoxide. Let me mention at this point that for nitrogen-14, as is well known, the quadrupole moment is even larger and would yield spectra with widths of several MHz. So the nature of the problem is clear, and we see why this area of spin-1 nmr has not been approached in the same way that spin-$\frac{1}{2}$ nmr has.

What I would like to tell you about in these lectures are some concepts and results which are preliminary, but indicate that not only can we do high resolution spin-1 nmr but a whole new range of spin physics is open
to us. I won't cover the whole field of our recent developments, but will just give you some examples with only semiquantitative details to give you an idea of the approach and the potential of the new concepts. Before I begin describing to you the essence of the approach and its details, let me mention that the work in my laboratory was done by several of my colleagues. In particular the theory that I'll outline, which is an operator theory of double quantum nmr, was developed in a very elegant fashion by Dr. Shimon Vega, who is now on the staff of the Weizmann Institute of Science in Rehovot. Some of the experimental results that I'll describe were done together with Dr. Vega and some of my other co-workers; Dr. David Ruben, Tom Shattuck, and David Wemmer. The work on double quantum decoupling was done in collaboration with Professor M. Mehring at the Institute of Physics, University of Dortmund.

DOUBLE QUANTUM TRANSITION

To motivate the approach that was taken let us consider Figure 3. Although the energy levels \( m = +1, 0 \) and \(-1\) are shifted, because the quadrupole interaction is bilinear in angular momentum, we can see that the \(+1\) and \(-1\) levels are shifted by the same amount, they both shift up or down. So what occurs to us is the following: the way we do normal spin-\(\frac{1}{2}\) Fourier transform nmr is to apply a pulse between the \(\pm \frac{1}{2}\) levels, placing them in coherent superposition. The decay of the coherence is then monitored as a free induction decay. Fourier transformation of the decay gives a linear absorption spectrum. If we do either a multiple pulse experiment, or we decouple the abundant spins in the case of the observation of rare spins, we get a high resolution spectrum.
The corresponding statement for spin-1 would be that if we make a normal intense pulse on our deuterium spins and place all the levels +1, 0 and -1 in coherent superposition, then we induce a free induction decay the Fourier transform of which gives the linear absorption with quadrupolar splitting. However, the transition from +1 to -1 should remain sharp, in fact it should be independent of the quadrupole coupling and should contain only chemical shifts and other smaller couplings such as dipole-dipole couplings, etc. Thus, we consider the process in which we induce a transition from +1 to -1 with a two-photon transition, a double quantum process which is allowed, and place the levels ±1 in coherent superposition. We then hope that that coherence, when it decays, will in fact yield on Fourier transformation a sharp spectrum devoid of quadrupole splittings.

The idea is depicted schematically in Figure 4. We would like to pulse the deuterium spins with a "double quantum pulse", place m = ±1 in coherent superposition and something then decays. Let us tentatively call that something double quantum coherence. I have drawn that as a dotted line because it may or may not be directly observable. It is not clear that it is going to yield a oscillating magnetic signal. Simultaneously, we decouple the protons and we hope that that double quantum decay will be a high resolution one. I note here that multiple quantum transitions in continuous wave nmr are well known, but of little use in the case of high resolution solid state work where high power rf irradiation is required. I also note the beautiful coherent double quantum effects of Hatanaka, et al. and Brewer and Hahn, also not applicable to high resolution nmr and employing a less general formalism.
DOUBLE QUANTUM OPERATORS

A convenient way to treat the behavior of spin-$\frac{1}{2}$, as we all know from standard texts on magnetic resonance, is through the use of density matrices written in terms of the angular momentum operators. This is also true for arbitrary spin when the applied fields are extremely strong. We know that the three angular momentum operators $I_x$, $I_y$, $I_z$ satisfy commutation relations which give rise to behavior of the spins in terms of rotations. For example, if the spin density matrix is described by $I_z$ (equilibrium at high magnetic field and high temperature) and we put on an rf pulse which has the symmetry $I_x$ then we will induce a rotation of $I_z$ about $I_x$. A $\pi/2$ pulse means we stop after $I_z$ has ended up as $I_y$ along the $y$-axis in the rotating frame. Now what Dr. Vega has done is to write down a theory, a corresponding rotation theory, for the spin-1 case. What he did was to introduce fictitious spin operators$^{3,6}$ which play for the case of the spin-1 the analogue of the angular momentum operators for spin-$\frac{1}{2}$. These are shown in Table I and are grouped into three groups. As long as we have only bilinear operations, namely we have a quadrupole interaction, or linear angular operations, these nine operators are sufficient to describe any state of the system. Namely, any density matrix can be expanded as a linear superposition of these operators in a high temperature approximation.

Now, the important feature of these operators is that for each group, $p$, where $p = x$, $y$, or $z$, the three operators satisfy angular momentum commutation relations. In fact they are exactly fictitious spin-$\frac{1}{2}$ operators each one corresponding to two of the levels in our three level system. Each of these three subsets describes a three-dimensional space,
a fictitious spin-½ space which we refer to as p-space where p = x, y, z, i.e. x-space, y-space or z-space. In the case of the particular experiments that I will describe in these lectures the only space of consequence will be the z-space. We refer to this as double quantum space because the operators \( I_{z,1}, I_{z,2}, I_{z,3} \) contain matrix elements only between \( m = \pm 1 \) levels. In fact, if we are irradiating the spins only about the center unshifted Larmor frequency and inducing double quantum transitions, then we will see that these three operators completely describe the evolution of the system. Thus we can consider the spins as evolving in a three-dimensional space in which everything takes place as simple rotations.

Consider for example the case where our system starts magnetized along z, i.e., as \( I_{z,1} \) (which is in fact \( \frac{1}{2} I_z \)). If we can impose a perturbation which has the symmetry \( I_{z,2} \) with our pulse, then \( I_{z,2} \) will induce \( I_{z,1} \) to rotate into \( I_{z,3} \). This in fact, is the philosophy of the preparation of double quantum coherence, its description in terms of operators, and its application to the technique which we have termed Fourier Transform Double Quantum NMR.¹⁰

**DOUBLE QUANTUM HAMILTONIAN**

To see the application of these operators, let us consider the Hamiltonian for a spin-1 system in which we irradiate the nuclear spins at resonance, namely between the two quadrupolar satellites with a weak rf field. In the laboratory frame, the Hamiltonian is given by:

\[
\mathcal{H} = -\omega_0 I_z - 2\omega_1 I_x \cos \omega_0 t + \frac{1}{3} \omega_0 Q (3I_z^2 - I_1^2)
\]  

(3)
where the first term is the Zeeman coupling, the second term corresponds to the rf irradiation of intensity $2\omega_1$ and the third term is the quadrupole coupling, Equations (1), (2). Transforming this to the rotating frame and discarding time-dependent terms we obtain:

$$\mathcal{H} = -\omega_1 I_x + \frac{1}{3} \omega_Q (3I_z^2 - I_x^2)$$

Now, casting this in terms of our fictitious spin-$\frac{1}{2}$ operators from Table I, this can be written as:

$$\mathcal{H} = -2\omega_1 I_{x,1} + \frac{2}{3} \omega_Q (I_{x,3} - I_{y,3})$$

What I would like to show now is what I pointed out before, namely that this can be written totally in terms of $z$-operators (double quantum operators) after an appropriate transformation. In fact, let us now transform the Hamiltonian by the unitary transformation operator:

$$T = \exp(-i\theta I_{x,2})$$

where $T$ denotes a tilted frame $^{11,12}$ and

$$\theta = \tan^{-1} \left( \frac{2\omega_1}{\omega_Q} \right), \quad \omega_e = (4\omega_1^2 + \omega_Q^2)^{1/2}$$

The transformed Hamiltonian is:

$$\mathcal{H}_T = -\frac{1}{2} (\omega_e - \omega_Q) I_{z,3} + \frac{2}{3} \omega_Q + \frac{1}{2} (\omega_e - \omega_Q) (I_{x,3} - I_{y,3})$$

Note two things now. First of all, the second term in Equation (8) commutes with all the $z$ operators (this can be checked by looking at Table I).
and will therefore play no role in any system where we start in thermal equilibrium. Thus, we drop it. Secondly, since \( \omega_1 \ll \omega_Q \), we can expand the coefficient of the first term and obtain the double quantum Hamiltonian (on resonance):

\[
\mathcal{H}_{DQ} = -\frac{\omega_1^2}{\omega_Q} I_{z,3}
\]  

We refer to such an rf pulse with \( \omega_1 \ll \omega_Q \) as a double quantum pulse. Now all this was done in the case that \( \omega_1 \) is applied at resonance, i.e., the oscillating rf field is applied exactly at \( \omega_0 \). In the general case, we will have a resonance offset term which we denote \( \delta \omega \), (or sometimes \( \Delta \omega \) if it is not necessarily small) namely we irradiate at \( \omega_0 \pm \delta \omega \). The whole development then carries through as before and we obtain the double quantum (DQ) Hamiltonian:

\[
\mathcal{H}_{DQ} = -2\delta \omega I_{z,1} - \frac{\omega_1^2}{\omega_Q} I_{z,3}
\]  

Let us examine Equation (10). It contains two terms in exact analogy to the spin-\( \frac{1}{2} \) case. The first term corresponds to a resonance offset of \( 2\delta \omega \) along the \( z,1 \) axis. The second term corresponds to an rf field of intensity \( \frac{\omega_1^2}{\omega_Q} \) along the \( z,3 \) axis. This is exactly analogous to the spin-\( \frac{1}{2} \) case where we have a resonance offset \( \delta \omega \) along the \( z \)-axis and an rf field \( \omega_1 \) along the \( x \)-axis. In this case the 1-axis plays the role of \( z \) and the 3-axis plays the role of \( x \).
DOUBLE QUANTUM COHERENCE

We can now discuss the evolution of the spin density matrix under the Hamiltonian of Equation (10), namely during a double quantum rf pulse. Assume the density matrix is initially given in equilibrium by:

\[ \rho_0 = 2\beta \omega_0 I_{z,1} \]  

(11)

The time evolution is given by:

\[ \rho(t) = \exp(-it \mathcal{H}_{DQ}) \rho_0 \exp(it \mathcal{H}_{DQ}) \]  

(12)

Taking \( \mathcal{H}_{DQ} \) from Equation (10) and assuming

\[ \frac{\omega_1^2}{\omega_Q} \gg 2\delta \omega \]  

(13)

we can neglect \( 2\delta \omega \) during the pulse and obtain to a good approximation:

\[ \rho(t) = \exp(i \frac{\omega_1^2}{\omega_Q} I_{z,3}) 2\beta \omega_0 I_{z,1} \exp(-i \frac{\omega_1^2}{\omega_Q} I_{z,3}) \]  

(14)

which is easily solved, since it is a spin-1/2 problem, as:

\[ \rho(t) = 2\beta \omega_0 \left[ I_{z,1} \cos \frac{\omega_1^2}{\omega_Q} t - I_{z,2} \sin \frac{\omega_1^2}{\omega_Q} t \right] \]  

(15)

Thus we see that we are rotating the effective density matrix around the \( z,3 \) axis at an angular frequency of \( \frac{\omega_1^2}{\omega_Q} \). This we might term "double quantum rotary free induction decay" and it has already been treated and observed by Hatanaka et al.\(^4\). We define a \( \frac{\pi}{2} \) double quantum pulse:
\[
\frac{t}{\frac{\omega_1}{\omega_Q}} = \frac{\pi}{2}
\]  
(16)

in which case we obtain the density matrix after preparation as

\[
\rho = -2\beta_0 I_{z,2}
\]  
(17)

Before we enquire into the evolution of this double quantum state let me try to give you a visual picture of what has happened here. This is most easily done by observing Figure 5, which shows the symmetry of the three relevant double quantum operators, \(I_{z,1}', I_{z,2}', \) and \(I_{z,3}'.\) The system started in equilibrium in the state \(I_{z,1}'\), we applied a pulse whose symmetry corresponds to \(I_{z,3}\) and we have now created a state of the system corresponding to \(I_{z,2}'\). This double quantum state is a state of quadrupolar coherence in the \(x,y\) plane. This means that we have a coherent macroscopic electric quadrupole moment in the \(x,y\) plane. Now, several things should be obvious just by looking at the symmetry, also clear in the work of Hatanaka et al.\(^4\): a) The precession frequency of this double quantum state after the \(\pi/2\) double quantum pulse should occur at \(2\delta\omega\) because the symmetry is such that it comes back to itself every \(180^\circ\). b) We can see that there should be no observable magnetization. This has a quadrupolar symmetry and so it would be observable only by a quadrupole detector, with an enormously small voltage. So our double quantum decay is not directly observable and we will have to probe it somehow. c) The two conjugate states \(I_{z,2}'\) and \(I_{z,3}'\) are \(\frac{\pi}{4}\) apart, so a \(\frac{\pi}{4}\) phase shift of the rf might induce spin locking. We'll see that later.
Assume now that at time 0 we have a state corresponding to $I_{z,2}$ as given by:

$$\rho(0) = I_{z,2}$$

where I have dropped the coefficients from Equation (17). This state will evolve during $\tau$ under only the first term of the Hamiltonian (10) since we have removed the rf, and a very simple calculation gives us the result:

$$\rho(t) = I_{z,2} \cos 2\omega \tau - I_{z,3} \sin 2\omega \tau$$

The fact that $I_{z,2}$ and $I_{z,3}$ commute with the quadrupole Hamiltonian is the quantum mechanical statement of the claim that the double quantum decay is unaffected by the quadrupole coupling. I would like to point out that the theory is quite general and will treat not only the case of double quantum irradiation but irradiation anywhere in the spectrum. It is a powerful and general theory, applicable not only to the case of magnetic resonance but to any three-level system, including, for example, two photon laser phenomena. Also, it can be directly extended to higher order coherent multiphoton effects.

Now, quantum mechanically the statement that Equation (19) gives no observable induction signal is

$$\text{Tr}\{I_{+}\rho(t)\} = 0$$

How can we then observe the double quantum decay? Well, one way to do that is just to apply another pulse which will serve the purpose of an
observation pulse. We hope that if at a particular time $t$ we apply a strong pulse we will elicit a magnetization which will be proportional to the double quantum coherence at time $t$. This is in fact the case as depicted schematically by Figure 6. So one way to do the experiment is to make a double quantum pulse, wait a time $t$, put on our observation pulse and then observe the signal after the second pulse as a function of $t$. If you look at this carefully, you will see that this is a special case of the two-dimensional spectroscopy described by Ernst and Jeener in their lectures although in our case it is often unnecessary to do a double Fourier transformation. We do this, however, when we wish to get the double quantum behavior for a particular quadrupolar satellite or range of $\omega_Q$'s.

In practice, if you look at Figure 6, you will see that the signal after the second pulse will occur in dispersion mode. Further, it is difficult to observe directly because the quadrupolar decay is so rapid that receiver recovery time after the pulse interferes. So we use other pulse sequences for which I shall not go into the details of either the theory or the technique. I am sure many possibilities will occur to you. I will show you only one example of a sequence which we have used, in Figure 7. This is a nice way to observe double quantum free induction decays for the purpose of deuterium nmr spectroscopy. We make a double quantum pulse $P_1$, the system evolves during $t$ and we then make another double quantum pulse $P_2$ which returns the system back to the $z$-axis. Two intense pulses $P_3$ and $P_4$ will give us a spin echo $M(t)$ whose intensity is proportional (with some distortion) to the double quantum coherence $Q(t)$ just before $P_2$. Fourier transformation of $M(t)$ should then give us a high resolution double quantum spectrum.
Okay, so much for the simple aspects of the theory, let's now see some experimental results depicting our first results on nmr spectra of deuterium. In Figure 8, we see one of the features of the double quantum effect. This experiment was done on the deuterium spins of 100% deuterated oxalic acid dihydrate. In (a) a double quantum pulse was applied at resonance and the decay monitored as I have just described. We see a free induction decay lasting almost 1 millisecond or so demonstrating that in fact we have effectively removed the quadrupole coupling, because the quadrupole splitting in this case is of the order of 200 KHz. Now we repeat the experiment after shifting ~2 KHz of resonance and we get a resonance offset oscillation. Fourier transforming the two decays from a and b we get the spectra at the bottom which are shifted by ~4 KHz showing the 26ω effect that we expected. In addition, the lines are ~37 ppm wide, which is considerably narrower than the width of the quadrupolar satellites in the original single quantum spectrum, so that we are eliminating inhomogeneous distributions of quadrupole couplings as well. The resolution is dominated here by deuterium-deuterium dipolar coupling.

To see if we can resolve a deuterium chemical shift the same experiment was performed but this time on a 10% deuterated crystal. The double quantum decay was monitored while decoupling the protons and a typical result is shown in Figure 9. In (a) we see the double quantum decay and in (b) the Fourier transform. There are two chemically different types of deuterium in this compound, the carboxyl deuterium and the deuterium of the water of hydration. We see that we can actually resolve them and we
obtain in fact the spin-$\frac{1}{2}$ spectrum from the deuterium that we would expect if we did high resolution proton nmr. Again, here from a spectrum which is something like 200 KHz wide we obtain an essentially high resolution solid state nmr spectrum.10

We can also measure the chemical shift anisotropy of the deuterium and the first such measurement is shown in Figure 10.10,16 Here the double quantum peak of the carboxyclic deuterium was monitored as the crystal was rotated and compared with the chemical shift measured from a single quantum experiment. The latter is done in a good crystal by observing the quadrupolar satellites with high resolution while proton decoupling.16

The case of the powder is also interesting and Fourier transform double quantum nmr was applied to a long outstanding problem, that of the solid state nmr spectrum of the protons in benzene. The chemical shift anisotropy is expected to be small and so previous techniques have not been successful. Dr. Vega and David Wemmer took monodeuterobenzene 10% doped into normal protonated benzene, decoupled the protons at -50° and observed the double quantum free induction decay. Upon Fourier transformation it gives the spectrum shown in Figure 11, yielding a chemical shift anisotropy for the deuterium spins of -6.5 ppm.17 Indeed it is small, it is negative as expected by theory, and in fact is quite well resolved by our technique from the original spectrum which is ~ 140 KHz wide. I should mention that these last two deuterium experiments were done at ~ 28 MHz.
DEUTERIUM SPIN DECOUPLING--INTRODUCTION

I would like to now show you that the theory and the whole double quantum concept is applicable not only to Fourier transform double quantum nmr but to other potentially useful double quantum phenomena as well. In particular, one of the first things that we did with double quantum nmr effects was to perform deuterium decoupling in the solid.\textsuperscript{18} This was essentially a direct extension of the work of Meiboom and his group on deuterated liquid crystals.\textsuperscript{19}

In the case of solids we wish to decouple deuterium from protons allowing us to observe the high resolution proton nmr of the residual protons in perdeuterated materials. This poses a problem similar to the one we have discussed up to now in that in order to decouple, as shown by Figure 12, we need to irradiate the deuterium spins which can cover a frequency of \( \sim 200 \) KHz. Thus, using the normal concepts of decoupling we would need a tremendously large \( \omega_1 \), practically impossible. However, remember that the double quantum transition is sharp and we are in fact able to decouple through this transition as explained by Meiboom et al.\textsuperscript{19} This is shown in Figure 13 where the residual protons in 99.5\% deuterated DMSO yield a sharp spectrum upon deuterium decoupling even with \( \omega_1 \ll \omega_Q \).

This effect is very sensitive to the deuterium irradiation frequency.

Can we treat this decoupling quantitatively, using the double quantum operator formalism? The answer is yes, we can predict the \( ^1H \) linewidth dependence on both deuterium irradiation frequency and intensity \( \omega_1 \). In order to see how we treat double quantum decoupling quantitatively let us quickly review the case of the spin-\( \frac{1}{2} \) and then I will show you that you can do the spin-1 case by direct analogy, just substituting the fictitious
spin-$\frac{1}{2}$ double quantum operator in each case for the appropriate real spin-$\frac{1}{2}$ operator.

**SPIN-$\frac{1}{2}$ DECOUPLING**

For the case of spin-$\frac{1}{2}$ decoupling we have two unlike spin-$\frac{1}{2}$ nuclei $I$ and $S$ coupled by dipolar coupling. We assume $S$ is dilute and $I$ abundant. The Hamiltonian in the rotating frame is given by:

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}_{IS}$$  \hspace{1cm} (21)

where

$$\mathcal{H}_o = -\Delta \omega I_z - \omega_1 I_x$$  \hspace{1cm} (22)

and

$$\mathcal{H}_{IS} = \sum_I b_I I_z S_z$$  \hspace{1cm} (23)

where we neglect $\mathcal{H}_{II}$. We assume the $I$-$S$ coupling term $\mathcal{H}_{IS}$ to be characterized by a dipolar parameter $D$ which is a characteristic $b_I$. The problem is the following, as we can see. We apply off resonance by an amount $\Delta \omega$ an rf field of intensity $\omega_1$ on the $I$-spins to decouple them from the $S$-spins to yield a sharp $S$ spectrum. We would like to study how efficient this is as a function both of $\omega_1$ and $\Delta \omega$. Namely, how sensitive is it to the offset frequency from the middle of the $I$-spin resonance and to the intensity $\omega_1$.

An excellent way to treat this problem of decoupling is to use the coherent averaging formalism, some aspects of which are described
in the lectures by Waugh. What we do is to look at the effect of $\mathcal{H}_0$ upon $\mathcal{H}_{IS}$. $\mathcal{H}_0$ will modulate $\mathcal{H}_{IS}$ and we will expand the average $\mathcal{H}_{IS}$ due to the modulation in a series of terms which we will call the average Hamiltonian. It turns out that in our case the only terms of the average Hamiltonian which are relevant are the first and the third, namely;

$$\tilde{\mathcal{H}}^{(0)}_{IS} = \cos \theta \mathcal{H}_{IS}$$  \hspace{1cm} (24)$$

$$\tilde{\mathcal{H}}^{(2)}_{IS} = \left( \frac{P^2}{\omega_1} \right) \mathcal{H}^\prime_{IS}$$  \hspace{1cm} (25)$$

where

$$\cos \theta = \sqrt{\frac{\omega_1}{\omega_1^2 + \Delta \omega^2}}$$  \hspace{1cm} (26)$$

$\tilde{\mathcal{H}}^{(1)}_{IS}$ is not important since it commutes with the S-spin operators and will not cause a broadening to first order. $\tilde{\mathcal{H}}_{IS}$ is an operator with structure similar to that of $\mathcal{H}_{IS}$. Now using Equations (24) and (25) we can describe the behavior of the S-spins as occurring essentially under the influence of $\tilde{\mathcal{H}}^{(0)}_{IS} + \tilde{\mathcal{H}}^{(2)}_{IS}$. In the case that we are off resonance the first term $\tilde{\mathcal{H}}^{(0)}_{IS}$ is non-zero and we will take it to constitute the average IS Hamiltonian and neglect Equation (25). In the case that we are on resonance, $\cos \theta = 0$ and we will take as the first non-zero term $\tilde{\mathcal{H}}^{(2)}_{IS}$ in (25).

Let us discuss these two cases in sequence. First, off resonance decoupling. In this case the I-S Hamiltonian is given by Equation (24)
and thus the S-linewidth due to the I-S coupling will go as \( \cos \theta \), since \( \mathcal{H}_{IS} \) is scaled down by \( \cos \theta \), i.e.:

\[
\frac{\delta}{\delta_0} \sim \cos \theta = \frac{\Delta \omega}{\sqrt{\omega_1^2 + \Delta \omega^2}}
\]  

(27)

where \( \delta \) is the linewidth of the S-spins during irradiation of the I-spins, and \( \delta_0 \) is the S-spin rigid linewidth without I-spin decoupling. We see from this that decoupling will become inefficient when \( \Delta \omega \) is of the order \( \omega_1 \). This is simply restating what is well known, that in order to effect decoupling if you are off resonance by \( \Delta \omega \) your field \( \omega_1 \) must be larger than \( \Delta \omega \).

For the second case of on resonance decoupling, we use Equation (25). In this case we see that \( \frac{\delta}{\delta_0} \) should go as \( \frac{D^2}{\omega_1^2} \), where \( D \) characterizes the I-S dipolar coupling. This was pointed out previously by Haeberlen\(^2\) for the spin-\( \frac{1}{2} \) case, and means that if we are on resonance: a) For large \( \omega_1 \) (and I would like to remind you that this whole theory is valid only for large \( \omega_1 \)):

\[
\frac{\delta}{\delta_0} \sim \frac{D^2}{\omega_1^2}
\]  

(28)

b) In order to have efficient decoupling \( \omega_1 \) must be at least as large as \( D \), the rigid S-linewidth. If I-I coupling is included, the situation is more complicated if \( |\mathcal{H}_{II}| > |\mathcal{H}_{IS}| \).

**DOUBLE QUANTUM DECOUPLING**\(^{17b,21}\)

We can now take over these results to the case of double quantum
decoupling using the fictitious spin-$\frac{1}{2}$ operators. Here we have a spin-$1$ with quadrupolar coupling $\omega_Q$ coupled to a dilute spin-$\frac{1}{2}$ $S$. In this case the Hamiltonian is again given by:

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}_{IS}$$

(29)

and we write $\mathcal{H}_o$ and $\mathcal{H}_{IS}$ in terms of the fictitious spin-$\frac{1}{2}$ operators. $\mathcal{H}_o$ is the $I$ double quantum operator from (10):

$$\mathcal{H}_o = -2\Delta \omega I_{z,1} - (\omega^2_I/\omega_Q)I_{z,3}$$

(30)

where we assume a constant characteristic $\omega_Q$ and

$$\mathcal{H}_{IS} = \sum_{i} 2b_{i} I_{i z,1} S_z$$

(31)

again characterized by a dipolar coupling $D \sim b_{i}$. This is identical to the spin-$\frac{1}{2}$ case if we make the correspondence $x,y,z \rightarrow 3,2,1$, $\Delta \omega \rightarrow 2\Delta \omega$, $\omega_1 \rightarrow \omega_Q$. So we can write down the average Hamiltonian directly, namely, the average $\mathcal{H}_{IS}$ due to the decoupling field $\mathcal{H}_o$ and we obtain for the first two important terms:

$$\mathcal{H}_{IS}^{(0)} = \cos \theta \mathcal{H}_{IS}$$

(32)

and

$$\mathcal{H}_{IS}^{(2)} = \frac{D^2 \omega^2_Q}{\omega^4_1} \mathcal{H}_{IS}$$

(33)

where by direct analogy to (27)
\[
\cos \theta = \frac{2b w}{\sqrt{1 + \frac{b^2}{4}}} \tag{34}
\]

By direct analogy to (27) we obtain for the relative S-linewidth when we decouple off resonance:

\[
\frac{\delta}{\delta_0} \sim \cos \theta = \frac{2b \omega_0}{\sqrt{\omega_1^4 + 4\Delta \omega^2 \omega_1^2}} \tag{35}
\]

From this we see that the decoupling will become inefficient and that \(\frac{\delta}{\delta_0}\) of the S resonance will become of the order of 1 when \(\Delta \omega\) is of the order of \(\frac{1}{4}(\omega_1^4/\omega_Q^4)\omega_1^4\). This explains the extreme sensitivity of the deuterium decoupling to the irradiation frequency of the deuterium. If we shift off by a small amount compared to \(\omega_Q\) the decoupling becomes inefficient as long as \(\omega_1 << \omega_Q\), even though at resonance for the deuterium the decoupling can be very efficient.

Similarly, we can find the condition for on resonance decoupling from the Hamiltonian in (33) by analogy to (28):

\[
\frac{\delta}{\delta_0} \sim \left(\frac{D^2 \omega^2}{\omega_1^4}\right) \tag{36}
\]

Thus we predict for double quantum decoupling that the S-linewidth, in this case the proton linewidth, should go as \(\frac{1}{\omega_1^4}\) for large \(\omega_1\). In addition, we find that for the onset of decoupling namely for \(\frac{\delta}{\delta_0}\) to be reduced from 1 we need \(\omega_1^2\) to be of the order of \(D \omega_Q^2\). This is exactly the double quantum condition which we predicted by very simple arguments previously.

Now let's see that these quantitative predictions are in fact borne out. First, Figure 14 shows the off resonance decoupling behavior of
solid benzene-d$_6$. We are looking here at the residual protons in 99% deuterated benzene while irradiating the deuterium spins, plotting the residual proton linewidth as we shift the deuterium rf off resonance by an amount $\Delta v$. The solid line is $\cos \theta$ given by (34) with no parameters, assuming only that the S-line is Gaussian.

The on resonance decoupling behavior is shown in Figure 15 showing the experimental proton linewidth as the deuterium $\omega_1$ field is increased. The theoretical (solid) line is calculated using precise values of D with no other parameters for benzene showing the expected $\frac{1}{\omega_1^4}$ dependence.

We note also that the onset of decoupling occurs at a deuterium $\nu_1$ of about 6 KHz, which is considerably less than the quadrupole coupling, again bearing out quantitatively our theoretical predictions. Let me close this section by mentioning that Professor Mehring and his students have used deuterium double quantum decoupling together with multiple-pulse nmr to produce some really nice high resolution proton spectra.

**PROTON NMR AND MOTION IN ICE**

As an example of more chemical interest, we have studied the application of deuterium decoupling to the resolution of the proton chemical shift in several deuterated materials. Here I shall show you one example in Figure 16, that of ice. What we see is the spectrum of the residual protons in 99% deuterated ice at -90° C. The top spectrum of the figure is without deuterium decoupling, and the lower one is with decoupling, showing the first resolution of the proton chemical shift tensor of ice. The chemical shift anisotropy is large, of the order of 35 ppm due to strong hydrogen bonding.
In the case of ice, and in other cases as well, we were able to go further than to resolve only the proton or the deuterium chemical shift. We were able to actually see the effects of motion on the spectra and I would like to show you one example. The idea here was to show a simple case of motion of a particular symmetry on an anisotropic nmr lineshape. The reason for this is a recent beautiful theory developed by Alexander, Baram and Luz which allows one to use simple group theoretical arguments to describe motion in polycrystalline samples. The same problem has been treated in numerical calculations and experiments by Spiess et al. and by us.

The problem is depicted in Figure 17. We have a probe, in this case our chemical shift tensor of the proton in ice, which has a symmetry. This is imbedded in a molecule, or we have particular sites that this probe is going to move in, which transform according to the symmetry. The number of parameters describing the motion is reduced tremendously by the group theoretical statement in Figure 18. Namely, the only irreducible representations of the point group describing the motion, which are relevant, are those which contain the totally symmetric representation of . Using this simple theory we are able to predict the expected spectra when the nuclei move according to a particular symmetry.

Figure 19 shows a nice example of this in the case of ice. On the left side we see experimental spectra of the residual protons in heavy ice with deuterium decoupling as a function of temperature. At low temperature we get the axially symmetric rigid spectrum and at -5° we see that the protons are moving around rapidly enough that we are getting
essentially a single line at the isotropic position. The other spectra show what happens at intermediate temperatures and we see that the spectra contain structure expected from the calculations. The spectra on the right are simulated assuming motion of the protons according to tetrahedral symmetry. This is precisely the motion expected for the protons in ice-I. The packing in the hexagonal lattice has each oxygen surrounded tetrahedrally by four others with protons hydrogen bonding between them. This is described in detail in the lecture by Gränicher. Thus the motion of the protons can be described as a tetrahedral pseudo-rotation of a water molecule amongst six equivalent positions. We see in Figure 19 that the correspondence between theoretical and experimental spectra is quite satisfying and gives us a direct way to study the reorientational part of the proton motion in these crystals, which is not always the case for dielectric relaxation and diffusion measurements.

**DOUBLE QUANTUM SPIN LOCKING**

As one final example I would like to discuss the question of spin locking. The case of spin locking for spin-$\frac{1}{2}$ is extremely well known. I have tried to depict in Figure 20 the symmetry aspects of spin locking. Remember that I am a chemist and love to think of atomic and molecular orbitals. Assume that we apply a $\pi/2$ pulse along the $x$-direction in the rotating frame. It has the symmetry of a vector, a $p_x$ orbital, as shown in the top left corner. The spins have been prepared so that they lie along the $y$-axis with the symmetry of a $p_y$ orbital. If we now phase shift the rf by $90^\circ$ we go from $x$ to $y$, aligning our $H_1$ field with the magnetization and causing spin locking. The magnetization can now decay
only by spin lattice processes, and the coherent state between \( m = \pm \frac{1}{2} \) is thus prolonged dramatically. This is very useful in many many applications, in particular motional studies and double resonance. Similarly, with a 180° phase shift we go from \( H_\perp \) to \( -H_\perp \) and this gives us a mechanism for producing spin echoes, as is well known.

Now, what is the analogous situation for the spin-1 case? In order to understand this let us look at the effect of rf phase shift on the double quantum Hamiltonian given by (10). This Hamiltonian was derived for the case that the rf field in the rotating frame is applied along the \( x \)-axis. Now let us assume that our irradiation was along an arbitrary axis, namely with phase angle \( \phi \) in the rotating frame, given by:

\[
H = -2\delta \omega I_{z,1} - 2\omega_1 (I_{x,1} \cos \phi + I_{y,1} \sin \phi)
\]  

Applying the same tilt transformation as we did in (6) again with \( \omega_1 \ll \omega_Q \) we derive this time the effective double quantum Hamiltonian:

\[
H_{\text{DQ}} = -2\delta \omega I_{z,1} - \frac{\omega_1^2}{\omega_Q} (I_{z,3} \cos 2\phi + I_{z,2} \sin 2\phi)
\]

where again the commutative term \( (I_{x,3} - i I_{y,3}) \) has been dropped. Thus an rf phase shift of \( \phi \) corresponds to a shift of \( 2\phi \) in the double quantum frame.

This is depicted schematically in Figure 21 using orbitals of quadrupolar symmetry, the \( d \) orbitals. Assume that we would like to effect spin locking of the double quantum state. We apply a \( \frac{\pi}{2} \) double quantum pulse and prepare the state \( I_{z,2} \). The conjugate operator which
created this state is \( I_z, 3 \). Looking at the picture we see that a 45° phase shift will make the effective rf operator align with the spin state and should thus effect quadrupolar spin locking. Similarly, if we would like to make spin echoes we should make a 90° phase shift which will show up in the double quantum frame as a 180° phase shift.

We have done both experiments: I will show you only one example, that of spin locking. If you look at Figure 22 you see a normal double quantum free precession on the deuterium spins of solid perdeuterated oxalic acid dihydrate monitored with a single probing pulse. The whole double quantum decay is over due to deuterium-deuterium dipole-dipole couplings in a few hundred microseconds. In Figure 23 I show you what we observed when the same experiment was done but the double quantum pulse was followed with a phase shifted weak rf pulse, namely a phase shifted double quantum pulse. You see that the oscillations have been removed and that the decay has been considerably prolonged exactly as in the case of normal spin-\( \frac{1}{2} \) spin locking. Similar behavior has been observed in the pure quadrupole regime by Hahn and his group.

This whole concept allows us to consider the possibility of double quantum cross polarization. Namely, can we cross polarize from the protons the double quantum deuterium transition, so that we could then do high resolution double quantum nmr spectroscopy with high sensitivity. In fact we have done this but with the limited time of my lectures I will not describe it to you. All of these things will be published soon.

I hope I have given you some feel for this new field of Fourier Transform Double Quantum NMR and the large number of its potential applications. I hope to see some of you trying out similar experiments
in the future. I would like to acknowledge helpful and enjoyable discussions not only with the colleagues whom I have already mentioned who participated in the research and did all the work but with my friends Erwin Hahn, Robert Harris and Michael Mehring, who helped us tremendously.
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14. R. R. Ernst, Lectures at this school, page

15. J. Jeener, Lectures at this school, page


17. a) S. Vega, D. E. Wemmer and A. Pines, to be published.


20. J. S. Waugh, Lectures at this school, page


27. E. L. Hahn, Lectures at this summer school, page
Table I. Fictitious Spin-$\frac{1}{2}$ Operators for 3-Level System and Matrix Representation (Matrices are multiplied by 2).

| $I_{x,1}$ | $\frac{1}{2} I_x$ | \(
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\) |
| $I_{x,2}$ | $\frac{1}{2}(I_y I_z + I_z I_y)$ | \(
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & -i \\
0 & i & 0
\end{pmatrix}
\) |
| $I_{x,3}$ | $-\frac{1}{2}(I_y^2 - I_z^2)$ | \(
\begin{pmatrix}
0 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\) |
| $I_{y,1}$ | $\frac{1}{2} I_y$ | \(
\begin{pmatrix}
0 & 0 & 1 \\
0 & 0 & 0 \\
1 & 0 & 0
\end{pmatrix}
\) |
| $I_{y,2}$ | $\frac{1}{2}(I_z I_x + I_x I_z)$ | \(
\begin{pmatrix}
0 & 0 & i \\
0 & 0 & 0 \\
-i & 0 & 0
\end{pmatrix}
\) |
| $I_{y,3}$ | $-\frac{1}{2}(I_z^2 - I_x^2)$ | \(
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\) |
| $I_{z,1}$ | $\frac{1}{2} I_z$ | \(
\begin{pmatrix}
0 & i & 0 \\
-i & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\) |
| $I_{z,2}$ | $\frac{1}{2}(I_x I_y + I_y I_x)$ | \(
\begin{pmatrix}
0 & 0 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\) |
| $I_{z,3}$ | $-\frac{1}{2}(I_x^2 - I_y^2)$ | \(
\begin{pmatrix}
0 & 0 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\) |

\[ [I_{p,j}, I_{p,k}] = i I_{p,l} \]

$p = x, y, z$

$j, k, l = 1, 2, 3$ or cyclic permutation
Figure 1. Energy levels for quadrupolar spin-1 in high magnetic field. The quadrupolar interaction gives rise to two "allowed" transitions at frequencies $\omega_0 \pm \omega_Q$ where $\omega_0$ is the Larmor frequency.
Figure 2. Deuterium nmr spectrum of solid perdeuterated dimethylsulfoxide, showing large linewidth due to quadrupolar broadening.
Figure 3. Double quantum transition for spin-1.
Double-Quantum Preparation and Evolution

Figure 4. Schematic diagram of Fourier Transform Double Quantum NMR experiment to yield high resolution nmr spectrum of deuterium. A double quantum pulse places m = ±1 in coherent superposition and the coherence Q(τ) decays without quadrupolar interaction while protons are decoupled.
Figure 5. Symmetry of double quantum z-operators in the rotating frame. $I_{z,1}$ corresponds to a z-magnetization while $I_{z,2}$ and $I_{z,3}$ correspond to the two coherent double quantum states in the x-y plane. These are fictitious spin-$\frac{1}{2}$ operators for the double quantum transition with commutation relation $[I_{z,1}, I_{z,2}] = iI_{z,3}$ and cyclic permutation of 1,2,3.
Figure 6. Evolution and detection of double quantum coherence by simple
two pulse sequence. The normalized expressions on the figure are written for the
ideal case of a pure double quantum pulse \((\omega_1 \ll \omega_Q)\) followed by a normal
single quantum pulse \((\omega_1 \gg \omega_Q)\). Fourier transformation of the signal
yields a dispersion-like line with intensity proportional to \(\langle I_{z2}(\tau)\rangle = \cos 2 \delta \omega \tau\), thus allowing a plot of the double quantum free induction decay.
Figure 7. Pulse sequence (2 double quantum pulses and 2 single quantum pulses) for double quantum free induction decay.
Figure 8. Double quantum free induction decay of deuterium in crystal of perdeuterated oxalic acid dihydrate. a) near resonance and b) $\delta \omega = 2$ KHz off resonance. The lower figure contains the Fourier transform of those decays showing the double quantum offset is $2\delta \omega = 4$ KHz.
Figure 9. Double quantum free induction decay and Fourier transform of deuterium in 10% deuterated crystal of oxalic acid dihydrate. The chemical shifts of the two types of deuterium nuclei, carboxyl and water are resolved.
Figure 10. Chemical shift of carboxyl deuterium as the crystal is rotated, showing the large chemical shift anisotropy.
Figure 11. Fourier Transform Double Quantum (FTDQ) NMR spectrum of deuterium in polycrystalline benzene-$d_1$ (10% in normal benzene) at $T \sim -50^\circ\text{C}$. 
Figure 12. Coupled pair of proton and deuterium spins showing schematic spectra, the top for a crystal and the lower for a powder. We would like to spin decouple the deuterium by irradiation to observe a sharp proton spectrum, but the deuterium line can be \( \sim 200 \text{ KHz} \) wide.
Figure 13. Double quantum decoupling of deuterium in solid perdeuterated dimethylsulfoxide, with a weak deuterium $\omega_1$ field $\omega_1 \ll \omega_Q$ on resonance.
Figure 14. Double quantum decoupling (linewidth of residual protons) of deuterium in solid perdeuterated benzene as a function of deuterium resonance offset $\Delta \nu$, showing the sensitivity to resonance condition when $\omega_Q$ is large. The solid line is from theory with no parameters.
Figure 15. Double quantum decoupling (linewidth of residual protons) of deuterium in solid perdeuterated benzene as a function of deuterium $H_1$ field. The solid line depicts the $\alpha \frac{1}{\omega_1^4}$ behavior from theory with no parameters.
Figure 16. Nmr spectra of residual protons in perdeuterated ice-I with and without double quantum deuterium decoupling.
Figure 17. Schematic diagram of molecule (or nucleus) moving according to symmetry $G$ while we observe lineshape of probe with symmetry $g$. 
Which irreducible representations of $G$ are induced by the totally symmetric representation (A) of $g$?

Figure 18. The problem of the effect of motion on lineshape can be reduced using symmetry. The only irreducible representations of $G$ which are relevant are those which contain the totally symmetric representation of $g$. Very often there are only two such representations of $G$ making the problem a $2 \times 2$ one which is analytically solved.
Figure 19. Nmr spectra of residual protons in ice with deuterium decoupling at various temperatures. The spectra on the right are calculated for the case of protons moving according to tetrahedral symmetry, i.e., G of Figure 18 corresponds to the tetrahedral group and g corresponds to the chemical shielding tensor. The numbers on the right are proton jump rates in Hz.
Figure 20. Symmetry of linear angular momentum (spin-$\frac{1}{2}$) operators; phase shift of $90^\circ$ takes $I_x$ to $I_y$ and can thus induce spin locking. A phase shift of $180^\circ$ takes $I_y$ to $-I_y$. 
Figure 21. Symmetry of double quantum (fictitious z-space spin-\(\frac{1}{2}\)) operators.

A phase shift of 45° takes \(I_{z,2}\) to \(I_{z,3}\) and can thus induce double quantum spin locking. A phase shift of 90° takes \(I_{z,3}\) to \(-I_{z,3}\).
Double Quantum Free Induction Decay

Figure 22. Deuterium double quantum free induction decay in crystal of perdeutero oxalic acid dihydrate with small resonance offset. The intensity of the signal after the second pulse is plotted versus $\tau$. The first pulse is a $\frac{\pi}{2}$ double quantum pulse.
Figure 23. The same as Figure 22 except that during $\tau$ a 45° phase shifted rf irradiation with $\omega_1 \ll \omega_Q$ is continued after the double quantum pulse. This causes locking of the double quantum state, removing the resonance offset oscillation and prolonging the double quantum decay by an order of magnitude.
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