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Abstract

When a spin-1 with quadrupole interaction $\omega_Q$ is irradiated near resonance $\omega_o (\omega_o - \omega = \Delta \omega)$ with an rf field $\omega_1$ such that $\omega_1 \ll \omega_Q$ the density matrix essentially evolves in a three dimensional frame of reference defined by the operators $I_{z,1} = \frac{1}{2} I_z$, $I_{z,2} = \frac{1}{2} (I_I + I_II)$, $I_{z,3} = - \frac{1}{2} (I^2_x - I^2_y)$. In this frame, which we term "z-space" or the "double quantum frame" the effective rf intensity is $\frac{\omega_1}{\omega_Q}$ and the effective resonance offset is $2\Delta \omega$. We demonstrate in this paper that an rf phase shift of $\phi$ corresponds to a $2\phi$ shift of $\frac{\omega_1}{\omega_Q}$ in the double quantum frame. This is used to perform double quantum phase reversal and double quantum spin locking. Applications to high resolution deuterium nmr in solids are also illustrated.

In this lecture we discuss some of the novel theoretical and experimental developments in pulsed Double Quantum (DQ) NMR in solids. Using this approach, we have performed and analysed DQ spin-decoupling, measured the deuterium chemical shift in single crystals and the chemical shift anisotropy of deuterium in polycrystalline benzene-d$_1$ ($\Delta \sigma = -6.5 \pm 1.5$ ppm), and performed proton deuterium DQ cross-polarization experiments. Here we will discuss the extension of the theory to DQ phase reversal and spin-locking.

The basic theoretical framework is the development of a fictitious spin-$\frac{1}{2}$ operator formalism for the behavior of a spin-1 nucleus subject to a Zeeman interaction $H_o$ with Larmor frequency $\omega_o$, radio frequency irradiation $H_1(t)$ of intensity $\omega_1$ at frequency $\omega$ ($\omega_o - \omega = \Delta \omega$) and a quadrupolar interaction with quadrupolar splitting frequency parameter $\omega_Q$. In the rotating frame the Hamiltonian for this system is given by:

$$H = -\Delta \omega I_z - \omega_1 I_x + \frac{1}{3} \omega_Q (3I^2_z - I(I+1))$$  (1)

Following our field theory we define the following nine fictitious spin-$\frac{1}{2}$ operators $I_p, I$ in terms of the spin-1 angular momentum operators $I_p$:
The usefulness of these operators derives from the fact that for each
\( p = x, y, z \) the operators \( I_{p,i} \) fulfill spin-\( \frac{1}{2} \) angular momentum commutation relations:

\[
[I_{p,i}, I_{p,j}] = i I_{p,k} \quad i, j, k = 1, 2, 3
\]

Thus each \( p \) describes a fictitious two level spin-\( \frac{1}{2} \) subspace (an SU(2) subgroup of the full SU(3) group), which we term the \( p \)-space.

To demonstrate the application of this, let us consider the spin-1 system in equilibrium in high magnetic field for which the reduced high temperature density matrix can be written in the high temperature approximation:

\[
\rho_o = \beta \omega_o I_z = 2 \beta \omega_o I_{z,1}
\]

We now enquire about the evolution of (4) under the Hamiltonian in (1) with \( \Delta \omega << \omega_Q \), i.e., a weak rf field near the unperturbed deuterium Larmor frequency. To a good approximation the Hamiltonian in terms of the operators in (2) can be written:

\[
\mathcal{H} \approx -2 \Delta \omega I_{z,1} - \frac{\omega_1^2}{\omega_Q} I_{z,3} + \frac{2}{3} \omega_Q (I_{x,3} - I_{y,3})
\]

Since the last term in (5) is commutative with the first two and with \( \rho_o \) in (4) it can be essentially discarded. Furthermore, the first two terms contain matrix elements only between the \( m = \pm 1 \) magnetic sublevels of the spin-1 and we refer to the \( z \)-space defined by the operators \( I_{z,1} \) as the DQ space. This is a fictitious spin-\( \frac{1}{2} \) space with 3 cartesian axes \( 1, 2, 3 \) with effective rf irradiation field \( \frac{\omega_1^2}{\omega_Q} \) along the \( z,1 \) axis and resonance offset \( 2 \Delta \omega \) along the \( z,3 \) axis. From (3) we find easily that the vector defining the density matrix precesses about an effect we find defined by the DQ operator.

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

at angular frequency \( \omega_e = \left( 4 \Delta \omega^2 + \frac{\omega_1^4}{\omega_Q^2} \right)^{\frac{1}{2}} \) in strict analogy to the spin-\( \frac{1}{2} \) case.

Taking a 90° DQ pulse \( t = \frac{\pi}{2} \) with \( \omega_1^2 \omega_Q \gg \Delta \omega \) the density matrix \( \rho_o \)
in (4) is transformed by (6) into $2\beta\omega I_{z,2}$ which is in a state of transverse quadrupolar order reflecting a coherent superposition of the $m = \pm 1$ levels and yields a high resolution DQ free induction decay. To see the effect of the rf phase on the DQ phase let us consider $\mathcal{H}_1(t)$ to have a general phase in the rotating frame, i.e., we take as a generalization of (1) the rotating frame Hamiltonian:

$$\mathcal{H} = -\Delta\omega I_z - \omega_1 (I_x \cos\phi + I_y \sin\phi) + \frac{1}{3} \omega_Q (3I_z^2 - I(I+1))$$

(7)

A straightforward calculation with the same conditions used to derive (6) gives the DQ Hamiltonian:

$$\mathcal{H}_{DQ} \approx -2\Delta\omega I_{z,1} - \frac{\omega_1^2}{\omega_Q} (I_{z,3} \cos 2\phi + I_{z,2} \sin 2\phi)$$

(8)

Thus a phase change of $\phi$ in $\mathcal{H}_1(t)$ corresponds to a change of $2\phi$ for the effective rf irradiation in the double quantum frame. Thus to effect a $180^\circ$ phase reversal of $\omega_1^2$ we need a $90^\circ$ rf phase shift and for a $90^\circ$ phase shift of $\omega_Q^2$ for spin locking we need a $45^\circ$ rf phase shift.

To examine this experimentally, experiments were performed on a single crystal of deuterated oxalic acid dihydrate oriented in such a way that the carboxyl deuterons had a quadrupolar splitting of $\nu_Q = 90^\circ$ kHz. In the first set of experiments, we examined the effect of a $90^\circ$ rf phase shift. An rf phase of intensity $\nu_1 = 20$ kHz $< \nu_Q$ and duration $\tau$ and $\Delta\omega = 0$ was applied to the spin system followed by an intense $90^\circ$ probing pulse. The intensity of the signal following the probing pulse $S(\tau)$ is clearly proportional to $I_{z,1}$ at the end of the first weak pulse and can be calculated from (4) to (6):

$$S(\tau) \sim \beta\omega_0 \cos \left(\frac{\omega_1^2}{\omega_Q} \tau\right) f(\tau)$$

(9)

where $f(\tau)$ takes account of relaxation. Experimental results for $S(\tau)$ are shown in figure 1(a) and are in good agreement with (9) ($T_2$ of $f(\tau) = 485 \mu$s) and the experiments of reference 7. In figure 1(b) results of the same experiment are shown except that after $\tau = 165 \mu$s the phase of the weak rf pulse is shifted by $90^\circ$. As can be seen, this results in a $180^\circ$ phase shift for the DQ rotary decay, in agreement with (8).

In the second set of experiments a $90^\circ$ DQ pulse $\omega_1^2, t = \frac{\pi}{2}$ was applied $\Delta\nu = 2.5$ kHz off resonance followed a time $\tau$ later by a probing pulse giving a signal intensity $S(\tau)$ proportional to the expectation value of $I_{z,2}$ at time $\tau$, i.e.,
Experimental values for this DQ free induction decay are compared with the theoretical line in figure 2(a) with $T_2$ of $f(\tau) = 218 \mu\text{sec}$. The experiment was then repeated but during $\tau$ the weak rf irradiation was continued but with a phase shift of $45^\circ$. According to equation (8) the first pulse should cause $\rho_0$ to evolve to $2\beta\omega_0 I_{z,2}$; the $45^\circ$ phase shift then induces the effective operator $\frac{\omega_0}{\omega_Q} I_{z,2}$ so the system should be spin locked eliminating the $2\Delta\omega$ oscillation and prolonging the decay. Indeed, the results in figure 2(b) show just this effect yielding a DQ $T_{1\rho}$ of 2.2 msec.

Applications of these concepts can be made to high resolution deuterium nmr, double resonance, and dipolar coupling. Recent examples on crystals and polycrystalline samples will illustrate this.

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References

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FIGURE 2

(a) Double quantum free induction decay after a 90° double quantum pulse \(\frac{\omega_0}{2} t = \frac{\pi}{2}\) on the carboxyl deuterons of crystalline oxalic acid dihydrate. The experimental points are compared with the theoretical line from equation (10). In (b) the 45° phase shifted rf is expected to induce double quantum spin locking according to (8) and indeed the resonance offset oscillation is removed and the decay prolonged.
Double Quantum Rotary Decay

(a) Double quantum rotary free induction decay on the carboxyl deuterons of crystalline oxalic acid dihydrate. The experimental points are compared with the theoretical line of equation (9) using the parameters in the figure. In (b) the rf phase was shifted by 90° after 165 μsec. This is predicted by equation (8) to induce a 180° phase shift in the double quantum decay as is indeed observed.

FIGURE 1
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