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THEORY OF DOUBLE-QUANTUM COHERENCE AND HIGH RESOLUTION DEUTERIUM NMR IN SOLIDS*

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Abstract

When a spin-1 with quadrupole interaction ω_Q is irradiated near resonance ω_o ($\omega_o - \omega = \Delta\omega$) with an rf field ω_1 such that $\omega_1 \ll \omega_Q$ the density matrix essentially evolves in a three dimensional frame of reference defined by the operators $I_{z,1} = \frac{1}{2} I_z$, $I_{z,2} = \frac{1}{2}(I_x I_y + I_y I_x)$, $I_{z,3} = -\frac{1}{2}(I_x^2 - I_y^2)$. In this frame, which we term "z-space" or the "double quantum frame" the effective rf intensity is $\frac{\omega_1^2}{\omega_Q}$ and the effective resonance offset is $2\Delta\omega$. We demonstrate in this paper that an rf phase shift of ϕ corresponds to a 2ϕ shift of $\frac{\omega_1^2}{\omega_Q}$ 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.[1] Using this approach, we have performed and analysed DQ spin-decoupling,[2] measured the deuterium chemical shift in single cyrstals[3] and the chemical shift anisotropy of deuterium in polycrystalline benzene-d_1 ($\Delta\sigma = -6.5 \pm 1.5$ ppm)[4], and performed proton deuterium DQ cross-polarization experiments.[5] 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-½ operator formalism for the behavior of a spin-1 nucleus subject to a Zeeman interaction H_o with Larmor frequency ω_o, radio frequency irradiation $H_1(t)$ of intensity ω_1 at frequency ω ($\omega_o - \omega = \Delta\omega$) and a quadrupolar interaction with quadrupolar splitting frequency parameter ω_Q. In the rotating frame the Hamiltonian for this system is given by:

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

Following our field theory we define the following nine fictitious spin-½ operators $I_{p,i}$ in terms of the spin-1 angular momentum operators I_p:

$$I_{p,1} = \frac{1}{2} I_p$$
$$I_{p,2} = \frac{1}{2} (I_q I_r + I_r I_q) \qquad p,q,r = x,y,z$$
$$I_{p,3} = -\frac{1}{2} (I_q^2 - I_r^2) \qquad \text{or cyclic permutation} \qquad (2)$$

The usefulness of these operators derives from the fact that for each p (p = x,y,z) the operators $I_{p,i}$ fulfill spin-½ angular momentum commutation relations:

$$[I_{p,i}, I_{p,j}] = i\, I_{p,k} \qquad i,j,k = 1,2,3 \text{ or cyclic permutation} \qquad (3)$$

Thus each p describes a fictitious two level spin-½ 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:

$$\rho_o = \beta\omega_o I_z = 2\beta\omega_o I_{z,1} \qquad (4)$$

We now enquire about the evolution of (4) under the Hamiltonian in (1) with ω_1, $\Delta\omega << \omega_Q$, 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:[1]

$$\mathcal{H} \simeq -2\Delta\omega I_{z,1} - \frac{\omega_1^2}{\omega_Q} I_{z,3} + \frac{2}{3}\omega_Q (I_{x,3} - I_{y,3}) \qquad (5)$$

Since the last term in (5) is commutive with the first two and with ρ_o in (4) it can be essentially discarded. Furthermore, the first two terms contain matrix elements only between the m = ±1 magnetic sublevels of the spin-1 and we refer to the z-space defined by the operators $I_{z,i}$ i=1,2,3 as the DQ space. This is a fictitious spin-½ 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.

$$\mathcal{H}_{DQ} \simeq -2\Delta\omega I_{z,1} - \frac{\omega_1^2}{\omega_Q} I_{z,3} \qquad (6)$$

at angular frequency $\omega_e = (4\Delta\omega^2 + \frac{\omega_1^4}{\omega_Q^2})^{½}$ in strict analogy to the spin-½ case.

Taking a 90° DQ pulse $\frac{\omega_1^2}{\omega_Q} t = \frac{\pi}{2}$ with $\frac{\omega_1^2}{\omega_Q} >> \Delta\omega$ the density matrix ρ_o

in (4) is transformed by (6) into $2\beta\omega_o I_{z,2}$ which is in a state of transverse quadrupolar order reflecting a coherent superposition of the $m = \pm 1$ levels[6,7] 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:

$$\mathcal{H} = -\Delta\omega I_z - \omega_1(I_x \cos\phi + I_y \sin\phi) + \frac{1}{3}\omega_Q(3I_z^2 - I(I+1)) \qquad (7)$$

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

$$\mathcal{H}_{DQ} \simeq -2\Delta\omega I_{z,1} - \frac{\omega_1^2}{\omega_Q}(I_{z,3}\cos 2\phi + I_{z,2}\sin 2\phi) \qquad (8)$$

Thus a phase change of ϕ in $\mathcal{H}_1(t)$ corresponds to a change of 2ϕ for the effective rf irradiation in the double quantum frame. Thus to effect a 180° phase reversal of $\frac{\omega_1^2}{\omega_Q}$ we need a 90° rf phase shift and for a 90° phase shift of $\frac{\omega_1^2}{\omega_Q}$ for spin locking we need a 45° 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 ν_Q = 90° kHz. In the first set of experiments, we examined the effect of a 90° rf phase shift. An rf phase of intensity ν_1 = 20 kHz << ν_Q and duration τ and $\Delta\omega$ = 0 was applied to the spin system followed by an intense 90° 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):

$$S(\tau) \sim \beta\omega_o \cos\left(\frac{\omega_1^2}{\omega_Q}\tau\right) f(\tau) \qquad (9)$$

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 µsec) and the experiments of reference 7. In figure 1(b) results of the same experiment are shown except that after τ = 165 µsec the phase of the weak rf pulse is shifted by 90°. As can be seen, this results in a 180° phase shift for the DQ rotary decay, in agreement with (8).

In the second set of experiments a 90° DQ pulse $\frac{\omega_1^2}{\omega_Q} t = \frac{\pi}{2}$ was applied $\Delta\nu$ = 2.5 kHz off resonance followed a time τ later by a probing pulse giving a signal intensity $S(\tau)$ proportional to the expectation value of $I_{z,2}$ at time τ, i.e.,

$$S(\tau) \sim \beta\omega_o \cos(2\Delta\omega\tau) f(\tau) \qquad (10)$$

Experimental values for this DQ free induction decay are compared with the theoretical line in figure 2(a) with T_2 of $f(\tau) = 218$ µsec. The experiment was then repeated but during τ the weak rf irradiation was continued but with a phase shift of 45°. According to equation (8) the first pulse should cause ρ_o to evolve to $2\beta\omega_o I_{z,2}$; the 45° phase shift then induces the effective operator $\frac{\omega_1^2}{\omega_Q} I_{z,2}$ 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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1. S. Vega, J. Chem. Phys., 63, 3769 (1975).
   S. Vega and A. Pines, Operator Formalism for Double Quantum NMR, submitted to Physical Review.
2. A. Pines, D. J. Ruben, S. Vega and M. Mehring, Phys. Rev. Lett., 36, 110 (1976).
3. S. Vega, T. W. Shattuck and A. Pines, Phys. Rev. Lett., 37, 43 (1976).
4. S. Vega, D. E. Wemmer and A. Pines, Fourier Transform Double Quantum NMR of Solid Benzene-d_1, to be published.
5. T. W. Shattuck, Ph.D. thesis, Berkeley, 1976.
6. R. G. Brewer and E. L. Hahn, Phys. Rev. A., 11, 1641 (1975).
7. H. Hatanaka, T. Terao and T. Hashi, J. Phys. Soc. Japan, 39, 835 (1975).
   H. Hatanaka and T. Hashi, J. Phys. Soc. Japan, 39, 1139 (1975).

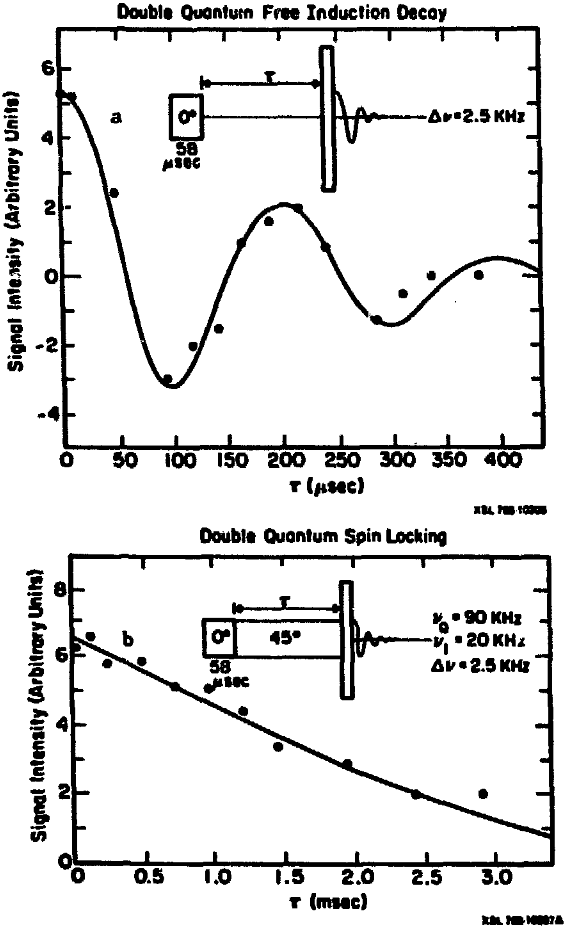

FIGURE 2

(a) Double quantum free induction decay after a 90° double quantum pulse $\frac{\omega_1^2}{\omega_Q} t = \frac{\pi}{2}$ 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.

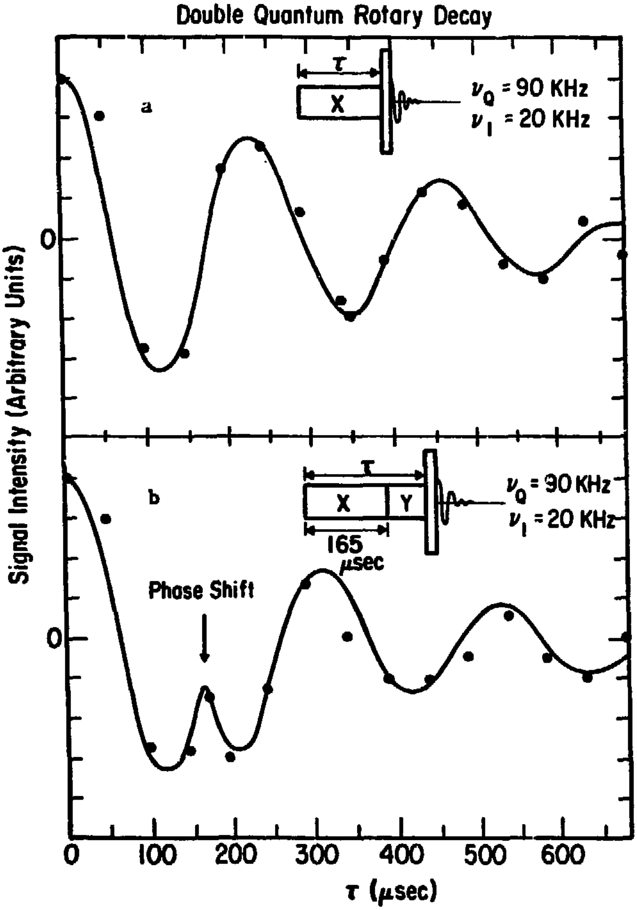

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FIGURE 1

(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.