COMMENTS ON NMR RESOLUTION OF THE CHEMICAL SHIFT IN SOLIDS

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Several errors of principle and fact in a recent letter are pointed out and some additional comments made on new NMR experiments in progress.

This journal recently published some theoretical predictions about a pulsed NMR method for reducing the effects of static dipolar interactions in solids while retaining electronic screening and other inhomogeneous shifts of the Larmor frequencies [1]. We feel it appropriate to criticize that account on the following grounds: a) the experiment has already been performed and discussed elsewhere [2], rendering further predictions unnecessary, b) the theory is incorrect in both conception and detail, thus making the predictions erroneous (and in fact at odds with experimental evidence [2]). c) some aspects of previous [2-4] work have been misstated or miscontrued. A detailed discussion of this and related methods will appear shortly [5]: For the present we content ourselves with mentioning the principal errors of ref. 1, for which we adopt its notation insofar as possible.

The method in question deals with a spin system characterized by a static internal Hamiltonian $\mathcal{H}$ consisting of dipolar interactions $\mathcal{H}_1$ and inhomogeneous shifts $\mathcal{H}_c$, polarized initially along the x axis of the rotating reference frame. The system is repeatedly subjected to a cycle [5] of two 90° r.f. pulses polarized alternately along the $\pm x$ axis, so spaced in time that the density matrix after $\frac{1}{2}N$ cycles (N even) is

$$\rho(t=2N\tau) = O^{\dagger \frac{1}{2}N} I_x O^{\frac{1}{2}N} \tag{1}$$

$$O = \exp(i\mathcal{H}\tau) R \exp(i\mathcal{H}_2\tau) R^\dagger \exp(i\mathcal{H}\tau) \tag{2}$$

where $R = \exp(\frac{1}{2}i\pi I_x)$.

The two parts of $\mathcal{H}$ commune if and only if all the shifts δ_i contained in $\mathcal{H}_c$ are the same, as they were in our experiment [2]. The authors neglect the commutator for arbitrary δ_i's thus vitiating from the outset their complaint that our chemical shift was not "real".

They then proceed to approximate the long-time development (1) and (2) by

$$O^{\frac{1}{2}N} = P_c^{\frac{1}{2}N} P_1^{\frac{1}{2}N} + \text{correction terms} \tag{3}$$

$$P_c = \exp(i\mathcal{H}_c\tau) R^\dagger \exp(i\mathcal{H}_c 2\tau) R \exp(i\mathcal{H}_c\tau)$$

$$P_1 = \exp(i\mathcal{H}_1\tau) R^\dagger \exp(i\mathcal{H}_1 2\tau) R \exp(i\mathcal{H}_1\tau)$$

The claim is made that the lowest correction terms to $\langle I_x(t)\rangle$ are of order τ^4. In fact it is easily verified by direct expansion that these terms are of order $N^4\tau^4$, i.e. t^4. This is an example of a well known difficulty of perturbation theory [3], and means that although the authors are concerned with the behavior of $\langle I_x\rangle$ for $t \gg T_2$, their expression is valid only in the opposite limit. (They have also apparently overlooked the fact that their eq. (4) fails to satisfy the requirement of time-reversal invariance, and thus might be expected to give spurious corrections of order t^3. Proper symmetrization would have avoided this problem.)

A more carefully treated time-expansion theory [2.5] shows that, roughly stated, the effective damping time of $\langle I_x\rangle$ for $\tau \to 0$ is of order, not $T_{2\epsilon}$, but δ^{-1}, where δ is the largest inhomogeneous shift. That is, in terms of frequency

spectra obtainable by Fourier transformation of $\langle I_x(t) \rangle$, the dipolar broadening can be effectively reduced just to the point of resolving the largest shift, and no further. This is true whether the shifts are "real" or otherwise.

For liquids, where dipolar broadening is absent, $\langle I_x(t) \rangle$ could have been calculated even after the mistakes mentioned. Unfortunately the authors' calculation for two spin-$\frac{1}{2}$ species with shifts δ_1 and δ_2 [their eq. (6)] is again in error. We suspect that the difficulty lies in their stated neglect of off-diagonal terms in P_c for $\sin \delta_{1,2} \tau \ll 1$. This can be dangerous when P_c is raised to a high power. However we cannot identify the trouble with certainty because the authors do not specify the representation in which the off-diagonal terms are neglected. In any case, the correct version of their eq. (6) is

$$\langle I_x(t) \rangle / \langle I_x(0) \rangle = \tfrac{1}{2} \{ \cos (\tfrac{1}{2}\sqrt{2}\delta_1 t) + \cos (\tfrac{1}{2}\sqrt{2}\delta_2 t) \} \qquad (4)$$

The explicit result for arbitrary τ is given elsewhere [5]. The interesting reduction of the effective shifts by $\sqrt{2}$ has been verified experimentally [6], is characteristic of the pulse sequence employed, and is valid for complex systems of arbitrary spins.

The authors state [1]: "It was first pointed out by Mansfield and Ware that experiments using coherent pulse trains as above, effectively remove the dipolar interaction in solids, and thus are analogous to other line narrowing experiments involving physical rotation of the specimen about the axis inclined to H_0 at the special angle $\arccos \tfrac{1}{3}\sqrt{3}$." The first half of this sentence is a direct misstatement of fact [4,7]. The analogy drawn in the second half is spurious.

Pulse experiments *are* possible [5] which succed in eliminating secular dipolar broadening altogether while preserving chemical shifts and scalar couplings. Some of these, in the limit $\tau \ll T_2$, do have an interesting analogy to the experiment of Lee and Goldburg [8], in which a strong steady r.f. field H_1 is applied to a sample off resonance by ΔH_0 such that $(H_1 / \Delta H_0) = \sqrt{2}$. A trivial example is an experiment in which the fields H_1 and ΔH_0 are simultaneously pulsed, but many others are possible which require pulsing of H_1 alone. Some can be elaborated in such a way as to ameliorate certain difficulties of the Lee-Goldburg experiment (e.g. inhomogeneity of H_1). A general theory of such experiments, including the possibility of rather general vectorial modulations of H_1 and H_0, has been developed and will be reported when warranted by the availability of sufficient supporting experimental results.

References

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