

Comments on Spin-Dynamics Calculations

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Received November 25, 1985

One of the areas of NMR which receives considerable attention and which still leads to confusion is the analytical calculation of the spin dynamics of single or groups of spins. This confusion is partly due to the fact that spin systems have a finite number of states and it is easy to represent the spin Hamiltonian in most bases. In spite of this ease, for a few coupled spins or larger-than- $\frac{1}{2}$ spin magnitudes, the dimensions become large enough that analytical calculations are lengthy unless care is taken in setting up the problem.

There are three decisions to be made in the treatment of spin dynamics which arise in the analysis of multipulse sequences. The first is whether to use the indirect method, i.e., to calculate the eigenvectors ψ_{IM} and eigenvalues E_{IM} of the spin Hamiltonian or to use the direct method which was first applied to NMR by Banwell and Primas (1) which calculates directly the spin-density matrix (i.e., the one discussed by Fano (2)) and the multi-quantum frequencies. The second decision is whether to choose a basis as primitive products (3, 4), fictitious spins $\frac{1}{2}$ (5, 6), or spherical tensor operators (7-9). The third choice is to decide how to calculate the time dependence of the operators. Two approaches for the direct method evaluate the spin-density operator by either a sum of commutators ordered in time, T , written formally as

$$\rho(t) = T \exp \left[-i \int_0^t dt' \mathcal{H}(t') \right] \rho(0) T \exp \left[i \int_0^t dt' \mathcal{H}(t') \right] \quad [1]$$

or by calculating only one commutator and leaving the quantum Liouville equation as a differential equation

$$i\hbar \frac{d}{dt} \rho(t) = [\mathcal{H}, \rho(t)] \dots \quad [2]$$

For a number of years this author has been exploiting the direct method and the coupled set of differential equations approach. This is only viable if a spherical tensor operator basis is used. Recently a comparison between these three steps of spin-dynamics calculations has been given which argues for the spherical tensor or multipole formulation (10). Even so, publications are appearing in which the direct method is used but which remain pessimistic about the approach. For example, Grivet (11), after treating a pair of spins- $\frac{1}{2}$ (AX system) concludes: "... the present method suffers from the drawback that all spin operators defined for the system of interest

must be treated on an equal footing. Thus the 4^n commutators and 4^{2n} expectation values characteristic of an n -spin system will probably discourage implementation of this scheme for $n \geq 3$.

A similar statement was made by Andersen a number of years earlier (4) in treating the same system as Grivet. These conclusions would not have been drawn had a spherical tensor operator (multipole) basis been used (see (12) for the multipole treatment of two spins $\frac{1}{2}$). In the first place, it is not necessary to generate a table of 4^n commutators. Grivet's equation [7]

$$[\hat{u}_i, \hat{u}_k]_- = -i \sum_p C_{ik}^p \hat{u}_p \quad [3]$$

correctly defines the C_{ik}^p as structure factors (a term used in group theory or Lie algebra) and then by choosing for an AX system the primitive products of the spin operators, i.e., linear I_i, S_k , and bilinear, $I_i S_k$ operators, he generates a 16×16 commutator table. If, in marked contrast, the \hat{U}_i 's are taken as spherical tensor operators (10), the structure factors are simply Clebsch-Gordan coefficients and reduced matrix elements (the well known Wigner-Eckart theorem). These are all given in one expression for all spin magnitudes and for any number of spins. One simply does not need to generate tables of commutation relations as the Sørensen, Eich, Levitt, Bodenhausen, and Ernst (3) basis requires or as the fictitious-spin- $\frac{1}{2}$ basis requires (5).

With respect to the second pessimistic remark regarding the drawback of treating all spin operators on an equal footing, within a spherical basis, this is incorrect. For single spins, the polarizations have well defined physical meanings describing the multi-quantum coherences and spherical tensor rank. The tensor rank k is the operator analog of the spin magnitude I for the state vector label while the spherical component q is the operator analog of the spin projection M . k and q are quantum numbers. For ^{79}Br in crystals of KBr most of the multipole polarizations have been measured and found to have distinct relaxation times (13). Similar unpublished experiments of ^{127}I in KI crystals give further corroboration that the spherical tensor polarizations are individually detectable. For groups of spins, the spherical tensor basis describes spin clusters of simultaneous single, double, triple, etc., spin polarizations. Moreover, since simultaneously correlated spin polarizations of three or more spins are less likely than single spin polarizations, e.g., $\langle I_{1x} I_{2y} I_{3x} \rangle$ is likely to occur with a lower probability than $\langle I_{1x} \rangle \langle I_{2y} \rangle \langle I_{3x} \rangle$, the multipole basis gives a convenient way for putting the spin operators on an unequal footing and helps in making approximations.

A more recent paper by Man, Theveneau, and Papon (14), considering the central line of half-integral spins, is related to the above discussion in that they treat selective excitation by using [1] and a fictitious-spin- $\frac{1}{2}$ basis. The purpose of their article is to rationalize the Rabi (15) relation for the central transition $(I + \frac{1}{2})\omega_1 t$. This is also relevant to nutation spectroscopy (16, 17). The only real advantage of using fictitious-spin- $\frac{1}{2}$ bases is for selective excitation, as the earlier work of Vega (18) and paper V show. Both these works give the reasons for the change in the effective rf frequency. In the author's paper V (19), moreover, use of a spherical tensor basis for various selective pulses, it is shown that for any selective single quantum transition between levels M and $M + 1$ the effective rf frequency becomes

$$\omega_{1,\text{eff}} = (I(I + 1) + M(M - 1))^{1/2} \omega_1 \quad [4]$$

For the central transition, $M = \frac{1}{2}$ and clearly

$$\omega_{1,\text{eff}} = (I + \frac{1}{2})\omega_1. \quad [5]$$

Man *et al.* also include the spherical part of the quadrupole interaction while the pulse is on (their [5]) yet after a lengthy calculation find that the central transition does not depend upon the quadrupole frequency (their [17]). The treatment in paper V (19) shows that not only is the rf frequency increased to $\omega_{1,\text{eff}}$ but also the quadrupole frequency is decreased to $\omega_{Q,\text{eff}}$ for selective multi-quantum excitation. In fact a selective single quantum excitation has zero effective quadrupole frequency, $\omega_{Q,\text{eff}} = 0$ (20) which means that no matter how large the quadrupole, a selective excitation of the central line is described only by a pure rotation. This is the reason why Eq. [17] of Man *et al.* does not depend on ω_Q , a point the fictitious-spin- $\frac{1}{2}$ formulation does not reveal without calculation.

The spherical tensor basis approach to spin dynamics gives considerably more than mathematical convenience. It reveals physically measurable quantities and provides natural insight into the phenomena presently being studied via multi-quantum multipulse NMR.

ACKNOWLEDGMENT

This work is supported by a research grant from the Natural Sciences and Engineering Council of Canada (NSERC).

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