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# New Approach to High-Resolution Proton NMR in Solids: Deuterium Spin Decoupling by Multiple-Quantum Transitions

A. Pines,* D. J. Ruben, and S. Vega
*Department of Chemistry, University of California, Berkeley, California 94720, and*
*Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720*

and

M. Mehring
*Institute for Physics, University of Dortmund, Dortmund, West Germany*

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Deuterium spin decoupling by double-quantum transitions in the manner of Meiboom and co-workers is applied for the first time to solids, opening the way for a new approach to high-resolution proton NMR. With use of this approach, the first resolved proton NMR spectrum of polycrystalline ice is presented and the chemical shielding tensor elements are determined. A simple treatment of the double-quantum process shows why decoupling is possible even though the deuterium spectral width is ~200 kHz as a result of quadrupolar broadening.

It is well known that nuclear magnetic resonance lines in diamagnetic solids are dominated by magnetic dipole-dipole interactions between the nuclear spins. Hidden in these broad lines is a wealth of information derived from much smaller interactions of interest to physicists and chemists, in particular chemical shifts. Two primary approaches have been adopted recently for the effective elimination of the dipolar couplings and the extraction of the smaller interactions. The first is applicable to abundant isotopes such as $^{1}H$ and $^{19}F$, and involves selective modulation of the spin interactions by multiple-pulse sequences.[1] The second approach, applicable to dilute isotopes (e.g., $^{13}C$, $^{15}N$, or artificially or chemically dilute) involves spin decoupling by strong resonant radio-frequency irradiation of an abundant isotope while observing the resonance of the isotope of interest.[2]

There are several reasons why the second approach is more attractive than the former. Firstly, it is considerably simpler technically, since the stability requirements for modulating first-rank tensor interactions are more modest than those for their second-rank counterparts. Secondly, there is a possibility for isotopic labeling, thus extending the technique to larger molecules. This is particularly clear for the case of the important abundant nucleus $^{1}H$, which poses a serious challenge for multiple-pulse techniques because of its small chemical shifts and strong dipolar interactions. Indeed, only a relatively small number of systems have been studied, confined mostly to small molecules.[3] As a striking example of the difficulties, one of the simplest and most "desirable" of proton-containing solids, ice, has eluded such studies, as a result of its strong dipolar interactions and extremely short

$T_2$.[4]

An appealing idea would be to immerse the protons in a bath of deuterium nuclei, thus rendering them isotopically dilute. The solid-state $^1$H high-resolution spectrum could then be created by deuterium spin decoupling. This has been used to observe $^1$H dipolar spectra in selectively deuterated molecules dissolved in liquid crystals by Meiboom and co-workers.[5] Why then, has this not been attempted to date in solids? In order to appreciate the difficulty, let us examine the situation depicted schematically in Fig. 1. The $^1$H linewidth is dominated by dipolar coupling to the deuterium. Imagine that we apply at the deuterium frequency a rotating field of intensity $\omega_1$ (in angular frequency units). The criterion for spin decoupling is that the rate of transitions between the deuterium magnetic sublevels induced by $\omega_1$ must be comparable to the dipolar coupling.[6] If the quadrupolar splitting were absent, this rate would be proportional to $\omega_1^2$; so this means

$$\omega_1^2 \sim D^2, \tag{1}$$

an easily attainable experimental situation. However, with the quadrupolar splitting $Q/2\pi \sim 200$ kHz $\gg D/2\pi$, the criterion for decoupling is that we need to "cover" the spectral width of the deuterium,

$$\omega_1^2 \sim Q^2, \tag{2}$$

i.e., a rotating field $H_1 \sim 300$ G, which is quite simply prohibitive for continuous irradiation.

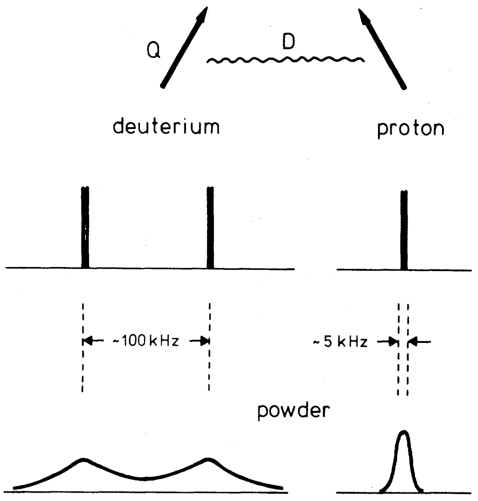

FIG. 1. Schematic representation of dipolar-interacting proton and deuterium spins and NMR spectra. The dipolar coupling is $D$ and the deuterium is characterized by quadrupolar splitting $Q$ from an axially symmetric electric-field-gradient tensor. The problem with spin-decoupling deuterium comes from the large spread of frequencies (~200 kHz).

Nevertheless, as Fig. 2 demonstrates, the experiment is indeed possible, in clear violation of this logic. Shown is the Fourier-transform spectrum of residual protons in a sample of ~99% deuterated water frozen to − 90°C, with and without resonant irradiation at the deuterium frequency. The spectra were obtained on a home-built double-resonance spectrometer operating at 185 MHz for protons. This is, to our knowledge, the first proton NMR spectrum in a solid obtained with deuterium spin decoupling and the first high-resolution proton NMR spectrum of ice. The deuterium decoupling reveals a proton powder spectrum derived from a chemical shielding tensor with axial symmetry. The principal elements of the tensor relative to external tetramethysilane (TMS) are

$$\sigma_{\parallel} = 15 \pm 2 \text{ ppm}, \quad \sigma_{\perp} = -19 \pm 2 \text{ ppm}.$$

There is an isotropic shift of 2 ± 1 ppm from liquid water. We have also studied other materials in this manner, but have preferred to present here the results for ice—we believe it to be a particularly good prototype for these experiments, for the following reasons: (a) The proton dipolar couplings are large, making the application of multiple-pulse techniques exceedingly difficult. (b) The deuterium quadrupolar interaction is large (in excess of 200 kHz), making it an ex-

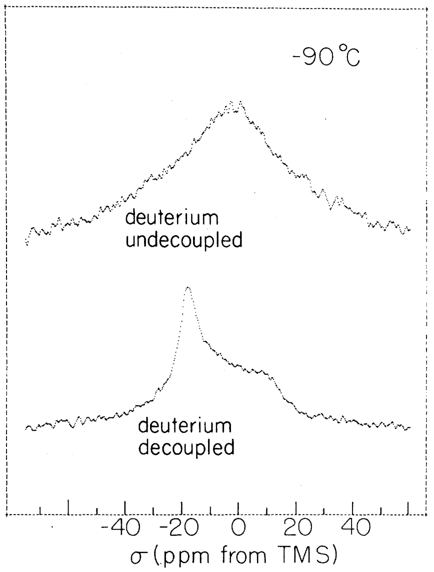

FIG. 2. Fourier-transform NMR spectrum of residual protons in 99% deuterated ice.

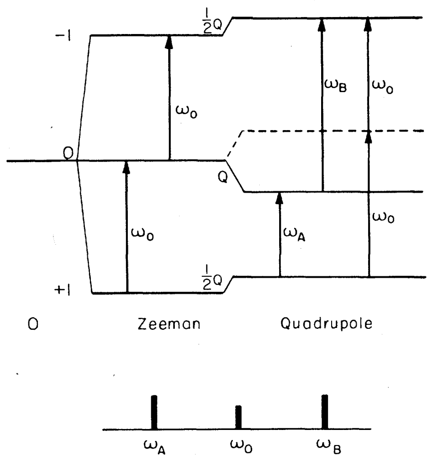

FIG. 3. Energy-level diagram for discussion of deuterium spin transitions. A double-quantum transition $1 \rightarrow -1$ occurs at the unshifted central frequency $\omega_0$.

cellent test case for the spin decoupling. (c) The proton dynamics are of interest and controversy[7] and can be studied by observing the high-resolution line shapes. Such a temperature-dependent study has indeed been carried out by us and will be described in detail in a separate paper.

We need now to understand why the experiment works. Figure 3 provides the basis for the discussion. The arguments given at the beginning for the transition probabilities and decoupling were based, of course, on the allowed deuterium transitions, $m = +1 \rightarrow 0$ and $m = 0 \rightarrow -1$, labeled $\omega_A$ and $\omega_B$. As recognized by Meiboom and coworkers,[5] decoupling might also be effected by the "forbidden" transition $m = +1 \rightarrow -1$, which could occur by a double-quantum process at the unshifted frequency $\omega_0$. We can provide an extremely simple but illustrative argument to assess this effect. Consider again the applied field $\omega_1$ at the central frequency $\omega_0$, with $Q \gg D$. The probability $W$ for the double-quantum transition is easily calculated by second-order perturbation theory:

$$W \sim \frac{\omega_1^4 |\langle 1|I_x|0\rangle|^4}{(\omega_0-\omega_A)^2} \sim \frac{\omega_1^4}{Q^2}. \tag{3}$$

With employment again of our spin-decoupling condition $W \sim D^2$ as before, this means we need

$$\omega_1^2 \sim QD. \tag{4}$$

This is considerably less than required by (2), is attainable in practice, and is indeed precisely what we observe experimentally. This, then, explains why the experiment is possible even with

$$Q \gg \omega_1 \gg D.$$

Although the double-quantum process is inherently less probable than the allowed single-quantum processes (if both are induced on resonance), it is *resonant* for all the deuterium spins, whereas the allowed ones are not. Full details on our rigorous theory will be presented elsewhere.

To summarize, we give some final comments, which will be enlarged upon in a full paper:

(1) The technique, with its technical simplicity (deuterium-decoupling powers of only several hundred watts), opens the way for an alternative approach to high-resolution proton NMR in solids. Samples can be selected from a wide and available range of predeuterated materials with observation of the residual protons. Where too many lines might render the spectrum intractable, isotopic labeling can be used to emphasize selectively particular nuclear sites.

(2) The experiment can be combined with multiple-pulse techniques using partially deuterated materials. This reduces the requirement of short pulse cycle time and enhances the proton signal-to-noise ratio. It also forms a useful way to solve the broadening induced by isotopic labeling as in (1) above. We have used this to observe fine splittings in crystal samples.

(3) The arguments and experiments presented in this paper hold not only for deuterium-proton systems. The same reasoning exactly can be invoked for the spin decoupling of two strongly dipolar-coupled, like spin-$\frac{1}{2}$ nuclei from a third unlike nuclear spin. Consider for example the case of two protons ($I$) coupled to a $^{13}$C spin ($S$) as in high-resolution $^{13}$C spectroscopy. Here, double-quantum transitions occur between the energetically lowest and highest proton triplet states: $|\alpha\alpha\rangle \leftrightarrow |\beta\beta\rangle$. This explains why proton decoupling of $^{13}$C is considerably simpler than might be guessed from the width of the proton lines, i.e., even when

$$\gamma \|\mathcal{H}_{II}\| \gg \omega_1 \gg \gamma \|\mathcal{H}_{IS}\|.$$

In methylene groups ($^{13}$CH$_2$) of liquid crystals, this fact was originally quite surprising[8] since it might be expected that we require $\omega_1 \sim \gamma \|\mathcal{H}_{II}\|$.[6]

(4) The treatment and experiments can be generalized to higher-order multiple-quantum transitions. For example, for $n$ equivalent coupled protons, of spin $n/2$ with axial symmetry, to be decoupled from an unlike spin, we need multiple-quantum transitions of order $n$, $n-2$, $n-4, \ldots,$

etc.

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*Alfred P. Sloan Fellow.

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## COMMENTS

# Nonlinear Crossover between Critical and Tricritical Behavior

J. F. Nicoll, T. S. Chang, and H. E. Stanley
*Physics Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*
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Recently *approximate* solutions to renormalization-group equations were used to calculate the double-power "tricritical" scaling equation of state. We show that this equation can be simply calculated using our *exact* renormalization-group trajectories. The equation of state is expressed *explicitly* in terms of nonlinear scaling fields.

In a recent Letter[1] it was suggested that the crossover or "double-power" scaling functions[2] germane to "tricritical"[3-4] and critical points may be constructed using iteration techniques proposed by Wilson, Nauenberg, and Nienhuis,[5] together with an appropriate mean-field approximation, by matching the Wilson-Fisher critical behavior with a Landau-like expression with fluctuation corrections.

For the problem treated in Ref. 1, approximate solutions of the corresponding recursion relations were derived. On the other hand, we had previously derived[6] the exact $O(\epsilon)$ nonlinear solution of the renormalization group equations for the same problem.[6-8]

In this Comment we show (i) that our exact solutions are particularly convenient for a matching procedure of the sort introduced in Ref. 1, so that there is no necessity to produce approximate solutions, and (ii) that the equation of state[9] can be expressed directly in terms of the nonlinear scaling fields calculated in Ref. 6, permitting a completely *explicit* expression (automatically in asymptotic Griffiths form) for the equation of state, in contrast to the *implicit* equation given in Ref. 1. Our results validate the approach of Ref. 1 and support its claimed potential utility for problems where exact trajectories may not be easily found.

As in Ref. 1 we begin with a Hamiltonian density of the form

$$\mathcal{H} = \tfrac{1}{2}(\nabla\vec{s})^2 - \vec{h}\cdot\vec{s} + \tfrac{1}{2}r\vec{s}^2 + \tfrac{1}{4}u\vec{s}^4 + \tfrac{1}{6}v\vec{s}^6 + \ldots$$

in dimensions $d \equiv 4 - \epsilon$, where $\vec{s}(\vec{x})$ is an $n$-com-