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## Separated Local Field Spectra in NMR: Determination of Structure of Solids\*

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Various techniques of coherent averaging in NMR are applied in time sequence and the transient signal is doubly Fourier analyzed. The result is a two-dimensional NMR spectrum in which dipole-dipole spectra of spins having slightly different chemical shifts are separated from one another. The results are useful for determination of atomic positions in solids.

We report here the experimental demonstration of an NMR technique which may be generally useful in the determination of atomic positions in solids.<sup>1</sup> It has long been known that such information resides in the nuclear magnetic dipole-dipole interactions. While in liquids these interactions are motionally averaged to zero, there are so many such couplings in solids that the NMR spectrum, except in a few special cases,<sup>2</sup> has an unresolvable "wide-line" character. In principle the structural information is extractable via moment analysis,<sup>3</sup> but the difficulties, both experimental and theoretical, of obtaining higher-order moments preclude the application of this method to most solids.

We consider the spectrum of relatively dilute spins  $S$  which are coupled to abundant neighboring spins  $I$  through the interaction

$$\mathcal{H}_{IS} = -2 \sum_n \sum_k b_{nk} S_{zk} I_{zk}, \quad (1)$$

where  $b_{nk} = \gamma_S \gamma_I \hbar^2 r_{nk}^{-3} P_2(\cos \theta_{nk})$  contains the structural information. The  $I$  spins, because they are abundant, interact among themselves through

$$\mathcal{H}_{II} = \sum_i \sum_{k < l} b_{kl} (\vec{I}_k \cdot \vec{I}_l - 3 I_{zk} I_{zl}). \quad (2)$$

In addition the  $S$  spins have chemical shifts  $\Delta_n$  which might be resolvable in the absence of  $I$ - $S$  dipolar broadening<sup>4</sup>:

$$\mathcal{H}_{\Delta S} = \sum_n \Delta_n S_n. \quad (3)$$

Now we imagine giving the  $S$  spins an initial transverse polarization  $\langle S_+(0) \rangle = \langle S_x \rangle + i \langle S_y \rangle$  at time zero which is then allowed to decay in two stages. In the first time interval,  $t_1$ , a line-narrowing irradiation is applied to the  $I$  spins resulting in a suppression of  $\mathcal{H}_{II}$  and in a scaling of  $\mathcal{H}_{IS}$  by a factor  $\kappa$ .<sup>5</sup> Then  $\mathcal{H}_{IS}$  is suppressed in the second time interval,  $t_2$ , by strong resonant irradiation of the  $I$  spins while the remainder of the  $S$  free induction decay is recorded.<sup>4</sup> The signal observed at  $t_1 + t_2$  has the form

$$\langle S_+(t_1, t_2) \rangle = \langle \exp[i(\mathcal{H}_{\Delta S} + \kappa \mathcal{H}_{IS})t_1] \exp(i \mathcal{H}_{\Delta S} t_2) S_+ \exp(-i \mathcal{H}_{\Delta S} t_2) \exp[-i(\mathcal{H}_{\Delta S} + \kappa \mathcal{H}_{IS})t_1] \rangle. \quad (4)$$

Making use of  $S_+ = \sum_n S_{+n}$  and the local-field form of  $\mathcal{H}_{\Delta S}$  and  $\mathcal{H}_{IS}$ , Eq. (4) is readily simplified to

$$g(t_1, t_2) \equiv \langle S_+(t_1, t_2) \rangle / \langle S_+(0, 0) \rangle = \sum_n \exp\{i[\Delta_n t_2 + (\Delta_n + D_n)t_1]\} \quad (5)$$

with  $D_n = -2\kappa \sum_k b_{nk} m_k$ , where  $m_k$  is the magnetic quantum number of the  $k$ th neighboring  $I$  spin of  $S_n$ .

A Fourier analysis of  $g(0, t_2)$  with respect to  $t_2$  gives the pure chemical-shift spectrum  $f(\omega_2)$  of the  $S$  system<sup>4</sup>; a similar analysis of  $g(t_1, 0)$  with respect to  $t_1$  yields a sort of "wide-line" spectrum,  $f(\omega_1)$ , from which the effects of the  $I$ - $I$  interactions have been removed. Two-dimensional Fourier analysis<sup>6</sup>

yields an array,  $f(\omega_1, \omega_2)$ , from which dipolar spectra of each  $S$  spin can be separated.

The experiment was performed on a small single crystal of calcium formate,  $\text{Ca}(\text{HCO}_2)_2$ , of 6% isotopic abundance in  $^{13}\text{C}$ , and doped with  $\sim 0.1$  at. %  $\text{Mn}^{++}$  to shorten the proton spin-lattice relaxation time. The pulse sequence is shown in Fig. 1. The  $^{13}\text{C}$  spins ( $S$ ) were initially cross polarized using the protons ( $I$ ).<sup>4</sup> During  $t_1 = Nt_c$  a Waugh-Haber-Haeberlen four-pulse sequence<sup>5</sup> was applied to the protons with a cycle time  $t_c = 45 \mu\text{sec}$  to suppress the  $I$ - $I$  couplings. During  $t_2$  the  $I$  spins were continuously irradiated with an rf field  $H_1 = 15 \text{ G}$ , and the complex  $^{13}\text{C}$  signal was sampled at  $32\text{-}\mu\text{sec}$  intervals. Signals were averaged, and the process repeated for  $N = 1, 2, \dots, 20$ .

A two-dimensional transform of the data is shown as a contour plot in Fig. 2. The pure chemical-shift spectrum  $f(\omega_2)$  is shown vertically along the side, and the distorted "wide-line" spectrum  $f(\omega_1)$ , obtained by summing vertically, is shown along the top. The following features are evident: (1)  $f(\omega_1)$  itself shows some detail because the sample was a single crystal and because the spin Hamiltonian has a pure "local-field" character during  $t_1$ ; (2) dipolar splittings are observed in  $f(\omega_1, \omega_2)$ , each being symmetrical along the  $\omega_1$  axis about the locus  $\omega_1 = \omega_2 = \Delta_n$ ; (3) the observed splittings range from 1.1 to 12.3 kHz for  $\text{HCO}_2^-$  ions in various orientations in the unit cell; and (4) only seven rather than the expected eight lines are observed.

Using the known  $^{13}\text{C}$  shielding tensors,<sup>7</sup> and taking account of the experimentally determined scale factor  $\kappa = 0.53$ , we performed a computer

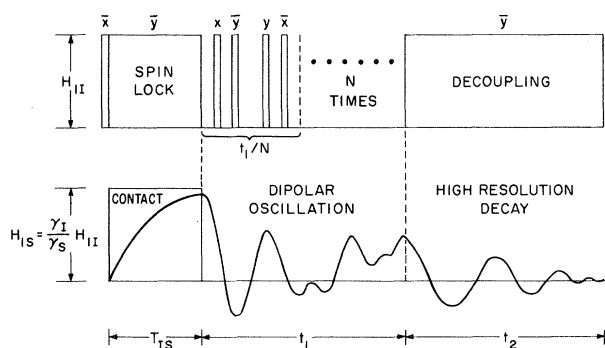


FIG. 1. Schematic diagram of the experimental procedure showing time-dependent rf fields and magnetizations.

search to determine the direction (initially unknown) of  $\vec{H}_0$  in crystal coordinates. Initially the C-H vectors were assumed to be of length 1.09 a.u. and to lie in the directions appropriate to the symmetry of the isolated  $\text{HCO}_2^-$  ion. The chemical shifts were reproduced easily within experimental error, but substantial errors remained in the dipolar splittings. The C-H directions were varied keeping  $r_{\text{CH}} = 1.09$  a.u. and obeying the symmetry restrictions of the  $P_{cab}$  space group. The residual errors were minimized when the direction cosines of  $\vec{r}_{\text{CH}}$ , in a coordinate system with the  $x$  axis along the  $C_2$  axis of the  $\text{CO}_2$  grouping and the  $z$  axis in the  $\text{COO}$  plane, were  $(-0.998, 0.025, 0.044)$  and  $(-0.995, 0.027, 0.094)$  for the two inequivalent classes of  $\text{HCO}_2^-$  in the unit cell. These directions represent bendings of  $2.9^\circ$  and  $5.5^\circ$  away from the free-ion direction.

We reported earlier an alternative method<sup>8</sup> that differs from the present one in that  $I$ - $S$  couplings manifest themselves in an oscillatory spin exchange, arising from terms of the form  $b_{nk} I_{\pm k} S_{\mp n}$ . These terms appear under double-resonance conditions when the Hartmann-Hahn condition is established.<sup>9</sup> That procedure, besides being experimentally more difficult, suffers from two defects as a result of the form of the effective coupling Hamiltonian. The first of these is that the desired parameters,  $b_{nk}$ , are not directly obtained from spectral splittings but must be related to the latter by detailed calculation. The other is

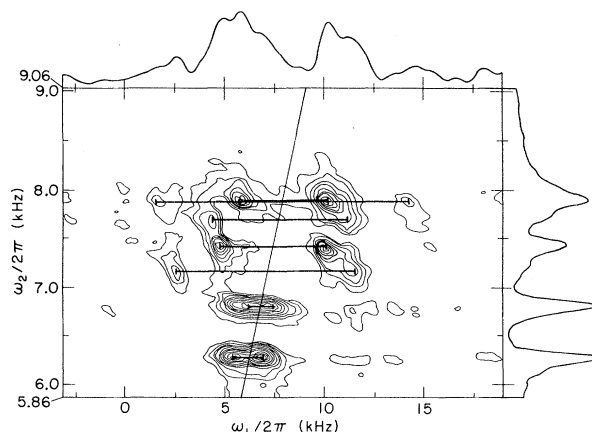


FIG. 2. Contour plot of function  $f(\omega_1, \omega_2)$ . Dipolar splittings for each of the observed seven lines are indicated by the heavy lines. The line bisecting the splittings is the locus  $\omega_1 = \omega_2 = \Delta_n$ . (The zeros of the two indicated frequency scales are different and arbitrary. Chemical shielding increases from top to bottom and from right to left.)

that the eigenfrequencies exhibit a tendency toward "locked modes," e.g., an S spin coupled to two I spins will exhibit a *single* eigenfrequency equal to the root mean square of the individual coupling strengths. For these reasons, and others,<sup>1</sup> we believe that the present approach has greater promise for the determination of the local geometrical structure of solids.

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## Universal Diamagnetism of Spinless Bose Systems

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I prove that the ground-state energy of an arbitrary system of nonrelativistic spinless Bose particles increases when any (arbitrarily strong or inhomogeneous) magnetic field is turned on.

Let

$$H(a) = -\sum_{j=1}^n (2\mu_j)^{-1} [\nabla_j - ie_j \vec{a}(x_j)]^2 + \sum_{j < k} v_{jk}(r_j - r_k) + \sum_j v_j(r_j), \quad (1)$$

where  $a$ ,  $v_{jk}$ , and  $v_j$  are arbitrary real-valued functions. My goal in this note is to prove the following elementary fact that appears to have escaped previous notice:

*Theorem.*—As an operator on either all square-integrable  $n$ -particle functions or on functions with Bose statistics on all of the particles,  $H(0)$  has a smaller ground-state energy than  $H(a)$ .

I emphasize that this result is not coming from a general inequality

$$\langle \psi, H(0)\psi \rangle \leq \langle \psi, H(a)\psi \rangle \quad (2)$$

for all  $\psi$ , for (2) is false! Equation (2) would imply an inequality on all eigenvalues but it is obvious that in the case  $n=1$ , and  $v$  spherically symmetric, energies of  $l \neq 0$  states decrease in lowest-order perturbation theory for a suitable choice of  $a$ . This remark shows that the theorem fails for fermions for the  $v_{ij}$  can be chosen zero! Note also that various analyses<sup>1</sup> of explicit ex-

amples of  $H(a)$  have noted the occurrence of an inequality  $E(a) \geq E(0)$  in these explicit examples.

I will prove the inequality

$$\langle |\psi|, H(0)|\psi| \rangle \leq \langle \psi, H(a)\psi \rangle. \quad (3)$$

Equation (3) implies the theorem by the variational principle,

$$E(a) = \inf_{\|\psi\|=1} \langle \psi, H(a)\psi \rangle \geq \inf_{\|\psi\|=1} \langle |\psi|, H(0)|\psi| \rangle \geq \inf_{\|\varphi\|=1} \langle \varphi, H(0)\varphi \rangle = E(0).$$

Notice that (3), unlike (2), does not imply anything about excited states because  $f - |f|$  destroys orthogonality. In addition, (3) tells us nothing about the fermion case since  $\psi \rightarrow |\psi|$  destroys Fermi statistics.

The inequality (3) follows from a more general inequality<sup>2</sup> of Kato proven for different purposes. By borrowing only part of his proof one can show (3) easily<sup>3</sup>: Since  $|\psi|^2 = \psi^* \psi$ , then with  $3n$ -dimensional gradients,

$$\begin{aligned} \langle |\psi|, |\nabla| \psi \rangle &= |\operatorname{Re}(\psi^* \nabla \psi)| = |\operatorname{Re}[\psi^* (\nabla - ia)\psi]| \\ &\leq \langle \psi, (\nabla - ia)\psi \rangle. \end{aligned}$$

Thus  $\langle |\nabla| \psi \rangle^2(x) \leq \langle (\nabla - ia)\psi \rangle^2(x)$ . Integrating over  $x$