PHYSICAL REVIEW VOLUME 151, NUMBER 1 4 NOVEMBER 1966

Nuclear-Magnetic-Resonance Line Shape in Solids

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(Received 16 June 1966)

The method of retarded Green's functions is applied to the calculation of rigid-lattice dipolar line shapes in solids. Some familiar results are derived for the case of isolated spins and spin pairs. The case of N interacting spins is also considered. An expression for the line shape is obtained by employing a frequency-dependent decoupling approximation. Simple constant decoupling approximations do not lead to damped line shape functions. The result is compared with early experimental data obtained by Bruce on the F^{19} resonance in a single crystal of calcium fluoride. The theoretical free induction decays obtained by Fourier-transforming the line shape are also compared with experimental data from Lowe and Norberg. The line shape derived is strongly dependent on the ratio of the fourth moment to the square of the second moment. Increases of this ratio, corresponding to inclusion of exchange interactions, are shown to produce dramatic narrowing of the absorption line, which ultimately approaches a Lorentzian function.

1. INTRODUCTION

The problem of calculating nuclear magnetic resonance line shapes in solids is an old one and has been considered in a number of early papers. One of the first contributions to this subject was by Van Vleck[1] who showed that the even moments of an absorption line shape centered at the Larmor frequency and in a high static magnetic field $\mathbf{H}_0$ could be exactly related to certain calculable lattice sums.

Attempts to derive the complete line shape based on the "Gaussian random frequency modulation" model were carried out by Anderson and Weiss[2] and Anderson.[3] This model is successful in predicting line-narrowing effects due to the presence of exchange interactions as well as spin-motional effects; although here a detailed experimental study of line shape shows some considerable deviations from the elementary theory as the transition between solid and liquid is made. In the case of no exchange interaction and when there is no atomic motion, the model predicts a Gaussian line shape. However, experimental studies of a number of solids reveal considerable departures from the Gaussian shape in many cases.

The first nonstochastic approach to the rigid-lattice line shape was made by Lowe and Norberg[4] (referred to as LN) on the fluorine resonance in a single crystal of calcium fluoride. They calculated the Fourier transform of the line shape or Bloch decay by considering the time evolution of a transverse magnetization (i.e., in a plane normal to the applied static magnetic field $\mathbf{H}_0$) under the influence of the dipolar interaction. As is well known, the Bloch decay in CaF_2 exhibits a beat structure which is recorded on some excellent experimental data. Fitting this curve and predicting the position of the beat zeros presents a rather exacting test of any theory. The fit obtained by Lowe and Norberg appears to be extremely good in spite of the approximations necessary to evaluate the decay.

The transverse decay can also be calculated with a simple series expansion in time. In this case the coefficients of even powers of time are the even moments of the absorption line shape as calculated by the method of Van Vleck.[1] The coefficients of odd powers vanish for a symmetric line shape. Unfortunately this series converges rather slowly but is nevertheless useful for calculating effects near zero time. This method has been used for calculating the more complex effects which occur in solids when a number of closely spaced 90° rf pulses are applied to the spin system. This situation has been shown to give rise to a "solid echo"[5,6] as well as other transient effects.[7]

Clough and McDonald[8] have re-examined the Lowe and Norberg calculation and have shown that the expression originally given for the transverse decay diverges from zero for large times. In a slightly modified method of calculation involving an additional transformation to a reference frame following the motion of the spins, they have so far not been able to improve on LN. The divergence arises because certain terms in the operator expansions have to be dropped in order to obtain an approximate, but closed-form, expression for the free induction decay. Further approximations introduced to make their series converge give rather poor agreement with the experimentally observed beat zeros in the Bloch decay. Abragam[9] has pointed out that series expansions of the form described above are not unique. As a rather intriguing example it is shown that the function

$$e^{-a^2t^2/2}\sin bt/bt,$$

where a and b are assignable constants, can be fitted to the experimental data for CaF_2 with remarkable agree-

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[1] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[2] P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1953).

[3] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

[4] I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

[5] J. G. Powles and P. Mansfield, Phys. Letters **2**, 58 (1962).

[6] J. G. Powles and J. H. Strange, Proc. Phys. Soc. (London) **82**, 6 (1963).

[7] P. Mansfield, Phys. Rev. **137**, A962 (1965).

[8] S. Clough and I. R. McDonald, Proc. Phys. Soc. (London) **86**, 833 (1965).

[9] A. Abragam, *The Principles of Nuclear Magnetism*, (Clarendon Press, Oxford, England, 1961).

ment over the entire Bloch decay. This is achieved by equating the coefficients of t^2 and t^4 in the expansion of the above expression to the second and fourth moments, respectively. On the basis of this empirical fact, it would seem possible to construct a plausible theory of dipolar line shape, largely dependent on the second and fourth moments.

Recently Tjon[10] has calculated the line shapes for the F^{19} resonance in CaF_2 by solving numerically an an integro-differential equation. The equation is first simplified using a Gaussian assumption.

In this paper, an attempt is made to calculate the rigid-lattice line shape for a number N of static interacting dipoles using the method of retarded Green's functions.[11] Tomita and Tanaka[12] have used the method to calculate line shapes in ferromagnetic resonance. Their results when applied to solids with dipolar broadening only give rather poor agreement with experiment in the paramagnetic region using the high-temperature approximation. The reasons for this are most likely attributable to the method of decoupling used, as well as to decoupling too soon. Brown[13] also has used a related method to calculate the intensities and the moments of dipolar broadened spectra in low external fields.

In the present work, a frequency-dependent decoupling approximation is used. This is evaluated using a physically intuitive approach. It is assumed that for a large number of interacting spins, the Green's functions occurring in the decoupling factor may be replaced by approximate smooth functions on the real axis. Plausible approximations for the form of these functions are introduced and an expression for the line shape in closed form is obtained. This is compared with experimental data, and it is shown that good agreement is obtained for the case of the fluorine resonance in a single crystal of CaF_2 when the external static magnetic field $\mathbf{H}_0$ is applied along the [100], [110], or [111] crystal axes.

The phenomenon of exchange narrowing for a single spin species is briefly discussed. It is shown that the theoretical line shape approaches a Lorentzian function when the exchange term begins to dominate over the dipolar interaction. Lack of suitable experimental data prevents a detailed comparison with the theory.

2. THE BASIC GREEN'S FUNCTION

The appropriate Green's function which describes the line shape is found by considering the complex susceptibility of a number N of interacting magnetic dipoles of spin I, placed in a uniform static magnetic field $\mathbf{H}_0$. The spin system is considered under the influence of a steady rf magnetic field ($H_R \cos\omega t$, $-H_R \sin\omega t$, 0). The total Hamiltonian for the system is

$$\hbar\mathcal{H}_T=\hbar(\mathcal{H}+\mathcal{H}_R)=\hbar(\mathcal{H}_0+\mathcal{H}_R+\mathcal{H}_1^{\text{tot}}), \qquad (1)$$

where the Zeeman term is $\mathcal{H}_0=-\omega_0 I_z$ and $I_z=\sum_i I_{z_i}$. $\mathcal{H}_R$ is the interaction between the applied rf field and the spin system and is equal to

$$\mathcal{H}_R=-\tfrac{1}{2}\gamma H_R(I_+e^{i\omega t}t+I_-e^{-i\omega t}).$$

$I\pm$ are the usual displacement operators. $\mathcal{H}_1^{\text{tot}}$ is the total spin-spin interaction. Let

$$\rho(0)=e^{-\beta\mathcal{H}}/\text{Tr}\{e^{-\beta\mathcal{H}}\}$$

be the initial thermal-equilibrium density matrix for the spin system, where $\beta=\hbar/kT$; k is the Boltzmann constant and T the absolute temperature. Tr denotes here the trace or diagonal sum. The equation of motion of a transformed density matrix $\rho^*(t)=e^{i\mathcal{H}t}\rho e^{-i\mathcal{H}t}$ under the influence of the applied rf field is

$$\frac{d\rho^*(t)}{dt}=-\tfrac{1}{2}i\gamma H_R[\rho^*,I_+(t)e^{i\omega t}+I_-(t)e^{-i\omega t}], \qquad (2)$$

where $I\pm(t)=e^{i\mathcal{H}t}I\pm e^{-i\mathcal{H}t}$. Where possible, the square bracket is reserved to denote the commutation of two operators. Assuming the spin system is initially in thermal equilibrium before the application of H_R then $\rho(-\infty)=\rho(0)=\rho^*(-\infty)$. Integrating Eq. (2) and transforming back to the laboratory frame we have in reiterative solution correct to first order in H_R

$$\rho(t)=\rho(0)-\frac{i\gamma H_R}{2}\int_{-\infty}^{t}[\rho(0),e^{i\mathcal{H}(\tau-t)}I_+e^{-i\mathcal{H}(\tau-t)}e^{i\omega\tau} + e^{i\mathcal{H}(\tau-t)}I_-e^{-i\mathcal{H}(\tau-t)}e^{-i\omega\tau}]d\tau. \qquad (3)$$

It is well known, however, that Eq. (2) has a coherent harmonic solution, no matter how small H_R is made. By this, we mean that H_R nutates the *total* thermal equilibrium magnetization. This is contrary to experience in actual spin systems; the apparent anomaly arises through neglect of spin-lattice relaxation. When account is taken of coupling to the lattice, it can be shown that for small H_R, $\rho(t)$ will not depart much from the thermal equilibrium value, thus replacement of $\rho(t)$ by $\rho(0)$ in the integrand of (3) is justified. This approximation then keeps the calculation adiabatic.

We wish to calculate the total transverse magnetization in the laboratory reference frame which is proportional to I_+. The ensemble average of an arbitrary operator A is calculated using

$$\langle A\rangle=\text{Tr}\{\rho A\}. \qquad (4)$$

Since the spin system is initially in thermal equilibrium before the rf is applied, we have $\langle I_+(t)\rangle=0$. Also, as we are interested in the line shape in high field, we take the part of $\mathcal{H}_1^{\text{tot}}$ which commutes with $\mathcal{H}_0$, i.e., $[\mathcal{H}_0,\mathcal{H}_1]$

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[10] J. A. Tjon, Phys. Rev. **143**, 262 (1966).

[11] D. N. Zubarev, Usp Fiz. Nauk **71**, 71 (1960) [English transl.: Sov. Phys.—Usp. **3**, 320 (1960)].

[12] K. Tomita and M. Tanaka, Progr. Theoret. Phys. **29**, 528 (1963); **29**, 651 (1963).

[13] L. S. Brown, IBM J. Res. Develop. **6**, 338 (1962).

$=0$. $\mathcal{H}_1$ is the truncated dipolar Hamiltonian[1] given by

$$\mathcal{H}_1=\sum_{k>j}(\tilde{A}_{jk}+A_{jk})\mathbf{I}_j\cdot\mathbf{I}_k+B_{jk}I_{zj}I_{zk}, \tag{5}$$

where

$$A_{jk}=-\tfrac{1}{2}\gamma^2\hbar(1-3\cos^2\theta_{jk})/r_{jk}^3,$$

$\tilde{A}_{jk}$ is the exchange-interaction coupling constant,

$$B_{jk}=\tfrac{3}{2}\gamma^2\hbar(1-3\cos^2\theta_{jk})/r_{jk}^3,$$

and r_{jk} is the internuclear distance between a pair of spins jk with the vector $\mathbf{r}_{jk}$ making an angle θ_{jk} with the applied static field $\mathbf{H}_0$. With these simplifications, and from Eqs. (3) and (4) we see that

$$\langle I_+(t)\rangle=\frac{i\gamma H_R}{2}\int_{-\infty}^{t}\mathrm{Tr}\{[\rho(0),I_+(t-\tau)]I_-e^{i\omega\tau}d\tau, \tag{6}$$

since $[\rho_0,\mathcal{H}]=0$. We assert that averages like $\langle[I_+(t-\tau),I_+]\rangle$ are zero at least in the high-temperature approximation. Introducing a step function

$$\begin{aligned}\theta(t)&=0 \quad t<0\\ &=1 \quad t>0\end{aligned} \tag{7}$$

and using the relation

$$\int_{-\infty}^{t}f(\tau)d\tau=\int_{-\infty}^{\infty}\theta(t-\tau)f(\tau)d\tau, \tag{8}$$

we obtain from Eq. (6) substituting $t'=t-\tau$:

$$\langle I_+(t)\rangle=\tfrac{1}{2}i\gamma H_Re^{-i\omega t}\int_0^{\infty}\theta(t') \times\mathrm{Tr}\{\rho(0)[I_+(t'),I_-]\}e^{i\omega'}dt' \tag{9a}$$

$$=H_Re^{-i\omega t}\chi(\omega). \tag{9b}$$

$\chi(\omega)$ is the complex susceptibility of the spin system defined by (9). Consider now the retarded, double-time Green's function[14]

$$\langle\langle I_+(t);I_-(0)\rangle\rangle=\theta(t)\langle I_+(t)I_-(0)-I_-(0)I_+(t)\rangle. \tag{10}$$

To ensure convergence it is more convenient to work with a related function

$$e^{-\epsilon t}\langle\langle I_+(t);I_-(0)\rangle\rangle \tag{11}$$

which equals (10) in the limit $\epsilon\rightarrow 0$. The Fourier transform of (11) is defined by

$$(1/2\pi)\int_0^{\infty}e^{-\epsilon t}\langle\langle I_+(t);I_-(0)\rangle\rangle e^{i\omega t}dt=\langle\langle I_+;I_-\rangle\rangle_{\omega+i\epsilon}. \tag{12}$$

We see immediately that the complex susceptibility is expressible in terms of (12), i.e.,[15]

$$\chi(\omega)=\lim_{\epsilon\to 0}i\gamma\pi\langle\langle I_+;I_-\rangle\rangle_{\omega+i\epsilon}. \tag{13}$$

3. EQUATIONS OF MOTION

The equation of motion of (10) under the influence of the total Hamiltonian is

$$\frac{d}{dt}\langle\langle I_+(t);I_-\rangle\rangle=\delta(t)\langle[I_+,I_-]\rangle+i\langle\langle[\mathcal{H},I_+];I_-\rangle\rangle. \tag{14}$$

Introducing the convergence factor and taking the Fourier transform, we obtain the more convenient form

$$\begin{aligned}(\omega+i\epsilon)\langle\langle I_+;I_-\rangle\rangle_{\omega+i\epsilon}\\ =(i/2\pi)\langle[I_+,I_-]\rangle+\langle\langle[I_+,\mathcal{H}];I_-\rangle\rangle_{\omega+i\epsilon}.\end{aligned} \tag{15}$$

The equation of motion contains a higher order Green's function which may be written in similar form to (15), thus a whole hierarchy of coupled Green's functions can be generated. The usual procedure is to terminate the hierarchy by a decoupling scheme which approximates a high-order Green's function by one of lower order. In this way a closed set of coupled equations is generated which may be solved. Before proceeding we note that

$$\begin{aligned}\langle\langle[I_+,\mathcal{H}];I_-\rangle\rangle_{\omega+i\epsilon}\\ =\omega_0\langle\langle I_+;I_-\rangle\rangle_{\omega+i\epsilon}+\langle\langle[I_+,\mathcal{H}_1];I_-\rangle\rangle_{\omega+i\epsilon}.\end{aligned} \tag{16}$$

Also using the high-temperature approximation for the spin-dependent part of the density matrix

$$\rho(0)=-\beta\mathcal{H}/\mathrm{Tr}\{1\}=aI_z,$$

we evaluate the average of the commutator

$$\langle[I_+,I_-]\rangle=\tfrac{2}{3}aNI(I+1)(2I+1)^N=A_{(+-)}{}^0. \tag{17}$$

More complex averages of the form $\langle[C_n,I_-]\rangle=A_{(+-)}{}^n$ occur in the development of the hierarchy, where $C_n=[[\cdots,[I_+,\mathcal{H}_1],\cdots],\mathcal{H}_1]_n$. The subscript n and the dots denote an n-fold commutation of $\mathcal{H}_1$ with I_+. Examination of these averages shows that

$$A_{(+-)}{}^n=\tfrac{2}{3}aNI(I+1)(2I+1)^NM_n$$

and $A_{(+-)}{}^{n+1}=0$, where n is an even integer and M_n is the nth moment of the line shape.

Defining the normalized Green's function as

$$G_{(+-)}{}^0=\langle\langle I_+;I_-\rangle\rangle_{\omega+i\epsilon}/K, \tag{18}$$

where

$$K=\tfrac{2}{3}aNI(I+1)(2I+1)^N$$

and substituting $\Delta\omega=\omega-\omega_0$ we write the hierarchy of

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[14] For an introduction to Green's-function methods see D. N. Zubarev (Ref. 11); also D. ter Haar, *Fluctuation, Relaxation and Resonance in Magnetic Systems* (Oliver and Boyd, Ltd., London 1961), p. 119.

[15] A similar generalized expression has been derived by G. Baym, Ann. Phys. (N. Y.) 14, 1 (1961).

coupled equations to stage 4 as

$$(\Delta\omega+i\epsilon)G_{(+-)}{}^0=(i/2\pi)+G_{(+-)}{}^1, \tag{19a}$$

$$(\Delta\omega+i\epsilon)G_{(+-)}{}^1=G_{(+-)}{}^2, \tag{19b}$$

$$(\Delta\omega+i\epsilon)G_{(+-)}{}^2=(i/2\pi)M_2+G_{(+-)}{}^3, \tag{19c}$$

$$(\Delta\omega+i\epsilon)G_{(+-)}{}^3=G_{(+-)}{}^4, \tag{19d}$$

$$(\Delta\omega+i\epsilon)G_{(+-)}{}^4=(i/2\pi)M_4+G_{(+-)}{}^5. \tag{19e}$$

4. DECOUPLING OF GREEN'S FUNCTIONS

A. System of Noninteracting Spins

We consider the Green's function for a simple system with no dipolar or exchange interaction. The result is of course trivial, but instructive. From Eq. (19a) if $\mathcal{H}_1=0$

$$G_{(+-)}{}^0=\frac{(i/2\pi)}{(\Delta\omega+i\epsilon)} \tag{20}$$

and since

$$(1/2\pi)\int_0^\infty \theta(t)e^{-\epsilon t}e^{i\Delta\omega t}dt=\frac{(i/2\pi)}{\Delta\omega+i\epsilon}, \tag{21}$$

the Bloch decay of this function is the step function $\theta(t)e^{-i\omega_0 t}$ defined in (7) in the limit $\epsilon\longrightarrow 0$. From Eq. (13) the susceptibility is

$$\chi(\omega)=\lim_{\epsilon\to 0}\frac{-\frac{1}{2}\gamma K}{\Delta\omega+i\epsilon}=-\tfrac{1}{2}\gamma K\left(-\pi i\delta(\Delta\omega)+\mathcal{P}\left(\frac{1}{\Delta\omega}\right)\right). \tag{22}$$

Here $\mathcal{P}$ means the Cauchy principal part.[16] The absorption line χ'' is thus a delta function centered at the Larmor frequency. The dispersive part is

$$\chi'=-\tfrac{1}{2}\gamma K/\Delta\omega.$$

B. System of Isolated Pairs of Spin-$\frac{1}{2}$

The two-spin Green's function can be derived by an exact decoupling method[17] as follows. From Eqs. (19a) and (19b) we have for the jkth pair

$$(\Delta\omega+i\epsilon)G_{(+-)}{}^0=\frac{i}{2\pi}+\frac{G_{(+-)}{}^0}{(\Delta\omega+i\epsilon)}\frac{G_{(+-)}{}^2}{G_{(+-)}{}^0}. \tag{23}$$

(To avoid additional notation, we do not add the subscripts jk to the Green's functions or eigenvalues in this section, but take them as understood.) We now examine the matrix elements of the quotient, i.e.,

$$\frac{G_{(+-)}{}^2}{G_{(+-)}{}^0}=\frac{\displaystyle\sum_{nn'}\frac{\langle n|I_+|n'\rangle\langle n'|I_-|n\rangle(\rho_n-\rho_{n'})[\Delta E_n-\Delta E_{n'}]^2}{E_n-E_{n'}+\omega+i\epsilon}}{\displaystyle\sum_{nn'}\frac{\langle n|I_+|n'\rangle\langle n'|I_-|n\rangle(\rho_n-\rho_{n'})}{E_n-E_{n'}+\omega+i\epsilon}}, \tag{24}$$

where ΔE_n is an eigenvalue of the dipolar interaction. The eigenstates in this case are well known, but we write down the energies for convenience

$$\begin{aligned}E_1&=-\hbar\omega_0+\Delta E_1=-\hbar\omega_0+\tfrac{1}{4}(A_{jk}+B_{jk}),\\E_2&=\Delta E_2=\tfrac{1}{4}(A_{jk}-B_{jk}),\\E_3&=\Delta E_3=-\tfrac{1}{4}(3A_{jk}+B_{jk}),\\E_4&=\hbar\omega_0+\Delta E_4=\hbar\omega_0+\tfrac{1}{4}(A_{jk}+B_{jk}).\end{aligned} \tag{25}$$

From the matrix elements of I_+ and I_- we see that the only energy differences to be considered are $[\Delta E_2-\Delta E_1]^2$ and $[\Delta E_4-\Delta E_2]^2$. Since these are identical, Eq. (24) becomes

$$G_{(+-)}{}^2/G_{(+-)}{}^0=\tfrac{1}{4}B_{jk}{}^2=M_{2_{jk}}=b_{jk}{}^2. \tag{26}$$

Substituting this result into Eq. (23) and rearranging we obtain the exact Green's function for a system of $\frac{1}{2}N$ isolated pairs of spin-$\frac{1}{2}$, i.e.,

$$G_{(+-)}{}^0=\sum_{k>j}\frac{i(\Delta\omega+i\epsilon)}{2\pi[(\Delta\omega+i\epsilon)^2-b_{jk}{}^2]}. \tag{27}$$

In the special case of equivalent pairs, $b_{jk}=b$ is constant. The summation in (27) may then be replaced by $\frac{1}{2}N$. The inverse Fourier transform of this function is then

$$\mathfrak{F}^{-1}G_{(+-)}{}^0=\tfrac{1}{2}Ne^{-i\omega_0 t}\theta(t)\cos bt \tag{28}$$

which as expected is an undamped cosine-modulated signal corresponding to the Bloch decay. The complex susceptibility, obtained from Eq. (27) in the limit as $\epsilon\longrightarrow 0$, is

$$\chi(\omega)=-\tfrac{1}{4}\gamma K\left\{\sum_{k>j}-\pi i[\delta(\Delta\omega+b_{jk})+\delta(\Delta\omega-b_{jk})]\right.$$
$$\left.+\mathcal{P}\left[\frac{1}{\Delta\omega+b_{jk}}+\frac{1}{\Delta\omega-b_{jk}}\right]\right\}. \tag{29}$$

This well-known result corresponds to $\frac{1}{2}N$ pairs of delta functions for the absorption line shape, symmetric about the Larmor frequency.

C. The Many-Spin Case

From the previous section we see that an exact decoupling scheme based on evaluating (24) in the case of N interacting spins is impractical since the eigenstates of such a system are unknown. In order to preserve the standard form for decoupling, we write Eqs. (19a) and (19b) together as

$$\begin{aligned}(\Delta\omega+i\epsilon)G_{(+-)}{}^0&=\frac{i}{2\pi}+\frac{G_{(+-)}{}^2G_{(+-)}{}^0}{(\Delta\omega+i\epsilon)G_{(+-)}{}^0}\\&=i/2\pi+\Pi(\Delta\omega+i\epsilon)G_{(+-)}{}^0.\end{aligned} \tag{30}$$

The standard decoupling procedure is equivalent to taking $\Pi(\Delta\omega+i\epsilon)$ approximately equal to $c/\Delta\omega$ where

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[16] See also C. P. Slichter, *Principles of Magnetic Resonance*, (Harper & Row, New York, 1963), p. 38.

[17] See, for example, K. W. H. Stevens and F. Persico, Nuovo Cimento **41**, 37 (1966).

c is a constant. In our case this is too crude an approximation, so we will attempt to evaluate it using arguments based on a somewhat physically intuitive approach. We assume that $\Pi(\Delta\omega+i\epsilon)$ is a smooth function [since $G_{(+-)}{}^2$ and $(\Delta\omega+i\epsilon)G_{(+-)}{}^0$ have the same poles, differing only in their strengths] and evaluate it using approximate expressions for the Green's functions in both numerator and denominator. That is to say, we assume that for small ϵ an actual Green's function in the complex plane can be replaced by a smooth approximate Green's function even on the real axis when $\epsilon=0$. We might expect from the equations of motion that $G_{(+-)}{}^2(0)=0$ (that there is no pole at the origin for the approximate function is shown later); also, that $\Pi(0)=(i/2\pi)/G_{(+-)}{}^0(0)$. To avoid difficulties at the origin we consider in some detail the approximation for $G_{(+-)}{}^2$. We first note that it may be obtained from Eqs. (19c), (19d), and (19e), i.e.,

$$(\Delta\omega+i\epsilon)G^2{}_{(+-)}=\frac{iM_2}{2\pi}+\frac{G_{(+-)}{}^4}{\Delta\omega+i\epsilon}. \tag{31}$$

As a very crude approximation (though in the spirit of the usual decoupling method), we decouple as follows

$$G_{(+-)}{}^4\simeq(M_4/M_2)G_{(+-)}{}^2. \tag{32}$$

Substituting this in Eq. (31) and solving we obtain for $\epsilon=0$ the inverse Fourier transform

$$G_2(t)=M_2e^{-i\omega_0t}\theta(t)\cos(M_4/M_2)^{1/2}t. \tag{33}$$

This is an undamped cosine modulated function and as we shall demonstrate is a rather poor approximation to the true expression. Lack of damping seems typical of the usual decoupling method in spin systems. This result is nevertheless interesting since it predicts the correct initial time dependence in $G_2(t)$. The exact form of $G_2(t)$ can be obtained directly from the moment expansion, i.e.,

$$G_2(t)=M_2e^{-i\omega_0t}\theta(t)\left[1-\frac{M_4}{M_2}\frac{t^2}{2!}+\cdots\right] \tag{34}$$

and is a strongly damped function. Except in the region of zero time, the envelope of this function is proportional to the second time derivative of the envelope of $G_0(t)$. Since $M_4>M_2{}^2$, the function $G_2(t)$ is much sharper than the Bloch decay. This point is exemplified in the particular case of a Gaussian decay function when the envelope $G_2(t)_{\mathrm{en}}$ oscillates slightly. In fact, any damped function which is expressible as an even-moment expansion will have a $G_2(t)_{\mathrm{en}}$ which crosses the abscissa at least once. The first zero will occur at a time

$$\tau=\sqrt{2}/a, \tag{35}$$

where $a^2=M_2[\alpha M_4/M_2{}^2]$ and α is an adjustable factor of value approximately unity.

We wish to replace the function $G_2(t)$ by a plausible approximation. Since it is proportional to $(d^2/dt^2\times G_0(t)_{\mathrm{en}}$ then

$$\lim_{\delta t\to0}\int_{0+\delta t}^{\infty}G_2(t)_{en}dt=\frac{d}{dt}G_0(t)_{en}\Big]_{0+\delta t}^{\infty}=0, \tag{36}$$

provided $G_0(t)_{\mathrm{en}}$ is an even-moment expansion which converges for large t. That is to say, the total area under $G_2(t)_{\mathrm{en}}$ is zero. Our approximation therefore must incorporate this result. It is precisely this point which makes $G_{(+-)}{}^2$ vanish for $\Delta\omega=0$, since Eq. (36) is the zero-frequency term in the Fourier transform of $G_2(t)_{\mathrm{en}}$. As a plausible approximation which satisfies our condition, we take

$$G_2(t)=M_2e^{-i\omega_0t}\{[\theta(t)-\theta(t-\tau)]-h[\theta(t)-\theta(t-\tau/h)]\}, \tag{37}$$

where h is less than unity and is arbitrary. Equation (37) is essentially the sum of two square-pulse functions: a positive pulse with width τ chosen to correspond to the first zero of $G_2(t)_{\mathrm{en}}$ as in (35), minus another pulse of equal area.

By Fourier transforming, the function $G_{(+-)}{}^2$ can be expressed as the difference of two other functions, i.e.,

$$G_{(+-)}{}^2=G_{(+-)}{}^{2A}-G_{(+-)}{}^{2B}, \tag{38}$$

where the superscript A refers to the positive pulse and B refers to the negative contribution.

We could in principle use this approximation for $G_{(+-)}{}^2$ and evaluate $G_{(+-)}{}^0$ directly from Eqs. (19a) and (19b). The arbitrariness of $G_{(+-)}{}^{2B}$ however, makes the behavior around the origin difficult to determine. It is certainly all right for high frequencies. By keeping the decoupling form we shall show that the behavior of $G_{(+-)}{}^0$ in the region of $|\Delta\omega|\simeq0$ can be obtained quite rigorously without knowing $G_{(+-)}{}^{2B}$ in detail.

Utilizing the above result, Eq. (38), the decoupling factor may be rearranged to give

$$\Pi(\Delta\omega)\equiv\frac{G_{(+-)}{}^{2A}}{\Delta\omega G_{(+-)}{}^0+G_{(+-)}{}^{2B}/\Pi(\Delta\omega)}. \tag{39}$$

Since $h<1$, $\Pi(\Delta\omega)$ in the denominator of (39) can be replaced by its value at the origin, i.e.,

$$\Pi(0)=-(i/2\pi)/G_{(+-)}{}^0(0). \tag{40}$$

This is a good approximation even when $\Pi(\Delta\omega)$ is only twice as broad as $G_{(+-)}{}^{2B}$. The approximation improves for $h\ll1$. In this case, the line shape approaches a Lorentzian function.

$G_{(+-)}{}^0(0)$ may be calculated approximately from the moment expansion for the Bloch decay as follows

$$\begin{aligned}G_{(+-)}{}^0(0)&=\lim_{\delta t\to0}\frac{1}{2\pi}\int_{0+\delta t}^{\infty}G_0(t)_{\mathrm{en}}dt\\&=\frac{f\tau}{2\pi}\simeq\frac{1}{2\pi M_2\tau},\end{aligned} \tag{41}$$

since $M_2\tau^2=1/f'$, where f, f' are numerical factors. For no exchange $f\simeq f'\simeq 1$ and τ has its previous meaning. To evaluate $G_{(+-)}{}^0(0)$ precisely would require a detailed knowledge of $G_0(t)$. Substituting Eq. (41) into Eq. (39) we obtain

$$\Pi(\Delta\omega)\simeq\frac{G_{(+-)}{}^{2A}}{\Delta\omega G_{(+-)}{}^0+(i/M_2\tau)G_{(+-)}{}^{2B}}. \tag{42}$$

From our pulse approximation, we readily obtain

$$G_{(+-)}{}^{2A}=\frac{M_2\tau}{2\pi}\left\{\frac{\sin\Delta\omega\tau}{\Delta\omega\tau}+i\frac{(1-\cos\Delta\omega\tau)}{\Delta\omega\tau}\right\}, \tag{43}$$

and

$$G_{(+-)}{}^{2B}=\frac{M_2\tau}{2\pi}\left\{\frac{\sin(\Delta\omega\tau/h)}{\Delta\omega\tau/h}+i\frac{(1-\cos(\Delta\omega\tau/h))}{\Delta\omega\tau/h}\right\}. \tag{44}$$

Substituting in Eq. (42), we check that

$$\Pi(0)\simeq -iM_2\tau\simeq -i/2\pi G_{(+-)}{}^0(0).$$

The last approximate equality follows from Eq. (41).

It is emphasized that $\Pi(\Delta\omega)$ in Eq. (42) involves no major approximations so far. We now wish to examine the denominator D of Eq. (42). In general the retarded Green's functions occurring in it are complex, i.e.,

$$G=G''+iG'.$$

The single- and double-primed parts would correspond to the dispersive and absorptive parts, respectively, of the complex susceptibility. Decomposing the denominator, we obtain

$$D=\{\Delta\omega G_{(+-)}{}^{0''}-G_{(+-)}{}^{2B'}/M_2\tau\}+i\{\Delta\omega G_{(+-)}{}^{0'}+G_{(+-)}{}^{2B''}/M_2\tau\}.$$

For $|\Delta\omega|\simeq 0$ we readily see that $D=i/2\pi$. Since the width of $G_{(+-)}{}^{2B}$ is arbitrary, we may choose it to be approximately as broad as the line shape without seriously violating Eq. (42). In this case the real part of D can be made to vanish approximately over the whole line shape.

If the real part of D vanishes, we can calculate the relationship of the imaginary parts of D as follows. The generalized dispersion relations for the retarded Green's function are

$$\mathrm{Re}G(\omega)=\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\mathrm{Im}\frac{G(\omega')d\omega'}{\omega'-\omega},$$

and

$$\mathrm{Im}G(\omega)=-\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\mathrm{Re}\frac{G(\omega')d\omega'}{\omega'-\omega}.$$

Substituting $G_{(+-)}{}^{0''}=(1/\Delta\omega)(G_{(+-)}{}^{2B'}/M_2\tau)$ into the second expression we have

$$G_{(+-)}{}^{0'}=-\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{G_{(+-)}{}^{2B'}(\omega')d\omega'}{M_2\tau(\omega'-\omega_0)(\omega'-\omega)}.$$

Rearranging this into partial fractions and using the first dispersion relation and the fact that $G_{(+-)}{}^{2B''}(\omega_0)=M_2\tau/2\pi$, we obtain

$$\Delta\omega G_{(+-)}{}^{0'}=-G_{(+-)}{}^{2B''}/M_2\tau+1/2\pi.$$

From this result we find that $D=i/2\pi$ for all $|\Delta\omega|$. We notice that exact cancellation of the real part of D occurs for Lorentzian-type functions. For broad line shapes, cancellation of the real part will only be approximately true over a limited frequency range. In the case of a Gaussian function, the approximation is quite good over most of the linewidth, as is readily checked by direct computation. For large $|\Delta\omega|$ however, D begins to decrease.

If we take $D=i/2\pi$ over the whole line for all line shapes, our approximation might be expected to affect the wings of broad Gaussian-type line shapes, causing them to converge to zero more slowly than is found experimentally. From Eq. (42) and the foregoing discussion, the decoupling factor is

$$\Pi(\Delta\omega)=\frac{M_2\tau}{i}\left\{\frac{\sin\Delta\omega\tau}{\Delta\omega\tau}+i\frac{(1-\cos\Delta\omega\tau)}{\Delta\omega\tau}\right\}. \tag{45}$$

We note in passing that by application of the convolution theorem, $\Pi(\Delta\omega)$ may be expressed as the Fourier transform of a correlation function $\Gamma(t)$, i.e.,

$$\Pi(\Delta\omega)=\mathfrak{F}\Gamma(t)=\mathfrak{F}\int_{-\infty}^{\infty}G^A(t-t')G_2{}^A(t')d't, \tag{46}$$

where

$$G^A(t-t')=\mathfrak{F}^{-1}\frac{1}{\Delta\omega G_{(+-)}{}^{0A}},$$

and

$$G_2{}^A(t')=\mathfrak{F}G_{(+-)}{}^{2A}$$

provided the inverse Fourier transforms exist. This is readily seen to be true in the case of Eq. (45) where

$$G^A(t-t')=(2\pi/i)\delta(t-t')$$

yielding

$$\Gamma(t)=(2\pi/i)G_2{}^A(t).$$

We now use our expression for $\Pi(\Delta\omega)$ in Eq. (30) to obtain $G_{(+-)}{}^0$, i.e.,

$$\lim_{\epsilon\to 0}G_{(+-)}{}^0=\frac{i/2\pi}{\Delta\omega+iM_2\{\sin\Delta\omega\tau/\Delta\omega+i(1-\cos\Delta\omega\tau)/\Delta\omega\}}. \tag{47}$$

The absorption line shape from Eq. (13) is therefore

$$\chi''=-\tfrac{1}{2}\gamma K\frac{M_2\sin\Delta\omega\tau/\Delta\omega}{[\Delta\omega-M_2(1-\cos\Delta\omega\tau)/\Delta\omega]^2+M_2{}^2[\sin\Delta\omega\tau/\Delta\omega]^2}. \tag{48}$$

If we use Eq. (38) directly to evaluate the line shape for high frequencies we obtain

$$\chi'' = -\tfrac{1}{2}\gamma K M_2 \sin\Delta\omega\tau/\Delta\omega^3 \qquad (49)$$

which agrees with the high-frequency limit of Eq. (48). This result will only be valid, however, when $G_{(+-)}{}^{2B} \simeq 0$, i.e., in the wings of the absorption line shape.

The periodic nature of χ'', arising directly from the pulse approximation, may be ignored because of heavy damping.

TABLE I. Theoretical values of M_2 in gauss and $M_4/M_2{}^2$ for the F^{19} resonance in a single crystal of CaF_2 with different directions of the external magnetic field.

	[100]	[110]	[111]
$M_4/M_2{}^2$	2.07	2.22	2.29
M_2(gauss)	14.40	5.02	2.34

5. COMPARISON WITH EXPERIMENT

The line shape, Eq. (48), is evaluated for the case of the fluorine resonance in a single crystal of CaF_2. Theoretical values of M_2 and M_4 are used with the

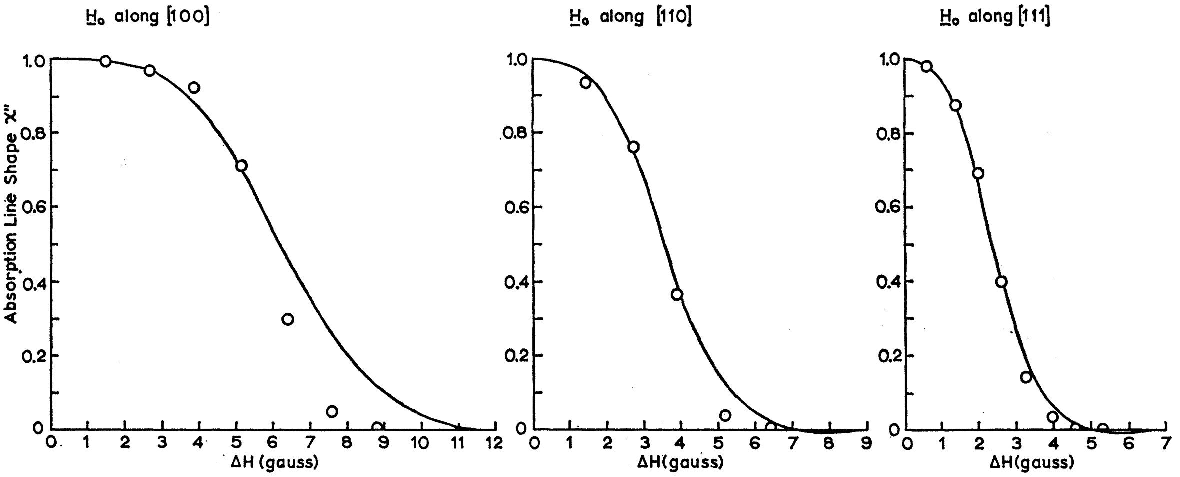

FIG. 1. Absorption line shape for the F^{19} resonance in a single crystal of calcium fluoride, with the external magnetic field along the [100], [110], and [111] directions. The solid line is the theoretical prediction, the circled points have been taken from Bruce's experimental data.

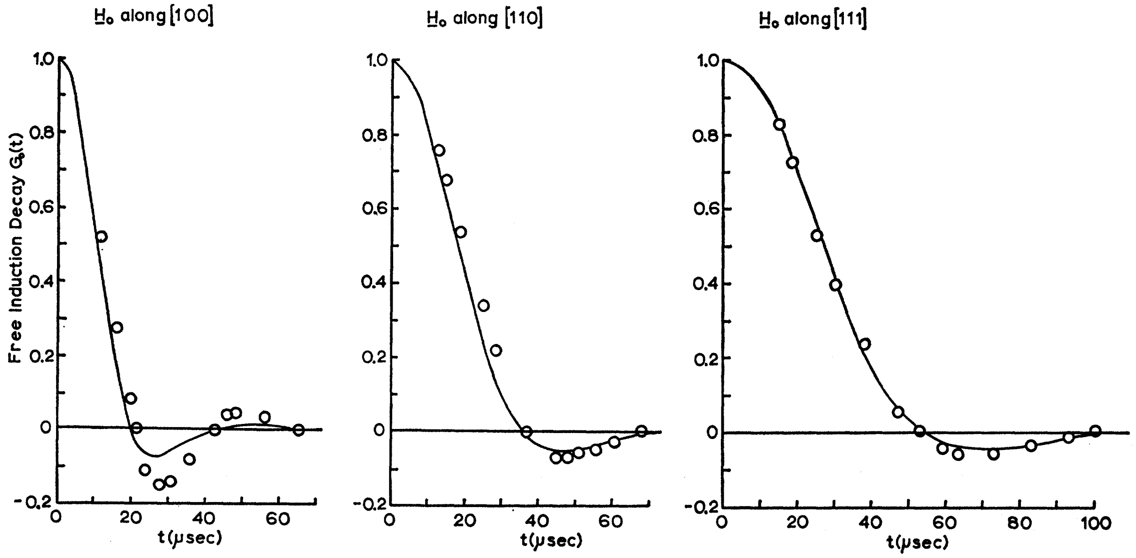

FIG. 2. Free induction decay envelopes for the F^{19} resonance in a single crystal of calcium fluoride with the external magnetic field along the crystal axes indicated. The solid line is the Fourier transform of the theoretical line shape, the circled points have been taken from Lowe and Norberg's experimental data.

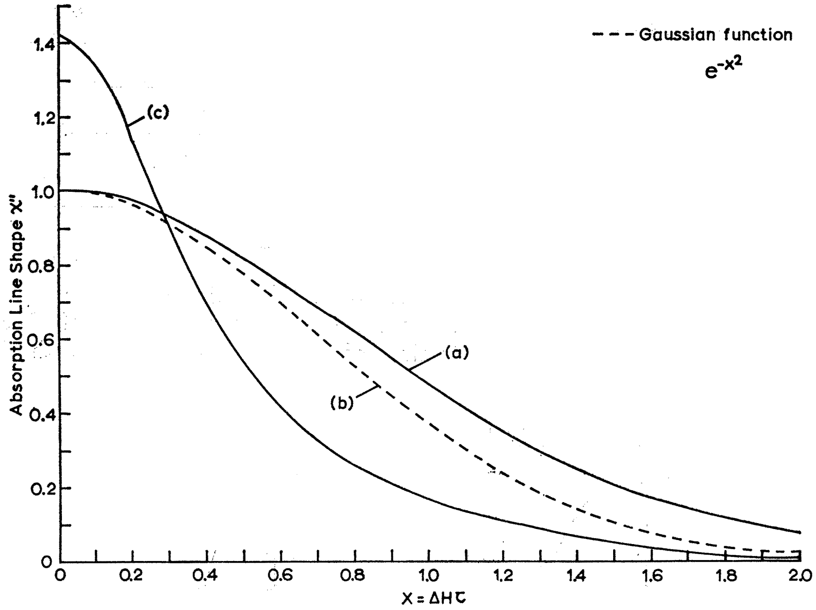

FIG. 3. Theoretical absorption line shapes for different values of the ratio M_4/M_2^2. Curve (a) corresponds to a ratio of 3 and is compared with the Gaussian-function curve (b). Curve (c) has a ratio of 6 and corresponds to an additional exchange contribution to the fourth moment equal to the purely dipolar part.

external magnetic field along the [100], [110], and [111] directions. The actual moments used are listed in Table I. The small contribution to the F^{19} moments arising from the very low natural abundance of Ca^{43} is entirely ignored.

The results for $\alpha=0.9$ are shown in Fig. 1 together with the experimental data of Bruce.[18] The value of α was chosen to fit the [100] data, and gives an even better fit for the other two orientations. The free induction decays obtained by taking the Fourier transform of the theoretical line shapes are compared with the experimental data of LN in Fig. 2.

6. CONCLUSIONS

The method of retarded Green's functions yields some familiar results for the line shape of simple spin systems. Simple decoupling of Green's functions is valid for dipolar broadened line-shape calculations in the case of isolated pairs of spin-$\frac{1}{2}$ and also possibly trios of spin-$\frac{1}{2}$. In this case exact results are obtained.

For the N-spin problem simple decoupling is inadequate. This leads to an undamped cosine modulated free induction decay with periodicity $2\pi/\sqrt{(M_2)}$. This corresponds to the replacement of the dipolar interaction by an average local field. For short times, however, this is a good approximation. Examination of the matrix elements of the decoupling factor shows that in general it will be a function of frequency. An exact evaluation would require a knowledge of the eigenstates of the N-spin problem. Using a physically intuitive approach we attempt to evaluate the decoupling factor using approximate Green's functions for both numerator and denominator.

We make three basic assumptions as follows:

(i) The actual Green's function for small ϵ may be replaced by a smooth approximate Green's function on the real axis. For a large number of interacting spins, this corresponds to the transition from a discrete to a continuous spectrum;

(ii) The square-pulse approximation for $G_2(t)$. This is a plausible approximation based on the moment expansion plus the physically realistic convergence of $G_0(t)$ for large times implicit in (i);

(iii) The denominator in the rearranged decoupling factor is constant, i.e., $D=i/2\pi$.

In view of the simplicity of the approximations made, the agreement between theory and experiment can only be regarded as an indication of the general correctness of the approach.

When exchange-type interactions are included in a spin system, with one spin species, they affect the fourth and higher moments only. We assume that the approximate equality Eq. (41) holds in this situation and in this case $f'\simeq M_4/M_4'$, where M_4' is the dipolar contribution to the fourth moment. In our expression, which is dependent on the ratio M_4/M_2^2, the line shape changes dramatically, narrowing to a Lorentzian shape near the center of the line for increasing values of the ratio. Thus the qualitative behavior of the line shape is explained by our expression. For a Gaussian shape, $M_s/M_2^2=3$. If we substitute this value into Eq. (48), and plot the absorption line versus a normalized variable $x=\Delta H\tau$, where ΔH is the off-resonance field and τ has its previous meaning, we obtain curve (a) of Fig. 3. This is compared with the Gaussian-function curve (b). We see that the differences are quite small. This is an interesting result, since it means that any broad line-shape function, including the Gaussian case can be characterized by a pulse correlation function $\Gamma(t)$. This agree-

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ment lends strong support to our initial assumptions regarding the evaluation of the decoupling factor.

The case when a fourth-moment exchange contribution equals the purely dipolar fourth moment is also plotted in curve (c). Here the line shape is practically Lorentzian near the center of the resonance, but is damped more rapidly for $|x|$ large. A test of this result is not possible at present since experimental exchange-narrowed line-shape data on suitable single crystals is lacking.

In conclusion a decoupling scheme, based on plausible assumptions is given which describes the many-spin line shape in cubic arrays. Similar assumptions may enable the method to be applied to other line-shape problems, in particular to artificially as well as thermally narrowed lines.

ACKNOWLEDGMENTS

The writer wishes to express his gratitude to Dr. G. A. Toombs for some stimulating discussions at the start of this work, and also to Professor K. W. H. Stevens for a number of discussions and suggestions.

PHYSICAL REVIEW VOLUME 151, NUMBER 1 4 NOVEMBER 1966

Triplet-State Electron Spin Resonance of an H-Atom–Methyl-Radical Complex in a Solid Matrix*

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(Received 9 May 1966; revised manuscript received 23 June 1966)

The electron spin resonance of paramagnetic species produced by γ irradiation of solid methane at 4.2°K has been observed. In addition to the expected signals from individual H and CH_3 radicals, weaker signals from exchange-coupled H and CH_3 radicals were observed. The exchange interaction is isotropic, but there is an anisotropic dipole-dipole interaction between the aligned electron spin moments which gives rise to a splitting of 91 G. Analysis of this interaction indicates the separation of the coupled H and CH_3 to be 6.76 Å. The hyperfine splitting by the H is 255 G and that by each proton of the CH_3 group is 11.5 G, or one-half those for the isolated H and CH_3. These features are shown to be in agreement with theoretical predictions. Similar effects were observed for CH_4 irradiated in a krypton matrix at 4.2°K.

EXCHANGE interaction is responsible for diverse phenomena in concentrated magnetic elements in solids. The most prevalent effects on magnetic resonance, those on linewidths and line shapes, have been treated theoretically by Van Vleck[1] and others.[2,3] Simultaneous flipping of two coupled spins was detected in diethyl copper acetate powder by Lancaster and Gordy,[4] who suggested that the spins might be coupled through exchange interaction. This species was studied further by Bleaney and Bowers[5] in single crystals, and the hyperfine structure of the coupled pairs of copper ions was measured and analyzed. Some weak satellite lines observed by Fletcher *et al.*[6] and by Feher *et al.*[7] in the resonance of phosphorus-doped silicon semiconductors have been attributed by Slichter[8] to exchange coupling. The present case, although analogous to that of copper acetate, is novel in that the exchange interaction arises between different magnetic species, in a magnetic-impurity site produced by irradiation. The interaction occurs between the two parts of a dissociated molecule. Although these measurements were not made on single crystals, it has been possible to resolve and analyze the electron-spin-resonance (ESR) spectra in some detail. From the analysis the separation of the two magnetic species in the matrix is found. We have observed these effects in the solid CH_4 matrix and in a krypton matrix at 4.2°K.

Figure 1 shows the first derivative of the ESR absorption curve of γ-irradiated CH_4 observed with high gain at 4.2°K. The spectrometer[9] and the experimental techniques[10] are described in previous reports from this laboratory. A γ-ray dosage of 6×10^5 R was given the sample from a $\frac{1}{2}$-kCi cobalt-60 irradiation source. The samples were irradiated in the microwave cavity, which was maintained at 4.2°K throughout the experiment. The observation frequency was 24 kMc/sec. The strong lines which saturate the receiver are due to

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* This study was supported by the U. S. Air Force Office of Scientific Research, Grant AF-AFOSR-493-66 and by the Army Research Office (Durham), grant DA-ARO(D)-31-124-G731.

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