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Nuclear Dipole Field Quenching of Integer Spins*

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For magnetic dipole-dipole coupling among integer nuclear spins in an asymmetric electric field gradient, the coupling is partially reduced by the asymmetry, and the coupling between integer spins and any nonresonant spins is highly reduced in first order. This "spin-quenching" mechanism is analogous to the quenching of electron orbital angular momentum of paramagnetic ions by low-symmetry crystal fields. These reductions in coupling are demonstrated by an examination of expectation values for the dipole-moment operator and, more formally, by calculating the Van Vleck second moment for a collection of identical spins $I=1$ in both axially symmetric and non-axially symmetric electric field gradients, with and without applied magnetic fields. The contribution to the second moment of an unlike set of half-integer spins by spins $I=1$, and its converse, is calculated as a function of applied magnetic field. The normal Van Vleck result is obtained, except that it is multiplied by a factor $z^2/(1+z^2)$, where z is proportional to the applied magnetic field, and is inversely proportional to the amount of asymmetry. The quenching effect is confirmed from Cl^{35} spin-echo double-resonance measurements of $BaClO_3 \cdot D_2O$, where the deuterium spins have $I=1$, and couple to the Cl^{35} spins which serve as a probe to measure the interspecies coupling.

I. INTRODUCTION

The dipole-dipole coupling interaction occurs as an important mechanism in a majority of nuclear magnetic resonance phenomena. In solids the magnetic dipole-dipole interaction broadens the resonance line, allows spins to couple to lattice modes of vibration, provides the mechanism for maintaining a spin temperature, and provides the coupling between different spin species which accounts for cross-relaxation and double resonance effects. In this investigation we deal with an effect, analogous to the quenching of electron orbital angular momentum of paramagnetic ions,[1] which can apply as well to nuclear quadrupole moments of integer spins coupled to crystalline electric field gradients of low symmetry. In zero or weak dc magnetic fields, the magnetic dipole-dipole coupling of any foreign spin species with an ensemble of such quadrupole coupled spins exhibits a quenching or a reduction far below that coupling predicted by the usual second moment calculations[2] for nuclear moments in a rigid lattice in high magnetic fields. Stevens[3] was the first to show that the second moment of interaction, formulated for differently oriented paramagnetic electronic ions, each with $S=1$, disappears as the external magnetic field is reduced to zero. In this paper we consider examples of coupled nuclear spin ensembles which are quite different from the ion-coupling case treated by Stevens. Our examples are chosen to be pertinent to nuclear quadrupole resonance spectroscopy experiments. Although the phenomenon of angular momentum quenching is well known in electron magnetism studies, the quenching effect upon zero-magnetic-field nuclear quadrupole spectra of integer nuclear spins has been studied little or overlooked in those cases where crystalline electric field gradients have a symmetry lower than axial.

The nuclear spin-quenching effect was reported earlier[4] in the case of coupling between Cl^{35} and D^2 spins, as measured by double resonance methods in $BaClO_3 \cdot D_2O$. In this case, the effect occurs because the deuterium nuclei have spin $I=1$, and each deuterium nuclear quadrupole is coupled to an asymmetric crystalline electric field gradient. Anomalously narrow nuclear quadrupole resonance lines for N^{14} ($I=1$) have been observed in $CO(NH_2)_2$ by O'Konski and Torizuka[5] and in thiourea by Cotts and Smith.[5]

II. THEORY

The spin-spin coupling either within a single spin species, or between different species, will be evaluated in terms of the second moment of the nuclear resonance line shape. It will first be done for a collection of identically oriented $I=1$ spins in axially symmetric and asymmetric electric field gradients, with and without an applied magnetic field. Also the contribution of a collection of $I=1$ spins to the second moment of $I=\frac{1}{2}$ spins as a function of magnetic field is calculated; and the converse case, the contribution of $I=\frac{1}{2}$ spins to the second moment of $I=1$ spins, is also obtained. However, before entering into a formal second moment computation, it is instructive to consider first some physical properties regarding the nature of quadrupole coupled integer nuclear spins, and some elementary properties of the dipolar coupling.

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[1] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932).

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

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[4] C. J. Gabriel, G. W. Leppelmeier, and E. L. Hahn, Bull. Am. Phys. Soc. **9**, 733 (1964).

[5] C. T. O'Konski and K. Torizuka (private communication); R. Cotts and D. Smith (private communication).

III. PURE QUADRUPOLE HAMILTONIAN

The pure nuclear quadrupole moment Hamiltonian in the principal axes system of the electric field gradient exclusive of dipolar coupling is given by[6]

$$h_Q=K\left[3I_z^2-I(I+1)+\frac{\eta}{2}(I_+^2+I_-^2)\right], \tag{1}$$

where $K=e^2qQ/4I(2I-1)$, $eq=|V_{zz}|$, Q is the nuclear quadrupole moment (in cm^2), and the asymmetry parameter is

$$\eta=(|V_{yy}|-|V_{xx}|)/|V_{zz}|\,.$$

Double subscripts of V signify second derivatives of the electric potential, evaluated at the site of the nucleus. The coordinate axes are defined such that $|V_{zz}|\geq|V_{yy}|\geq|V_{xx}|$. In the principal axes system, all off-diagonal elements of the tensor V are zero.

The eigenstates of the above Hamiltonian h_Q, for any integral spin, are such that the expectation values (or diagonal matrix elements) of all three components of spin angular momentum, I_x, I_y, and I_z, are zero for all eigenstates. Fundamentally, this lack of an invariant component of angular moment associated with the quenching effect, whether it occurs for electrons or nuclei, arises when the spin Hamiltonian is invariant under time reversal, and is applied to a problem where the effective particle spin is integer rather than half-integer. It follows, moreover, that if the system also interacts significantly with an external dc magnetic field which is not invariant under time reversal, then the quenching effect is reduced.

It is easily seen that the above remarks regarding complete quenching apply to the case $I=1$, such as deuterium, where the eigenfunctions ψ and corresponding eigenvalues E of the Hamiltonian of Eq. (1) are

$$\begin{aligned}\psi_\alpha&=\frac{1}{\sqrt{2}}(u_{+1}+u_{-1}), & E_\alpha&=K(1+\eta);\\ \psi_\beta&=\frac{1}{\sqrt{2}}(u_{+1}-u_{-1}), & E_\beta&=K(1-\eta);\\ \psi_\gamma&=u_0, & E_\gamma&=-2K;\end{aligned} \tag{2}$$

and u_{+1}, u_{-1} and u_0 are the eigenfunctions of the operator I_z. We shall have occasion to refer to this particular example in later discussions. As a general rule for any integer spin, the quenching effect arises when the actual eigenstates of the pure quadrupole Hamiltonian are expressed in terms of eigenstates of the operator I_z, which differ from one another in their characteristic quantum number m_I at least by $\Delta m_I=2$. For complete quenching, these eigenstates of I_z, when linearly combined to form a given quadrupole state, must be present in equal amounts. This is indicated explicitly by considering the Hamiltonian of Eq. (1), first when $\eta=0$. In this situation the states $\pm m_I$ are doubly degenerate. Since the asymmetry term in η connects only states which differ in m_I by $\Delta m_I=2$, it will lift the degeneracy for integer spins I, as shown in the example for $I=1$ [Eqs. (2)]. However, if I is half-integer the asymmetry term does not lift the degeneracy because the initially degenerate states $+m_I$ and $-m_I$ differ at least by an odd integer. When the degeneracy is removed by the η term, and the quadrupole Hamiltonian h_Q contains only even powers of the angular momentum operator, the time-reversal argument shows in general that a linear expansion of the eigenfunctions of h_Q, in terms of the eigenfunctions of I_z, will have only terms even in m_I or odd in m_I, but not both. The time reversal of h_Q of Eq. (1), which is quadratic in the spin operators I, does not change h_Q by reversing the sign of I. If h_{mn} is a matrix element of h_Q in the representation diagonal in I_z, then $h_{mn}=h_{-m-n}$. This last property can be used to show that if an eigenfunction of h_Q if given as

$$\psi_\alpha=\textstyle\sum_m a_m u_m\,,$$

then

$$\psi_\alpha'=\textstyle\sum_m a_{-m}u_m$$

is also an eigenfunction of h_Q with the same eigenvalue, where the u_m are eigenfunctions of I_z. This is possible only if there is a degeneracy, when $\eta=0$. For $\eta\neq0$, the degeneracy is removed and the condition $\psi_\alpha'=\psi_\alpha e^{i\varphi}$ (or $a_{-m}=a_m e^{i\varphi}$) applies to a given eigenstate, where φ is a phase factor. In this interesting situation, with the η term present, the eigenfunctions of h_Q for an integer spin have either the form

$$\psi_\alpha=a_0u_0+a_2u_2+a_2u_{-2}+\cdots$$

or the form

$$\psi_\alpha=a_1u_1+e^{i\varphi}a_1u_{-1}+a_3u_3+e^{i\varphi}a_3u_{-3}+\cdots.$$

The expectation values of I_x, I_y, and I_z in any of the eigenstates ψ_α above are all zero. Therefore, in zero-magnetic field the magnetic dipole-dipole coupling of any integer spin with any nonresonant neighboring spin is zero in first order when the dominant quadrupole interaction is asymmetric. It will be made clear later that this quenching effect is reduced by a modification of the above eigenstates by a magnetic field. Such a magnetic field could be externally applied, or could arise from the neighboring unlike spin itself. This unquenching effect of neighboring spins would occur in second order and is a difficult problem which is not treated in this paper. Only the effect of an externally applied field on the quenching will be handled in a rigorous fashion.

IV. EFFECT OF A MAGNETIC FIELD

The case of integer spin $I=1$ will be analyzed explicitly. Extensions of the following analysis to higher

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[6] T. P. Das and E. L. Hahn, *Solid State Physics* (Academic Press Inc., New York, 1958), Suppl. 1.

integer spins can as well be carried out. Previous investigators[7] have treated the NQR Zeeman splitting for $I=1$ by using the asymmetric η term of h_Q [Eq. (1)] and the applied Zeeman interaction as a perturbation, or conversely, by considering the entire quadrupole interaction as a perturbation upon a larger Zeeman interaction. A preferred approach here is to evaluate *exactly* the eigenfunctions and eigenvalues of the combined total quadrupole interaction and *one* of the components of an applied external magnetic field. Therefore, at most one need consider only two of the components of magnetic field as perturbations.

Consider the eigenfunctions, Eq. (2), of the quadrupole Hamiltonian Eq. (1). If one inspects the matrix elements of I_x, I_y, and I_z in this representation, one finds that the only nonzero elements of I_x connect the states α and γ; the only nonzero elements of I_y connect β and γ; and the only nonzero elements of I_z connect α and β. Obviously if a magnetic field H_0 is applied along a principal axis, one of the states α, β, or γ is unaffected, and the other two are mixed. Consequently, the Hamiltonian

$$h_0=h_Q-\gamma\hbar\mathbf{I}\cdot\mathbf{H}_0 \tag{3}$$

can be diagonalized exactly for H_0 either along the x, y, or z directions. For example, with H_0 along the z direction, the eigenvalues are

$$\begin{aligned} E_\alpha&=K[1+\eta(1+z^2)^{1/2}],\\ E_\beta&=K[1-\eta(1+z^2)^{1/2}], \end{aligned} \tag{4}$$

and

$$E_\gamma=-2K,$$

where

$$z=\gamma\hbar H_z/K\eta. \tag{5}$$

The corresponding eigenfunctions are

$$\begin{aligned} \psi_\alpha&=u_{+1}\cos\theta+u_{-1}\sin\theta,\\ \psi_\beta&=u_{+1}\sin\theta-u_{-1}\cos\theta, \end{aligned} \tag{6}$$

and

$$\psi_\gamma=u_0,$$

with

$$\cos\theta=\frac{1}{\sqrt{2}}[1+z^2+z(1+z^2)^{1/2}]^{-1/2},$$

$$\sin\theta=\frac{1}{\sqrt{2}}[1+z^2-z(1+z^2)^{1/2}]^{-1/2}.$$

The eigenfunctions of h_0, Eq. (3), for H_0 along the z axis determine spin-operator expectation values as follows:

$$\begin{aligned} &\langle I_x\rangle=\langle I_y\rangle=0 \text{ for all eigenstates},\\ &\langle I_z\rangle_{\alpha\alpha}=-\langle I_z\rangle_{\beta\beta}=-z/(1+z^2)^{1/2},\\ &\langle I_z\rangle_{\gamma\gamma}=0. \end{aligned}$$

Similarly, for H_0 along the x axis:

$$\begin{aligned} &\langle I_y\rangle=\langle I_z\rangle=0 \text{ for all eigenstates},\\ &\langle I_x\rangle_{\gamma\gamma}=-\langle I_x\rangle_{\alpha\alpha}=x/(1+x^2)^{1/2},\\ &\langle I_x\rangle_{\beta\beta}=0, \end{aligned}$$

where

$$x=2\gamma\hbar H_x/K(3+\eta). \tag{7}$$

And for H_0 along the y axis:

$$\begin{aligned} &\langle I_x\rangle=\langle I_z\rangle=0 \text{ for all eigenstates},\\ &\langle I_y\rangle_{\gamma\gamma}=-\langle I_y\rangle_{\beta\beta}=y/(1+y^2)^{1/2},\\ &\langle I_y\rangle_{\alpha\alpha}=0, \end{aligned}$$

where

$$y=2\gamma\hbar H_y/K(3-\eta). \tag{8}$$

The finiteness of certain $\langle I\rangle$ components given above is induced by the magnetic field in given directions, and signifies a removal of the dipolar field quenching. For a given spin which undergoes a transition from one eigenstate to another, a corresponding change in the static dipolar field will occur at the neighboring site of a different spin S. The coupling Hamiltonian between I and S is given by

$$\mathcal{H}_{IS}=\gamma_I\gamma_S\hbar^2r^{-3}[\mathbf{I}\cdot\mathbf{S}-3(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})r^{-2}], \tag{9}$$

where $\mathbf{r}$ is the vector distance between the two spins. If $|h_0|$ given by Eq. (3) is much larger than $|\mathcal{H}_{IS}|$, then $\mathcal{H}_{IS}$ may be regarded as a perturbation. With this assumption, each term of $|\mathcal{H}_{IS}|$ can be evaluated as products of matrix elements of S and I operators separately, in the diagonal representation of h_0. It is easily seen, therefore, how the effective magnetic dipole-dipole coupling between I and S is turned off or on, depending correspondingly upon whether H_0 is zero or finite. Of course, for $H_0=0$, or $H_0\approx h_s=\gamma_sS\hbar/r^3$, where h_s is the dipole field of spin S, the field h_s will remove the quenching to some extent. This intermediate case cannot be evaluated by the assumption of products of independent spin states.

V. EVALUATION OF SECOND MOMENTS

A knowledge of spin eigen and state functions is not explicitly required if the technique of diagonal sums is used to evaluate the second moment of the magnetic dipole-dipole interaction. The second moment of a symmetric line-shape function $f(\omega)$ centered at frequency ω_0, in the high-temperature approximation, is given by

$$\begin{aligned} M_2&=\int_{-\infty}^{\infty}d\omega(\omega-\omega_0)^2f(\omega)\\ &=-\mathrm{Tr}\{[\mathcal{H}_1',P]^2\}/\mathrm{Tr}\{P^2\}. \end{aligned} \tag{10}$$

This is the most general form for the trace evaluation of M_2. $\mathcal{H}_1'$ is that part of the total dipolar perturbation Hamiltonian $\mathcal{H}_1$ which commutes with the dominant

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[7] D. H. Smith and R. M. Cotts, J. Chem. Phys. **41**, 2403 (1964); P. A. Casabella and P. J. Bray, *ibid.* **28**, 1182 (1958).

zero-order Hamiltonian $\mathcal{H}_0$, where

$$\mathcal{H}_0=\sum_j h_{0j}+\sum_k h_{0k}, \tag{11}$$

$$\mathcal{H}_1=\sum_{j>k} h_{ik}, \tag{12}$$

with h_0 and h_{jk} given by Eqs. (3) and (9), respectively. The index k may pertain to a spin species different from the species referred to by index j; or in case of a single species, k pertains to a neighboring spin of j, and the sum over j and k is in pairs. The term h_{jk} is written as

$$\begin{aligned}h_{jk}=\gamma_j\gamma_k\hbar^2 r_{jk}^{-2}[&I_{xj}I_{xk}(1-3X_{jk}^2)\\&+I_{yj}I_{yk}(1-3Y_{jk}^2)+I_{zj}I_{zk}(1-3Z_{jk}^2)\\&+3(I_{xj}I_{yk}+I_{yj}I_{xk})X_{jk}Y_{jk}+3(I_{yj}I_{zk}+I_{zj}I_{yk})Y_{jk}Z_{jk}\\&+3(I_{zj}I_{xk}+I_{xj}I_{zk})Z_{jk}X_{jk}],\end{aligned} \tag{13}$$

where X_{jk}, Y_{jk}, and Z_{jk} are direction cosines of $\mathbf{r}_{jk}$. P is the sum of radiation spin operators $\sum_j I_{xj}$, $\sum_j I_{yj}$, or $\sum_j I_{zj}$ used to the extent that they connect pairs of eigenstates of h_{0j} that differ in energy by $\hbar\omega_0$.

Any term h_{jk} of Eq. (13) which commutes with $h_{0j}+h_{0k}$ in Eq. (11) will be denoted by h_{jk}'. Such a term will commute because

$$[h_{0j},h_{jk}']=[h_{0k},h_{jk}']=0, \tag{14}$$

or because

$$[h_{0j},h_{jk}']=-[h_{0k},h_{jk}']=\pm\hbar\omega_0 h_{jk}'. \tag{15}$$

Other noncommuting terms of h_{jk} are of course dropped because they would include spurious contributions to the second moment from higher order resonance lines not being measured. The condition (14) implies that h_{jk}' represents components of j and k spin orientation which cause static dipolar broadening. The condition (15) arises when energy is conserved for a mutual spin flip of j and k spin pairs, and therefore signifies a contribution to dynamic line broadening. Therefore, h_{jk}' connects eigenlevels of h_{0j} which differ in eigenfrequency by ω_0, and similarly for h_{0k}. The $+$ and $-$ signs signify that h_{jk}' acts for example as a raising operator for a j spin and a lowering operator for a k spin.

For any particular second moment calculation, the eigenstates of the dominant Hamiltonian must be examined. By rewriting the perturbation $\mathcal{H}_1$ in terms of proper linear combinations of operators, the pertinent h_{jk}' terms can be identified as the proper static or raising and lowering operators which must be retained in the calculation of M_2.

VI. SECOND MOMENT OF A SINGLE SPECIES $I=1$

Abragam and Kambe[8] have calculated the simplest case for nuclear quadrupole coupled nuclei of spin I with $\eta=0$ and $H_0=0$. In their result, as well as for other cases to follow in this paper, it is assumed that all sites of $I=1$ spins are equivalent with respect to electric field gradient and magnetic field axes, as viewed from the laboratory. We first rederive the second moment M_2 ($\eta=0$, $H_0=0$) for the simplest case because the form obtained for $\mathcal{H}_1'$ is needed for treating the less simple cases to follow. It is not logical to evaluate at first the most general result M_2 ($\eta\neq0$, $H_0\neq0$) because the most general useful form of $\mathcal{H}_1'$ reveals itself only for the $\eta=0$, $H_0=0$ case.

Case of $\eta=0$, $H_0=0$

When $\eta=0$ and $H_0=0$, Eq. (2) reveals a degeneracy ($E_\alpha=E_\beta$), and there is only one resonance line at $\hbar\omega=3K$. Now consider, for example, the first term $I_{xj}I_{xk}$ of the dipole-dipole Hamiltonian h_{jk} in Eq. (13). We would like to express it in terms of raising and lowering operators, and select those terms which satisfy Eq. (15). Obviously, $I_{xj}I_{xk}$ does not contribute static terms, according to Eq. (14), as seen from an inspection of the eigenstates [Eqs. (2)]. Making use of the commutation relations, one can write

$$\begin{aligned}I_{xj}I_{xk}=-I_{zj}I_{yj}I_{zk}I_{yk}-I_{yj}I_{zj}I_{yk}I_{zk}\\+I_{yj}I_{zj}I_{zk}I_{yk}+I_{zj}I_{yj}I_{yk}I_{zk}.\end{aligned} \tag{16}$$

The matrix algebra for a spin $I=1$ gives commutators

$$\begin{aligned}&[I_z^2,I_zI_y]=I_zI_y;\quad [I_z^2,I_yI_z]=-I_yI_z;\\&[I_z^2,I_zI_x]=I_zI_x;\quad \text{and}\quad [I_z^2,I_xI_z]=-I_xI_z,\end{aligned} \tag{17}$$

which are of the form given by Eq. (15). Consequently, in terms of the eigenstates of Eq. (2), I_yI_z lowers the state α to the state γ ($\alpha\rightarrow\gamma$), and I_zI_y raises the state γ to the state α ($\gamma\rightarrow\alpha$). Similarly, I_xI_z lowers β to γ($\beta\rightarrow\gamma$), and I_zI_x raises γ to β ($\gamma\rightarrow\beta$). Using Eq. (15) it is easily seen that h_{0j} does not commute with the first two terms of Eq. (16) because the j and k spins are both raised or lowered together in energy. The third and fourth terms are, however, products of raising and lowering operators and commute with $h_{0j}+h_{0k}$. Therefore, in truncating Eq. (16) we drop the first two terms and retain the last two terms as h_{jk}' terms. In this manner, the secular part of h_{jk} becomes

$$\begin{aligned}h_{jk}'=\gamma^2\hbar^2 r_{jk}^{-3}[&(I_{yj}I_{zj}I_{zk}I_{yk}+I_{zj}I_{yj}I_{yk}I_{zk})(1-3X_{jk}^2)\\&+(I_{xj}I_{zj}I_{zk}I_{xk}+I_{zj}I_{xj}I_{xk}I_{zk})(1-3Y_{jk}^2)\\&+I_{zj}I_{zk}(1-3Z_{jk}^2)+(I_{zj}I_{yj}I_{xk}I_{zk}+I_{yj}I_{zj}I_{zk}I_{xk}\\&+I_{xj}I_{zj}I_{zk}I_{yk}+I_{zj}I_{xj}I_{yk}I_{zk})(3X_{jk}Y_{jk})].\end{aligned} \tag{18}$$

The second moment of the line at $\hbar\omega_0=E_\alpha-E_\gamma$ [see Eqs. (2)] will be determined so that $P=\sum_j I_{xj}$ is the operator to be used in Eq. (10). This particular P only connects α with γ states. Therefore,

$$\begin{aligned}M_2(\eta=0,\ H_0=0)\\&=-\frac{\sum_{j>k}\mathrm{Tr}\{[h_{jk}',I_{xj}]^2\}}{\sum_j \mathrm{Tr}\{I_{xj}^2\}}\\&=\tfrac{1}{12}\gamma^4\hbar^4\sum_k r_{jk}^{-6}[8(1-3X_{jk}^2)^2+4(1-3Y_{jk}^2)^2\\&\quad+8(1-3Z_{jk}^2)^2-8(1-3Y_{jk}^2)(1-3Z_{jk}^2)\\&\quad+108X_{jk}^2Y_{jk}^2].\end{aligned} \tag{19}$$

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[8] A. Abragam and K. Kambe, Phys. Rev. **91**, 894 (1953).

With the fact that $X_{jk}^2+Y_{jk}^2+Z_{jk}^2=1$, this result is identical with that of Abragam and Kambe.[8] The second moment of the $\beta\rightleftarrows\gamma$ transition is evaluated if $P=\sum_j I_{yj}$ is used instead of $P=\sum_j I_{xj}$. This has the effect of interchanging X_{jk} and Y_{jk} in M_2 [Eq. (19)].

Case of $\eta\neq 0$, $H_0=0$

Referring to Eqs. (2), the degeneracy of the α and β levels is now removed for $\eta\neq 0$, $H_0=0$. There are three possible resonance lines, $\alpha\leftrightarrow\gamma$, $\beta\leftrightarrow\gamma$, and $\alpha\leftrightarrow\beta$. The first four terms of h_{jk}', Eq. (18), (operator coefficients of $1-3X_{jk}^2$ and $1-3Y_{jk}^2$) still commute with $h_{0j}+h_{0k}$, because these terms act as raising and lowering operators which conserve energy for transitions involving the same levels of j and k spins. However, a noncommuting term like $I_{zj}I_{yj}I_{xk}I_{zk}$ is dropped because it raises the jth spin from the state γ to α, and lowers the kth spin from the state β to γ, which does not permit energy conservation It is assumed that ηeqQ is sufficiently large compared to the dipolar broadening so that the transitions $\alpha\leftrightarrow\gamma$ and $\beta\leftrightarrow\gamma$ do not overlap. Since I_z is no longer diagonal, the $I_{zj}I_{zk}$ term in h_{jk}' now connects the states α and β. Now I_z can be decomposed into raising and lowering operators:

$$\begin{aligned} I_{z+}&=\tfrac{1}{2}I_z-\tfrac{1}{4}(I_+^2-I_-^2)\,,\\ I_{z-}&=\tfrac{1}{2}I_z+\tfrac{1}{4}(I_+^2-I_-^2)\,, \end{aligned} \tag{20}$$

where $I_\pm=I_x\pm iI_y$. The new operators I_{z+} and I_{z-} carry out the transitions $\beta\rightarrow\alpha$ and $\alpha\rightarrow\beta$, respectively. Use is made of Eq. (20) to make $I_{zj}I_{zk}$ function as a dynamic commutative term. Now that h_{jk}' of Eq. (18) will have missing from it the term in $X_{jk}Y_{jk}$, and using Eq. (10), the second moment of the $\alpha\leftrightarrow\gamma$ transition is

$$\begin{aligned} M_2(\eta\neq 0,\, H_0=0)=\tfrac{1}{12}\gamma^4\hbar^4\textstyle\sum_k r_{jk}^{-6}[&8(1-3X_{jk}^2)^2\\ &+4(1-3Y_{jk}^2)^2+4(1-3Z_{jk}^2)^2]. \end{aligned} \tag{21}$$

This result also gives M_2 for the $\beta\leftrightarrow\gamma$ transition if X_{jk} and Y_{jk} are interchanged, and gives the M_2 for the $\alpha\leftrightarrow\beta$ transition if X_{jk} and Z_{jk} are interchanged.

Case of $\eta=0$, $H_z\neq 0$

The energies and states of Eq. (3) are now

$$\begin{aligned} E_\alpha&=K+\gamma\hbar H_z\,, & \psi_\alpha&=u_{-1};\\ E_\beta&=K-\gamma\hbar H_z\,, & \psi_\beta&=u_{+1};\\ E_\gamma&=-2K\,, & \psi_\gamma&=u_0. \end{aligned} \tag{22}$$

It is assumed that H_z is much larger than the dipolar broadening so that the $\alpha\leftrightarrow\gamma$ and $\beta\leftrightarrow\gamma$ transitions cannot overlap. By examining the matrix elements of I_x and I_y in this case, it is advantageous to write them as

$$\begin{aligned} I_x&=\tfrac{1}{2}(I_zI_++I_-I_z-I_zI_--I_+I_z)\,,\\ I_y&=\frac{1}{2i}(I_zI_+-I_-I_z+I_zI_--I_+I_z)\,, \end{aligned} \tag{23}$$

where the binary operators connect states as follows:

$$I_zI_+:(\gamma\rightarrow\beta);\quad I_-I_z:(\beta\rightarrow\gamma);\quad I_zI_-:(\gamma\rightarrow\alpha)$$

and

$$I_+I_z:(\alpha\rightarrow\gamma)\,.$$

The dipole-dipole Hamiltonian [Eq. (13)] is rewritten in terms of the above operators, and the truncation procedure is carred out as outlined previously. Therefore,

$$\begin{aligned} h_{jk}'=\gamma^2\hbar^2r_{jk}^{-3}[&\tfrac{1}{4}(1-3X_{jk}^2)(I_{zj}I_{+j}I_{-k}I_{zk}\\ &+I_{-j}I_{zj}I_{zk}I_{+k}+I_{zj}I_{-j}I_{+k}I_{zk}+I_{+j}I_{zj}I_{zk}I_{-k})\\ &+\tfrac{1}{4}(1-3Y_{jk}^2)(I_{zj}I_{+j}I_{-k}I_{zk}+I_{+j}I_{zj}I_{zk}I_{-k}\\ &+I_{-j}I_{zj}I_{zk}I_{+k}+I_{zj}I_{-j}I_{+k}I_{zk})\\ &+(1-3Z_{jk}^2)I_{zj}I_{zk}]. \end{aligned} \tag{24}$$

The second moment expression of Eq. (10) for the $\alpha\leftrightarrow\gamma$ transition here will utilize $P=\sum_j I_{xj}'$, where $I_x'=\tfrac{1}{2}(I_+I_z-I_zI_-)$, as seen from Eq. (23). Therefore

$$M_2(\eta=0,\, H_z\neq 0)=(5/4)\gamma^4\hbar^4\textstyle\sum_k r_{jk}^{-6}(1-Z_{jk}^2)^2. \tag{25}$$

For a Zeeman interaction alone ($h_Q=0$) the coefficient 5/4 above is replaced by $\tfrac{3}{2}$, which shows that if the $\alpha\leftrightarrow\gamma$ and $\beta\leftrightarrow\gamma$ transitions are the same in frequency and therefore couple to one another, the extra dynamic broadening effect increases M_2 in Eq. (25) by a factor of 6/5.

Case of $\eta\neq 0$, $H_z\neq 0$

The eigenvalues and eigenfunctions for this case are given by Eqs. (4) and (6), respectively. The appropriate raising and lowering operators are

$$\begin{aligned} I_1&=-\tfrac{1}{2}I_+I_z+\tfrac{1}{2}AI_-I_z: && (\alpha\rightarrow\gamma);\\ I_2&=-\tfrac{1}{2}I_zI_-+\tfrac{1}{2}AI_zI_+: && (\gamma\rightarrow\alpha);\\ I_3&=\tfrac{1}{2}I_-I_z+\tfrac{1}{2}AI_+I_z: && (\beta\rightarrow\gamma);\\ I_4&=\tfrac{1}{2}I_zI_++\tfrac{1}{2}AI_zI_-; && (\gamma\rightarrow\beta);\\ I_{z+}&=\frac{1}{2(1+z^2)}\left[I_z-\frac{A}{2}I_+^2+\left(\frac{A}{2}+z\right)I_-^2\right]: && (\beta\rightarrow\alpha);\\ I_{z-}&=\frac{1}{2(1+z^2)}\left[I_z+\left(\frac{A}{2}+z\right)I_+^2-\frac{A}{2}I_-^2\right]: && (\alpha\rightarrow\beta). \end{aligned} \tag{26}$$

Relevant identities are given by

$$\begin{aligned} I_x&=\left(\frac{1+A}{1+A^2}\right)(I_1+I_2)+\left(\frac{1-A}{1+A^2}\right)(I_3+I_4)\,,\\ I_y&=\left(\frac{1+A}{1+A^2}\right)(I_4-I_3)+\left(\frac{1-A}{1+A^2}\right)(I_1-I_2)\,,\\ I_z&=I_{zs}+I_{z+}+I_{z-}\,, \end{aligned} \tag{27}$$

where

$$A=[(1+z^2)^{1/2}-z],\quad I_{zs}=\frac{z^2}{1+z^2}I_z-\frac{z}{2(1+z^2)}(I_+^2+I_-^2)\,,$$

and parameter z is defined by Eq. (5). I_{zs} is the part of I_z which commutes with $(h_Q-\gamma_I H_z I_z)$, and hence will make a static broadening contribution to the second moment. Selecting only secular terms of $\mathcal{H}_1$, Eq. (12), the truncated dipole-dipole pair interaction becomes

$$h_{jk}'=\frac{\gamma_I{}^2\hbar^2}{r_{jk}{}^2}\left\{(1-3X_{jk}{}^2)\left[\left(\frac{1+A}{1+A^2}\right)^2(I_{1j}I_{2k}+I_{2j}I_{ik})+\left(\frac{1-A}{1+A^2}\right)^2(I_{3j}I_{4k}+I_{4j}I_{3k})\right]\right.$$
$$+(1-3Y_{jk}{}^2)\left[\left(\frac{1+A}{1+A^2}\right)^2(I_{3j}I_{4k}+I_{4j}I_{3k})+\left(\frac{1-A}{1+A^2}\right)^2(I_{1j}I_{2k}+I_{2j}I_{1k})\right]$$
$$\left.+(1-3Z_{jk}{}^2)[I_{zsj}I_{zsk}+I_{z+j}I_{z-k}+I_{z-j}I_{z+k}]\right\}. \quad (28)$$

The part of I_x of Eq. (27) which connects the α and γ states is $[(1+A)/(1+A^2)](I_1+I_2)$, and therefore

$$P=\left(\frac{1+A}{1+A^2}\right)\sum_j(I_{1j}+I_{2j}). \quad (29)$$

One again takes the commutator of Eq. (29) with h_{jk}', Eq. (28), and follows the prescription of Eq. (10). The result is

$$M_2(\eta\neq0,H_z\neq0)=\frac{\gamma^4\hbar^4}{6(1+A^2)}\sum_k r_{jk}{}^{-6}\left\{(1+A^2)^{-1}[(1-3X_{jk}{}^2)(1+A)^2+(1-3Y_{jk}{}^2(1-A)^2]^2\right.$$
$$\times\frac{-8A^2z^2}{(1+A^2)^2}[(1-3X_{jk}{}^2)(1+A)^2+(1-3Y_{jk}{}^2)(1-A)^2](1-3Z_{jk}{}^2)$$
$$\left.+\frac{1}{2(1+A^2)}[(1-3X_{jk}{}^2)(1-A)^2+(1-3Y_{jk}{}^2)(1+A)^2]^2+\frac{2(1+A^2)(1+2z^4)}{(1+z^2)^2}(1-3Z_{jk}{}^2)^2\right\}. \quad (30)$$

Note that Eq. (30) reduces to Eq. (21) for $H_z\rightarrow0$, and reduces to Eq. (25) for $\eta\rightarrow0$. All of the results for M_2 so far have pertained to the $\alpha\leftrightarrow\gamma$ transition. Again, in this last case the appropriate permutations of the direction cosines in Eq. (30) must be made to give the M_2 expressions for the other two possible transitions.

It is interesting to compare the relative magnitudes of M_2 for the different cases obtained so far, except the last one which is too complex to consider. Arbitrary expressions for M_2 are computed by performing lattice sums over the k spins for a simple cubic lattice, assuming, unrealistically of course, that a spin j has a quadrupole interaction at a noncubic site. With d as the lattice spacing,

$$M_2(\eta=0,\ H_0=0)=28.4\gamma^4\hbar^4d^{-6},$$
$$M_2(\eta\neq0,\ H_0=0)=17.8\gamma^4\hbar^4d^{-6},$$
$$M_2(\eta=0,\ H_0=0)=16.7\gamma^4\hbar^4d^{-6},$$

and

$$M_2(K=0,\ H_0=0)=20.0\gamma^4\hbar^4d^{-6}.$$

The most significant difference occurs between the first two M_2 values above, which shows how the line narrows because of partial spin quenching when $\eta\neq0$. The quenching can never be complete because the dynamic broadening mechanism is always present among like spins. It can be nearly complete in the cases considered next where the line broadening due to unlike spins is considered.

Second-Moment Interaction between $I=1$ and $S=\frac{1}{2}$ Species ($\eta\neq0$, $H_0\neq0$)

The most important case of dipolar field quenching occurs between unlike I and S species, where the I spins now sum over the j index, and the S spins sum over the k index. The difference in resonance frequencies of the two species is taken to be extremely large compared to the linewidths. From the expression h_{jk}' given in Eq. (28), only the static terms apply here, so that

$$h_{jk}'=\gamma_I\gamma_S\hbar^2r_{jk}{}^{-3}(1-3Z_{jk}{}^2)$$
$$\times\left[\frac{z^2}{1+z^2}I_{zj}-\frac{z}{2(1+z^2)}(I_{+j}{}^2+I_{-j}{}^2)\right]S_{zk}. \quad (31)$$

And using $P=\sum_j I_{xj}'$, the same as used for M_2 ($\eta\neq0$, $H_z\neq0$) previously, the contribution of the S spins to the second moment of the I spins is

$$M_2(I)_S=\tfrac{1}{4}\gamma_I{}^2\gamma_S{}^2\hbar^4\frac{z^2}{1+z^2}\sum_k r_{jk}{}^{-6}(1-3Z_{jk}{}^2)^2. \quad (32)$$

To find the contribution of the I spins to the second moment of the S spins, one uses $P=\sum_k S_{xk}$, which gives

$$M_2(S)_I=\tfrac{2}{3}\gamma_I^2\gamma_S^2\hbar^4\frac{z^2}{1+z^2}\sum_j r_{jk}^{-6}(1-3Z_{jk}^2)^2. \quad (33)$$

If the magnetic field is applied along the x or the y axes, then the parameters z and Z_{jk} are replaced by x and X_{jk}, or by y and Y_{jk} respectively. We do not treat any case where H_z is varied for a given spin polarization due to a fixed H_x or H_y.

The expressions (32) and (33) are almost identical to those obtained by Van Vleck for the second-moment contribution to a magnetic resonance line by unlike spins. The only difference here is the factor $z^2/(1+z^2)$, where $z=\gamma_I\hbar H_z/K\eta$. The first-order calculation shows that the second-moment contribution disappears as $H_z\rightarrow 0$. In second order the local dipolar field of the S spins themselves would play the role of unquenching, similar to the effect of H_z. A second-order calculation might plausibly express z^2 as $z^2=(\gamma_I\hbar/K\eta)^2(H_z^2+H_L^2)$, where H_L^2 is some expression of the mean square local field. A fourth-moment calculation not carried out here may or may not show an entirely different behavior from that of the second moment. We cannot make any assertions about its variation because of dipolar field quenching, as H_z is varied.

VII. EXPERIMENTAL EVIDENCE OF SPIN QUENCHING

A thorough and rigorous experimental study of the spin-quenching effect remains to be carried out. The effect is strikingly shown by the double resonance spin-echo study of Cl^{35} coupling with D in $Ba(ClO_3)_2\cdot D_2O$. Although the Cl^{35} nucleus has spin $\frac{3}{2}$, it qualitatively plays the role of $S=\frac{1}{2}$, in the cases of Eqs. (32) and (33), because the transitions $\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ are very similar to those of the two level $S=\frac{1}{2}$ case. The Cl^{35} echo amplitude E_0 is observed in a two pulse 90–180° echo experiment in the absence of double resonance. If the D nuclear quadrupole transition is excited by a 180° pulse during the time of the 180° Cl^{35} pulse, the Cl^{35} echo amplitude E_{DR} is measurably reduced only if a magnetic field H_0 is applied to the sample. As H_0 is reduced in magnitude the echo amplitude change E_0-E_{DR} reduces toward zero, as seen in Fig. 1.

The model which explains the spin-echo double resonance effect has been discussed previously.[9] The local dipolar fields at Cl^{35} sites are made up in part by the contribution of D nuclei. A maximum Cl^{35} spin echo can be obtained as long as the local fields remain essentially static within the time 2τ of echo formation, where τ is the time between 90° and 180° pulses. If the D nuclear spins are inverted at time τ by a 180° pulse, their local-field contributions at Cl^{35} sites become scrambled and the Cl^{35} echo amplitude is correspondingly reduced. Let the normal echo from the S spins (Cl^{35}) be expressed as

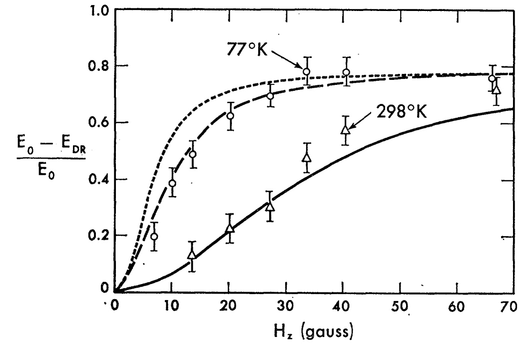

FIG. 1. Deuterium double resonance effect for spin-echo double resonance in $Ba(ClO_3)_2\cdot D_2O$ as a function of applied magnetic field H_z. Data points are from Ref. 10 (C. J. Gabriel, thesis). Curves are theoretical expectations as explained in the text.

$$E_0=e^{-C\langle\Delta\omega^2\rangle\tau^2}, \quad (34)$$

where C is a constant of order unity, and $\langle\Delta\omega^2\rangle$ is the second moment of the S spins due to *all* species of nuclear neighbors. When a 180° pulse is applied to the I spins (D), the echo signal is

$$E_{\mathrm{DR}}=\exp[-C(\langle\Delta\omega^2\rangle+\langle\Delta\omega_{IS}^2\rangle)\tau^2], \quad (35)$$

where $\langle\Delta\omega_{IS}^2\rangle\approx M_2(\eta\neq 0, H_z\neq 0)$ of Eq. (32) is the contribution of I spins to the second moment of the S spins. Using Eqs. (34) and (35) one obtains

$$(E_0-E_{\mathrm{DR}})/E_0=1-e^{-Sz^2/(1+z^2)}, \quad (36)$$

where

$$S=\tfrac{2}{3}C\tau^2\gamma_I^2\gamma_S^2\hbar^4\sum_j r_{jk}^{-6}(1-3Z_{jk}^2)^2.$$

The parameter S can be determined experimentally from the maximum double-resonance effect in high magnetic field ($H_0\sim 50$ G), when $z\gg 1$. The theoretical expression Eq. (36) can then be plotted for various values of z or H_z. All three plots in Fig. 1 use a value of $S=1.514$, obtained from the data at 77°K, which is determined by $1-e^{-S}=0.78=(E_0-E_{\mathrm{DR}})/E_0$. For single-crystal $BaClO_3\cdot D_2O$, nuclear quadrupole resonance measurements yield $\eta=0.091$, $K=61.8$ kc/sec, at 77°K; and $\eta=0.98$, $K=30.6$ kc/sec at 298°K. All the data in Fig. 1 were taken with the magnetic field H_0 perpendicular to the 180° symmetry axis of the D_2O molecules, and nearly, but not quite, parallel to the D-D direction. The maximum electric field gradient (z direction) is along the O-D direction, and therefore there was an angle of about 45° between the z direction and H_0. Thus $H_z\simeq 0.7H_0$ at 77°K. H_x was also about the same size, but can be safely ignored, because the denominator in x [Eq. (7)] is about 16 times larger than that in z [Eq. (5)]. The D_2O molecule is static at 77°K, but at 298°K it undergoes a

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[9] M. Emschwiller, E. L. Hahn, and D. E. Kaplan, Phys. Rev. **118**, 414 (1960).

hindered rotation[10] about the 180° symmetry axis which does some averaging of the electric field gradient. In this case the direction of maximum field gradient is along the D-D direction.[10] Since H_0 is nearly along this direction, H_x and H_y are small and shall be ignored. Two theoretical curves are plotted for 77°K: one with $H_z=H_0$ (short-dashed curve), and one with $H_z=0.7H_0$ (long dashes). The obvious preference for the latter shows that it is the component of field along the direction of maximum field gradient that is lifting the quenching, and not the total applied magnetic field. For H_z fields below 40 G, the transverse field components H_y and H_x yield parameters $y^2/(1+y^2)$ and $x^2/(1+x^2)$ [Eqs. (8) and (7)] which are negligibly small. In the region of $H_z\sim40$ to 50 G, agreement of the 298°K data with Eq. (36) is not good. This may be possible with $\eta\approx1$, and with some H_x and H_y present, because then the parameters involving y and x should not be neglected.

Our second-moment calculations indicate that the deuterium double-resonance line (interpreted in terms of the Cl^{35} echo amplitude versus deuterium NQR frequency ν) should be anomalously narrow. In fact the observed lines are anomalously broad ($\Delta\nu\sim10$ kc/sec). The source of this broadening is attributed to the presence of a 10% dilution of the deuterium by protons in our sample. The protons, having a different mass, have a thermal-vibration spectrum different from the deuterium nuclei. The random-site proton distribution will alter the temperature-dependent electric field gradient[11] at various deuterium sites, and a broadening of the line results, similar to crystal-field strain broadening. The broadening at 77°K is observed to diminish at 20°K, but it does not disappear because the zero-point motion is mass-dependent.

VIII. CONCLUSIONS

In pure nuclear quadrupole resonance the dipolar coupling of integer spin nuclei to neighboring like and unlike spins is reduced or quenched if the quadrupole interaction is significantly asymmetric. If the energy W_Q of the asymmetric component of quadrupole interaction exceeds by a large margin any nuclear magnetic interaction energy W_H, the dipolar field of the integer spin is effectively quenched for coupling to unlike spins, and partially reduced for coupling to like spins. These effects are shown by linewidth second moment calculations and by spin-echo measurements of the coupling among unlike spins. The usual second moment is reduced by a factor $(2W_H/W_Q)^2/[1+(2W_H/W_Q)^2]$ for coupling to unlike nuclei of half-integer spin. In the limit of a high externally applied field H, where $2W_H/W_Q\gg1$, the dipolar interaction is fully restored.

With a quadrupole asymmetry parameter of appropriate size, the quenching effect should make possible the high-resolution NQR spectroscopy of integer spin nuclei. The variation of line broadening as a function of external and internal magnetic fields is a behavior which should yield additional information about the asymmetry of internal crystalline fields. With these features, the D^2 and N^{14} nuclei with $I=1$ are particularly attractive for NQR studies of organic compounds. At low temperatures particularly, where NQR spin-lattice relaxation times are long, any measurable magnetic spin-lattice relaxation rate should also be quenched for asymmetry field coupled integer spins. The relaxation rates should be restored in the limit of high applied magnetic field.

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[10] T. Chiba, J. Chem. Phys. **39**, 947 (1963); C. J. Gabriel, thesis, University of California (unpublished).

[11] H. Bayer, Z. Physik **130**, 227 (1951).