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Diffusion of spin order in inhomogeneous systems

P. A. Fedders
Department of Physics, Washington University, St. Louis, Missouri 63130
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We derive equations for the transport or diffusion of Zeeman and of quadrupolar order among spin-1 particles whose difference in resonant frequencies (frequency offset) is much greater than the interspin dipolar interaction. Our results are exact in many cases. The mechanism is an extension of one applied earlier to spin-$\frac{1}{2}$ systems and depends on the existence of transverse spin fluctuations from an independent source, such as phonons or another reservoir of spins. Our exact results are qualitatively similar to but quantitatively different from results obtained by other investigators. The reasons for this difference as well as applications of our results to problems of current interest involving the spin diffusion among deuterium atoms in a-Si:H and in solid HD (or DT) are discussed.

I. INTRODUCTION

The term "spin diffusion" is used to denote the transport of spin order in solid nuclear spin systems. Usually the spin order is transported by the dipolar mediated flip-flop process whereby one spin flips up and a neighboring spin flips down. This process is effective when the spins are degenerate or nearly degenerate in that the difference between their resonant frequencies is less than or of order of the dipolar frequency. Thus the process is consistent with at least an approximate conservation of Zeeman energy.

In an earlier paper[1] (hereafter I) we considered a mechanism for spin diffusion when the spread of resonant frequencies is large compared to the dipolar frequency or bandwidth and thus the mechanism described in the preceding paragraph cannot operate. The paper derived equations for a spin $S=\frac{1}{2}$ system and discussed various applications. In part, it is the purpose of this paper to generalize the results of I to $S=1$ systems. This is a vital step because quadrupolar effects in general and quadrupolar effects on deuterium ($S=1$) are very important in many amorphous and/or glassy systems. In fact, the effect has been unequivocally observed in such a system.[2] Further, several restrictions were made concerning the nature of the transverse spin fluctuations which drive the spin diffusion. These restrictions for $S=\frac{1}{2}$ are partially removed in this paper. Reporting on independent work a paper by Suter and Ernst[3] (SE) addressed the same problem. A number of the results of SE are similar to, but different from, the exact results of this present paper for $S=1$. Thus we also wish to discuss this discrepancy.

In the rest of this section we shall discuss the basic idea of the calculation and some relevant notation. Section II contains an exact calculation for the transfer of Zeeman and of quadrupolar order between two $S=1$ spins feeling different electric field gradients and undergoing restrictive transverse fluctuations. These restrictions for $S=\frac{1}{2}$ are partially lifted in Sec. III. Section IV contains a comparison of our results to SE and examples containing calculations of the transverse fluctuations.

The basic idea behind our calculations is that the transfer of Zeeman or quadrupolar order between two spins can be driven by the transverse or T_2-like fluctuations of one or both of those spins in conjunction with the I_zS_z term in the dipolar Hamiltonian connecting these two spins. The mechanism is related to the mechanism causing the decay of the longitudinal magnetization of nuclear spins due to paramagnetic impurities. This process is, of course, much slower than the dipolar mediated flip-flop process. The transverse fluctuations can be caused by phonons, an independent reservoir of spins, or some other mechanism, and although the fluctuations are easiest to analyze if they are described by a Lorentzian shape, this is not a necessary condition. In any case, if these fluctuations are driven by some agency that operates independent of the two spins themselves and is also characterized by single relaxation rates, then exact equations describing the diffusion can be derived. This is a fundamental restriction that will limit most of this paper. Within this restriction, the problem divides itself into two parts. The first part, which this paper is mainly concerned with, is a derivation of the transport equations in terms of the transverse fluctuations. The second part, which will be addressed briefly in Sec. IV, is a derivation of the appropriate transverse fluctuations.

We note that the problem under consideration is closely connected to the problem of cross relaxation between different spin systems.[4-6] Although our results do not rigorously apply to this situation, they are relevant to an analysis of it. This will be discussed in Sec. III. Finally, we note that we are only concerned with single-quantum flips in this paper and do not consider higher-order multiple-quantum flips.[3]

In the rest of this paper we will be discussing Zeeman and quadrupolar order and various associated operators and relaxation rates. This will necessarily bring in operator combinations that are most conveniently expressed in terms of the irreducible multipole operators[7] A_{lm}. We will also need relaxation rates corresponding to these operators. It will be our convention to use the following notation for the decay rates:

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$$\begin{aligned} &\Gamma_{1d} \text{ for } l=1,\ m=0\ ,\\ &\Gamma_{2d} \text{ for } l=1,\ m=\pm 1\ ,\\ &\Gamma_{1q} \text{ for } l=2,\ m=0\ ,\\ &\Gamma_{2q} \text{ for } l=2,\ m=\pm 1\ , \end{aligned} \tag{1}$$

where d connotes dipolar and q connotes quadrupolar. Thus Γ_{1d} and Γ_{2d} correspond to T_1^{-1} and T_2^{-1}, respectively, and Γ_{1q} is the decay rate for quadrupolar order.

II. ONE PAIR

In this section we consider a single pair of $S=\frac{1}{2}$ or $S=1$ particles interacting with each other via the truncated dipolar Hamiltonian

$$\begin{aligned} H_d = \hbar\omega_d\{ & S_z(1)S_z(2) \\ & -\tfrac{1}{4}[S_+(1)S_-(2)+S_-(1)S_+(2)]\}\ , \end{aligned} \tag{2}$$

where $S_\alpha(i)$ is the α component of the spin operator at the site i. Further,

$$\omega_d=\omega_d(1,2)=\gamma^2\hbar(1-3\cos^2\theta_{12})/r_{12}^3\ , \tag{3}$$

where the two spins are separated by a distance r_{12} and θ_{12} is the angle that $\mathbf{r}_{12}$ makes with an external magnetic field that defines the z direction. In addition, for the $S=\frac{1}{2}$ case, we include a site-dependent Zeeman interaction,

$$H_0=-\sum_i \hbar\omega_0(i)S_z(i)\ . \tag{4}$$

For the $S=1$ case we assume a uniform Zeeman and a site-dependent quadrupole term

$$H_0=-\sum_i \{\hbar\omega_0 S_z(i)-\hbar\omega_q(i)[S_z^2(i)-\tfrac{2}{3}]\}\ . \tag{5}$$

We shall assume that the frequency offset $\omega_0(1)-\omega_0(2)$, $\omega_q(1)-\omega_q(2)$ or the combination is large compared to $\omega_d(1,2)$. Finally, we assume the existence of constant relaxation rates for any of the spin operators at sites 1 or 2. Thus the equation of motion for any spin operator $A_\alpha(i)$ is

$$[\partial A_\alpha(i)/\partial t]=(i\hbar)^{-1}[(H_0+H_d),A_\alpha(i)]-\Gamma_\alpha(i)A_\alpha(i)\ , \tag{6}$$

where α is a (collective) multipole index (l,m). Note that any of the relaxation rates $\Gamma_\alpha(i)$ may be zero.

The equations of motion for all of the spin operators can be solved exactly simply because there are only a finite number of operator combinations that can occur. For example, in the $S=\frac{1}{2}$ case, the operator equations for $S_z(1)$, $S_z(2)$, $S_+(1)S_-(2)$, and $S_-(1)S_+(2)$ form a closed set.[1] In what follows it is convenient to solve the equations as an eigenvalue problem by assuming that the operators evolve in time as $\exp(-\lambda t)$. The eigenvalues λ thus yield the decay or transfer rates. Alternatively, this can be viewed as Laplace transforming all of the equations. Although one can now obtain exact solutions, the equations are rather cumbersome unless some further approximation is made. Thus we assume that λ is small compared to the frequency offset between $S(1)$ and $S(2)$. This introduces a relative error of order ω_d squared divided by the frequency offset squared, and it is our assumption that this quantity is small.

This problem was solved for the $S=\frac{1}{2}$ case in I and the solution can be written as

$$[\lambda-\Gamma_{1d}(i)]S_z(i)=\omega_d(i,j)[S_z(i)-S_z(j)]g_{ij}(\omega_q(i,j))/8\ , \tag{7a}$$

$$g_{ij}(\omega)=\Gamma_{2d}(i,j)/\{\omega^2+[\Gamma_{2d}(i,j)]^2\}\ , \tag{7b}$$

where

$$\begin{aligned} &\omega_q(i,j)=\omega_0(i)-\omega_o(j)\ ,\\ &\Gamma_{2d}(i,j)=\Gamma_{2d}(i)+\Gamma_{2d}(j)\ . \end{aligned} \tag{8}$$

For $S=1$ the equations of motion can again be solved exactly, but the algebra is more formidable. In this case the equation for $S_z(i)$ can be written as

$$[\lambda-\Gamma_{1d}(i)]S_z(i)=[\omega_d^2(i,j)/3D(i,j)][S_z(i)-S_z(j)][\Gamma_b(i,j)\Gamma_c(i,j)\Gamma_d(i,j)+\omega_q^2(i)\Gamma_b(i,j)+\omega_q^2(j)\Gamma_c(i,j)]\ , \tag{9}$$

where

$$\begin{aligned} D(i,j)=&[\omega_q^2(i)-\omega_q^2(j)]^2+\omega_q^2(i)[\Gamma_a(i,j)\Gamma_b(i,j)+\Gamma_c(i,j)\Gamma_d(i,j)]\\ &+\omega_q^2(j)[\Gamma_a(i,j)\Gamma_c(i,j)+\Gamma_b(i,j)\Gamma_d(i,j)]+\Gamma_a(i,j)\Gamma_b(i,j)\Gamma_c(i,j)\Gamma_d(i,j) \end{aligned} \tag{10}$$

and

$$\Gamma_a(i,j)=\Gamma_{2d}(i)+\Gamma_{2d}(j),\quad \Gamma_b(i,j)=\Gamma_c(j,i)=\Gamma_{2q}(i)+\Gamma_{2d}(j),\quad \Gamma_d(i,j)=\Gamma_{2q}(i)+\Gamma_{2q}(j)\ . \tag{11}$$

These equations are more complicated than one might have hoped. If we assume that the ω_q's are much greater than the decay rates Γ, and further assume that the decay rates for spin 1 and spin 2 are the same, then Eq. (9) reduces to

$$(\lambda-\Gamma_{1d})S_z(i)=\omega_d^2(i,j)[S_z(i)-S_z(j)](\Gamma_{2d}+\Gamma_{2q})[\omega_q^2(i)+\omega_q^2(j)]/\{3[\omega_q^2(i)-\omega_q^2(j)]^2\}\ . \tag{9'}$$

Similarly, the equations of motion for the quadrupolar order $Q_z(i)$,

$$Q_z(i)=S_z^2(i)-\tfrac{2}{3}\ , \tag{12}$$

can be obtained. The result is

$$[\lambda-\Gamma_{1q}(i)]Q_z(i)=\omega_d^2(i,j)(Q_z(i)[\Gamma_a(i,j)\Gamma_c(i,j)\Gamma_d(i,j)+\Gamma_a(i,j)\omega_q^2(i)+\Gamma_d(i,j)\omega_q^2(j)] + Q_z(j)\{[\Gamma_a(i,j)+\Gamma_d(i,j)]\omega_q(i)\omega_q(j)\})/D(i,j)\ . \tag{13}$$

If we make the same assumptions that lead up to Eq. (9′), and also assume that $\Gamma_d=\Gamma_a$, then Eq. (13) simplifies to

$$(\lambda-\Gamma_{1q})Q_z(i)=[\omega_d^2(i,j)/2]\Gamma_a(\{[Q_z(i)-Q_z(j)]/[\omega_q(i)-\omega_q(j)]^2\}+\{[Q_z(i)+Q_z(j)]/[\omega_q(i)+\omega_q(j)]^2\})\ . \tag{13′}$$

The process that we are considering conserves magnetization, and thus the right-hand sides of Eqs. (7a) and (9) are proportional to $S_z(i)-S_z(j)$. However, quadrupolar order decays as well as diffuses by this process since the truncated dipolar Hamiltonian does not commute with the sum of $Q_z(i)$ over sites. Thus Eq. (13) or (13′) contains a term proportional to $Q_z(i)+Q_z(j)$ as well as the expected term proportional to $Q_z(i)-Q_z(j)$.

Although the above equations are exact within their range of validity, they do not in themselves constitute a solution to a given physical problem even if the relaxation rates are known. For example in Ref. 1, the results for $S=\frac{1}{2}$ were used to obtain the solution to problems where only "relaxation centers" possessed nonzero relaxation rates. Solving the equations is much easier in systems with a regular lattice of spins.

III. EXTENSIONS

In this section we shall lift several of the restrictions that apply to the calculations of Sec. II. First consider the restriction that only a pair of spins be considered. The obvious generalization is that each spin can interact with every other spin pairwise. Indeed, when this is done, the right-hand sides of Eqs. (7), (9), (9′), (13), and (13′) are replaced by sums over all terms $j\neq i$. There is another less trivial modification that can be made that describes the transport of spin from site 1 to site 3 via an intermediary site 2. This mechanism was investigated in I and was found to be quite small. Thus, the approximation of including only pairwise interactions is an excellent one.

Until now we have assumed that the transverse spin fluctuations are driven by some agency external to the spins themselves and can be described by a single relaxation rate. That is if there were no inhomogeneous broadening, the relevant line shape would be Lorentzian in frequency space. This will often be appropriate for discussing a set of spins with a broad inhomogeneous distribution of Zeeman or quadrupolar frequencies along with strong interactions with an independent spin reservoir or phonons. In the case of $S=\frac{1}{2}$ the assumption about the Lorentzian line shape can be relaxed.

In general, one can define a set of two-point spin correlation functions[8] $G_\alpha(i,j;t)$ that describe all of the spin fluctuations in a system,

$$G_\alpha(i,j;t)=\langle A_\alpha(i,t)A_\alpha^\dagger(j,0)\rangle\Theta(t)\ , \tag{14}$$

where $A_\alpha(i,t)$ is the irreducible multipole operator with $\alpha=(l,m)$ at the site i and the time t in the Heisenberg representation. The angular brackets $\langle\ \rangle$ denote the thermal average of the enclosed operators and $\Theta(t)$ is the step function. Since we are considering fluctuations induced by some mechanism independent of the spins themselves, the correlation functions are site diagonal,

$$G_\alpha(i,j;t)=G_\alpha(i,t)\delta_{ij}\ . \tag{15}$$

It is further convenient to Fourier transform $G_\alpha(i,t)$ in time to obtain the frequency-dependent correlation function $G_\alpha(i,\omega)$. Finally, it is useful to express $G_\alpha(i,\omega)$ in terms of a self-energy[8–10] or memory function $\Sigma_\alpha(i,\omega)$,

$$G_\alpha(i,\omega)=i/[\omega-\omega_\alpha(i)-\Sigma_\alpha(i,\omega)]\ , \tag{16}$$

where $\omega_\alpha(i)$ is the resonant frequency for the mode α. If α corresponds to $l=1,m$, then $\omega_\alpha(t)$ is $m\omega_0(i)$. The self-energy is usually expressed in terms of a real and imaginary part

$$\begin{aligned}\Sigma_\alpha(i,\omega)&=\Pi_\alpha(i,\omega)-i\Gamma_\alpha(i,\omega)\\&=\pi^{-1}\int_{-\infty}^{\infty}d\bar{\omega}\,\Gamma_\alpha(i,\omega')/(\omega-\omega'+i\delta)\ ,\end{aligned} \tag{17}$$

where $\delta\rightarrow 0^+$. The line-shape or spectral function for the operator α is given by

$$g_\alpha(i,\omega-\omega_\alpha(i))=\mathrm{Im}G_0(i,\omega)=\frac{\Gamma_\alpha(i,\omega)}{[\omega-\omega_\alpha(i)-\Pi_\alpha(i,\omega)]^2+[\Gamma_\alpha(i,\omega)]^2}\ , \tag{18}$$

since under the assumptions made above, $G_\alpha(i,\omega)$ and $\Sigma_\alpha(i,\omega)$ are functions of $\omega-\omega_\alpha(i)$. Note that both Lorentzian and Gaussian-like line shapes are easily accommodated by Eqs. (16)–(18). For a Lorentzian line shape $\Pi_\alpha(i,\omega)$ is zero and $\Gamma_\alpha(i,\omega)$ is a constant. For a Gaussian-like line shape $\Gamma_\alpha(i,\omega)$ is a function that falls off exponentially in $[\omega-\omega_0(i)]^2$.

The equation of motion of $S_z(i,t)$ involves operator pairs such as $S_+(i,t)S_-(j,t)$ and $S_+(j,t)S_-(i,t)$. If we still assume that the transverse fluctuations on i and j are independent (but not necessarily Lorentzian) then each can be described by independent spectral functions. Further, a product of functions in t space becomes a convolution in frequency space and thus Eq. (7) becomes

$$[\lambda-i\Gamma_{1d}(i)]S_z(i)=\omega_d^2(i,j)[S_z(i)-S_z(j)]g_{ij}[\omega_q(i,j)]/8\ , \tag{19}$$

where $\omega_q(i,j)=\omega_0(i)-\omega_0(j)$ and

$$g_{ij}(\omega_q)=\pi^{-1}\int_{-\infty}^{\infty}d\omega\, g_+(\omega-\omega_q)g_+(\omega)\ , \tag{20}$$

and $g_+(i,\omega)$ is the spectral function for $S_+(i)$.

Equation (20) is not a surprising result since it is similar to results obtained by several other authors in investigating cross relaxation between different spin reservoirs.[4-6,11,12] However, the numerical factors and the specific convolution derived here quite rigorously are different in detail from other treatments. The result given by Eqs. (19) and (20) is probably a pretty good approximation even if the spins fluctuating on sites i and j are not independent of each other since the fluctuations are usually correlated only to order $1/z$ where z is the coordination number. So far we have not been successful in deriving similar equations for $S=1$. Perhaps this is not too surprising when one compares the complexity of Eqs. (9) and (13) for $S=1$ with the much simpler Eq. (7) for $S=\frac{1}{2}$.

IV. DISCUSSION

In the last two sections we have derived equations for the transfer of Zeeman or quadrupolar order in inhomogeneous $S=\frac{1}{2}$ or $S=1$ spin systems. A knowledge of the transverse fluctuations (or decay mechanisms) of the spins involved is necessary in order to use these results, and that is the main topic of this section. However, first we wish to discuss our results with respect to the results of SE. Before we begin this we wish to point out that the difference between our results and the results of SE are primarily quantitative and not qualitative. Further, there are a number of cases included in SE that we have not considered.

The approximations made in SE between Eqs. (11) and (13) are similar to approximations made by other investigators, but they are nevertheless virtually impossible to characterize and, to our knowledge, are not exact in any limiting case. Thus we shall focus our discussion on the difference between their results and our results which are exact in at least some cases. We first consider the case of two $S=\frac{1}{2}$ spins in the presence of abundant I spins and form an equation for W_z, the transition rate for the transfer of spin between two spins,

$$d[S_z(1)-S_z(2)]/dt=-W_z[S_z(1)-S_z(2)]\ . \tag{21}$$

Our results from Eq. (7) and the results of SE from Eqs. (26) or (36) can be written

$$W_z=-[\omega_d(1,2)/2]^2g_{12}(\omega_q)\ , \tag{22}$$

where $g_{12}(\omega)$ is the "appropriate line-shape function" and ω_q is the frequency offset. The question of what the appropriate line-shape function is, however, is not a trivial question. Our results given by Eqs. (7b) and (20) are exact within their range of validity and relate g_{12} to the more familiar transverse fluctuation spectra. Equation (25) in SE is correct but cannot be related easily to more standard relaxation functions, and Eq. (32) in SE is inconsistent with our Eq. (20).

Next consider the case of spectral diffusion between two $S=1$ spins in the presence of abundant I spins. For two spins and constant relaxation rates we obtain the exact transfer rate

$$W_z=\{2[\omega_d(1,2)]^2/3D(1,2)\}[\Gamma_b(1,2)\Gamma_c(1,2)\Gamma_d(1,2)+\omega_q^2(1)\Gamma_b(1,2)+\omega_q^2(2)\Gamma_c(1,2)]\ , \tag{23}$$

where $D(1,2)$ is given by Eq. (10). On the other hand, using approximate solutions, SE obtain that the transfer of spin between two spins depends on a number of different rates:

$$W_z^{(23)}=\omega_d^2g^{(23)}(\delta_q)\ , \tag{46SE}$$

$$W_z^{(456)}=\tfrac{1}{2}\omega_d^2g^{(456)}(\sigma_q)\ , \tag{53SE}$$

$$W_z^{(46)}=\omega_d^2g^{(46)}(0)/\sigma_q^2\ , \tag{56SE}$$

$$\left.\begin{aligned}\sigma_q&=\omega_q(1)+\omega_q(2)\ ,\\ \delta_q&=\omega_q(1)-\omega_q(2)\ .\end{aligned}\right. \tag{44SE}$$

These results are quite different than ours. However, we both predict a diffusion rate that is proportional to the inverse square of a frequency offset.

There are at least two interesting and technologically important systems where spin diffusion among deuterium nuclear spins is important but is unlikely to occur directly because large random electric field gradients produce quadrupole splittings that are large compared to the relatively weak dipolar coupling between deuterium nuclear spins. One of these systems is solid DT (deuterium tritum) where spin diffusion among the T and D nuclear spins is vital if nuclear polarization of the targets is to be affected. This is an important objective in the laser fusion program, and experiments indicate that it is very difficult to polarize D. The other case is hydrogenated amorphous Si (a-Si:H) which is often deuterated in order to yield more information about the environment of the bonded H. However, in both of these systems spin diffusion can proceed via the H or T intermediary. Thus they fall into the category of spectral diffusion between $S=1$ spins in the presence of abundant $I=\frac{1}{2}$ spins where the S spins are D and the I spins are H or T.

In what follows we let $\omega_d(I,I)$, $\omega_d(S,S)$, and $\omega_d(I,S)$ be the magnitudes of the I-I, S-S, and I-S dipolar interactions, respectively. Since the magnetic moment of the proton or triton is considerably greater than the magnetic moment of the deuteron, we have that

$$\omega_d(I,I) \gg \omega(I,S) \gg \omega(S,S) \ . \tag{24}$$

Because of this the fluctuations of the I spins are almost entirely caused by the other I spins and not by the S spins. Thus the transverse fluctuations of the S spins are driven by the I spins, which is an agency independent of the S spins themselves. The size of these S-spin fluctuations can be crudely estimated by taking the square of the I-S coupling constant times the spectral function for the I-I spins. This yields a rate r

$$r \sim \omega_d(I,S)^2\omega_d(I,I) \sim \omega(S,s) \ . \tag{25}$$

The transverse line-shape functions ($l=2,1$; $m=+1$) for the S spins will now be calculated in terms of the correlation functions of the I spins. The Hamiltonian connects the I and S spin systems in the full dipolar Hamiltonian. However, we shall assume that the Lamor frequencies for the I and S spins, $\omega_0(I)$ and $\omega_0(S)$, respectively, are both much greater than $\omega_d(I,I)$. In this case the only secular part of the interaction Hamiltonian is the I_zS_z part. We now use the bubble[9] or Blume-Hubbard[10] approximation in order to obtain an equation for $\Gamma_\alpha(i,\omega)$ [see Eqs. (16) and (17)] for the S spins. In this case Γ_α stands for either the $l=1$, $m=+1$ mode or the $l=2$, $m=\pm 1$ mode, or any linear combination of them. The fact that they are the same is an accident of an $S=1$ system. Recalling that the appropriate correlation function is site diagonal, an easy calculation yields

$$\begin{aligned}\Gamma_\alpha(i,\omega) &= \pi^{-1}\int_{-\infty}^{\infty} d\omega' \sum_{j,k} a\,\omega_d(i,j)\omega_d(k,i) \\ &\qquad \times g_\alpha(i,\omega')f_0(j,k,\omega-\omega') \ , \\ a &= I(I+1)/3 \ ,\end{aligned} \tag{26}$$

where in $\omega_d(i,j)$ the i site is an S spin and the j site is an I spin. In this equation $f_0(j,k,\omega)$ is the spectral function for the $l=1$, $m=0$ or I_z correlation function

$$F_0(j,k,t) = a^{-1}\langle I_z(j,t)I_z(k,0)\rangle\Theta(t) \ . \tag{27}$$

Usually the bubble approximation is a reasonable but not a great approximation. However, in the present case it is exact (assuming that one knows f_0) to order $[\omega_d(IS)/\omega_d(II)]^2$. The reason is simply that all of the large-moment diagrams that correct the bubble approximation go into improving f_0. Physically this occurs because $\omega_d(II) \gg \omega_d(IS)$ and the expansion parameter $\omega_d(IS)/\omega_d(II)$ is small. Equation (26) is further simplified by noting that g_+ is a much narrower function than f_0. Thus g_+ in the integral can be well approximated by a δ function yielding

$$\Gamma_\alpha(i,\omega) = a\sum_{j,k}\omega_d(i,j)\omega_d(k,i)f_\alpha[j,k,\omega-\omega_\alpha(i)] \ . \tag{28}$$

If we are dealing with a Bravais lattice, Eq. (28) can be written in terms of the usual Fourier transforms[8] as

$$\Gamma_\alpha(i,\omega) = aN^{-1}\sum_q |\,\omega_d(q)\,|^2 f_0[q,\omega-\omega_\alpha(i)] \ , \tag{29}$$

where N is the number of points in the lattice and the summation over $\mathbf{q}$ is over all points in the first Brillouin zone.

In order to finish the calculation, we need a good approximation for f_0. Recently we have investigated the maximum-entropy approach to the problem of obtaining spin-correlation functions from a finite set of moments.[13] We found that the sequence of approximations involving more and more moments converges quite quickly and that applying the scheme to the self-energy yields better results than applying the scheme to the correlation function itself. There are only two nontrivial moments available for the $l=1$, $m=0$ dipolar correlation function in the literature[14,15] and in this case the maximum-entropy solution for a Bravais lattice is a Gaussian,

$$\begin{aligned}&\Gamma(\mathbf{q},\omega) = A(\mathbf{q})\exp[-\omega^2a^2(\mathbf{q})] \ , \\ &L_2(\mathbf{q}) = M_2(\mathbf{q}), \quad L_4(\mathbf{q}) = M_4(\mathbf{q}) - [M_2(\mathbf{q})]^2 \ , \\ &A(\mathbf{q}) = \{[\pi L_2(\mathbf{q})]^3/2L_4(\mathbf{q})\}^{1/2} \ , \\ &a^2(\mathbf{q}) = L_2 9\mathbf{q})/2L_4(\mathbf{q}) \ .\end{aligned} \tag{30}$$

The solution for a lattice with two atoms per unit cell is slightly more complicated and we refer the reader to the literature[14] for it. We believe that this approximation introduces errors of about 5%.

At this point we further assume that all of the $\omega_q(i)$ are much smaller in magnitude than $\omega_d(I,I)$. In that case the ω dependence of $\Gamma_\alpha(i,\omega)$ is unimportant and, to a good approximation, the relevant relaxation rates are the same and independent of frequency,

TABLE I. Transverse relaxation rate $\Gamma_{2d}=\Gamma_{2q}$ for $S=1$ spins interacting via $I=\frac{1}{2}$ spins in an hcp lattice. The rates are in units of $\hbar\gamma_s^2/a^3$ while Θ is the angle that the magnetic field makes with the c axis and ϕ is the angle that the projection of the magnetic field makes with an a axis.

Θ,ϕ	0,0	$\frac{1}{4}\pi,0$	$\frac{1}{2}\pi,0$	$\frac{1}{4}\pi,\frac{1}{6}\pi$	$\frac{1}{2}\pi,\frac{1}{6}\pi$
Γ_{2d}	50	35	83	46	47

TABLE II. Transverse relaxation rate $\Gamma_{2d}=\Gamma_{2q}$ for $S=1$ spins on Li sites interacting via $I=\frac{1}{2}$ sites on F sites in LiF. The rates are in units of $\hbar\gamma_s^2/a^3$. The crystallographic directions are the directions of the magnetic field.

Direction	[100]	[110]	[111]
Γ_{2d}	187	60	23

$$\Gamma_{\alpha}(i)=aN^{-1}\sum_{q}|\omega_d(q)|^2 f_0(q,\omega=0)\ . \tag{31}$$

We have computed these relaxation rates for the rate of D due to H in HD and for the ^{6}Li due to F in LiF. The results are presented in Tables I and II for different orientations. The rather extreme angular dependence for LiF arises because the dipolar interaction between a Li and the neighboring F's vanishes in the [111] direction.

We can now obtain a good estimate for the deuterium diffusion coefficient in HD in the limit where the inhomogeneous broadening of D nuclear spins is large. Since $\omega_d^2(i,j)$ falls off as $1/r^6$, only the 12 nearest neighbors in the lattice need be considered. Further, we average the dipolar interaction over the angles. This yields a diffusion coefficient

$$D=8(\gamma^2\hbar/a^3)^2a^2\Gamma_2/3\omega_q^2f^2\ , \tag{32}$$

where a is the lattice spacing, ω_q is an average $\omega_q(i)$, Γ_2 is Γ_{2d} or Γ_{2q}, and f is a correlation factor crudely defined as

$$[\omega_q(i)+\omega_q(j)]/[\omega_q(i)^2-\omega_q(j)^2]=2/\omega_q^2f^2\ . \tag{32'}$$

If sites near each other have nearly equal values of $\omega_q(i)$, then f is quite small. If the $\omega_q(i)$'s are uncorrelated then f is of order one. Using an average Γ_2 from Table I with $a=3.789$ Å and $\omega_q=4.15\times10^5$ s^{-1}, we obtain

$$D=4\times10^{-17}\ \mathrm{cm}^2/\mathrm{s}\ . \tag{33}$$

We note that $\omega_q=4.15\times10^5$ s^{-1} corresponds to the linewidth of 66 kHz in SiD$_4$. This is very broad, and even bad samples are probably an order of magnitude narrower. This yields a $D\sim4\times10^{-15}$ cm^2/s.

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