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Theoretical study of nuclear-spin–lattice relaxation in solid H_2

C. Ebner
Department of Physics, The Ohio State University, Columbus, Ohio 43210
and Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201

Charles W. Myles*
Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201

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Nuclear-spin–lattice relaxation in solid mixtures of ortho and para hydrogen is studied as a function of the o-H_2 concentration c. Equations of motion for the dynamical two-point angular momentum correlation functions are first obtained by the method of Blume and Hubbard. These equations are then impurity averaged by the Sung-Arnold method to obtain equations valid in the low-c regime. Numerical solutions to the latter equations are then used to obtain the nuclear-spin–lattice relaxation time T_1 as a function of c. The resulting T_1 displays the experimentally observed $c^{5/3}$ behavior at small c and its magnitude is shown to agree favorably with experiments at 10 K over the concentration range $0 \leq c \leq 0.5$.

I. INTRODUCTION

The properties of solid mixtures of ortho ($J=1$) and para ($J=0$) hydrogen molecules have been extensively studied both theoretically and experimentally in recent years.[1] A popular method of experimentally probing this system has been through nuclear-magnetic-relaxation studies.[2] Recently, such studies have been undertaken in both the large[3] and the small[4] ortho concentration regimes and over a wide range of temperatures.[3,4] Of particular interest in these experiments has been the dependence of the nuclear-spin–lattice relaxation time T_1 on the concentration c of the ortho molecules. Since a knowledge of the dynamical rotational angular momentum correlation functions of the o-H_2 is necessary in order to make a theoretical prediction for T_1,[3] the theoretical efforts in this area have been devoted to the development of theories for calculating these functions.[2,5–9]

In the high-concentration regime, Harris[2] has calculated the spectral functions for these correlation functions for both infinite and finite temperatures. He uses the method of moments plus a high-temperature expansion and obtains good agreement with the high-concentration experiments of Amstutz *et al.*,[3] with regard to both the temperature and concentration dependence of the relaxation time. More recently, Myles and Ebner,[9] also working in the high-concentration region, have used a high-temperature diagrammatic technique combined with a simple method of averaging over the distribution of o-H_2 molecules to calculate the $T=\infty$ spectral functions self-consistently for the first time. They obtain a $\sqrt{c}$ concentration dependence for T_1 which is in agreement with the data of Ref. 3 for all $c>0.5$. Also, the absolute magnitude of T_1 obtained in Ref. 9 is within 5% of the value obtained by extrapolating the data of Ref. 3 to $T=\infty$ for all concentrations larger than 0.5.

The low-concentration regime ($c<0.5$) has been explored by Sung,[6] Harris,[2] Hama, Inuzuko, and Nakamura,[7] and Ebner and Sung.[8] Sung[6] has applied the high-temperature statistical theory,[10,11] developed for paramagnetic resonance with a small concentration of spins, to the calculation of the angular momentum correlation functions and Harris[2] has used an improved version of the same theory. The T_1 resulting from these calculations has a concentration dependence of $c^{5/3}$, which is in agreement with the data of Weinhaus and Meyer[4] for $c<0.5$, but the magnitude of T_1 obtained in this way is in disagreement with that data by as much as 30% at some concentrations. Hama *et al.*,[7] have developed a theory which is capable of treating the $T=\infty$ correlation functions at all concentrations and which gives a concentration dependence and magnitude for T_1 which are in fair agreement with experiment for all c.[3,4] Both the method of Refs. 2 and 6 and the method of Ref. 7 suffer from the defect that the impurity-averaged correlation functions are obtained by statistically averaging assumed functional forms and no attempt is made to determine the shape of the spectral function from first principles. The first attempt in the small-c region to calculate the high-temperature correlation functions self-consistently and thus to overcome this defect was made by Ebner and Sung.[8] They used the Sung-Arnold[12] method of impurity averaging the Blume and Hubbard[13] correlation function theory and have obtained a T_1 which has the experimentally observed $c^{5/3}$ concentration dependence at small c. Their theory is only qualitative, however, since they have made no attempt to properly account for the anisotropy of the intermolecular interactions. For this reason, they did not obtain quantitative agreement with the experimental magnitude of T_1.

It is the primary purpose of this paer to improve the calculations of Ebner and Sung[8] by properly treating the anisotropy of the electric quadrupole-quadrupole (EQQ) interaction, which is the dominant orientationally dependent interaction between two o-H_2 molecules in solid H_2,[1,2] and which therefore almost totally determines the shape of the angular momentum spectral functions.[5-9] As in Ref. 8 the Sung-Arnold[12] method of impurity averaging the infinite-temperature Blume-Hubbard[13] correlation function equations is employed, but the equations are obtained using the full EQQ interaction rather than an isotropic approximation to it. The impurity-averaged correlation function equations are solved self-consistently and the spin-lattice relaxation time is computed as a function of the o-H_2 concentration using a formula for $1/T_1$ derived by applying the Blume-Hubbard[13] theory to the nuclear-spin correlation functions in this system. The resulting T_1 is compared to the data of Weinhaus and Meyer[4] at a temperature of $T = 10$ K and agreement is generally good with regard to both its magnitude and concentration dependence. Finally, the dense $(c = 1)$ Blume-Hubbard equations for the rotational correlation functions are solved self-consistently and the shapes of the spectral functions and the spin-lattice relaxation time obtained from this calculation are compared to both the high-c experiments of Ref. 3 and to the theoretical results of Myles and Ebner[9] at $c = 1$.

The remainder of this paper is organized as follows: In Part A of Sec. II the physical model and the notation are presented. Part B of Sec. II contains an outline of a matrix generalization of the Blume-Hubbard[13] correlation function formalism. In Part A of Sec. III, the formalism is applied to the particular case of spin-1 particles interacting via a quadrupole-quadrupole interaction, and the equations of motion for the rotational angular momentum correlation functions are derived for the dense system. The impurity-averaging method of Sung-Arnold[12] is briefly reviewed in Part B of Sec. III and is used to obtain equations for the impurity-averaged correlation functions. These equations have been solved numerically and the solutions are also presented in Sec. III B. In Sec. IV, a formula for $1/T_1$ is derived via the Blume-Hubbard technique. The impurity-averaged correlation functions are used in this expression and the resulting T_1 is compared with the experiments of Weinhaus and Meyer[4] at a temperature of 10 K for a variety of o-H_2 concentrations. In addition, a formula for $1/T_2$ is derived by the same method and the T_2 obtained from this expression is compared with experiment. In Sec. V the self-consistent solutions are obtained for the dense-system Blume-Hubbard[13] equations derived in Sec. III and the values for T_1 obtained from this calculation are compared with the experiments of Amstutz *et al.*[3] at large c and with the theoretical $c = 1$ results of Myles and Ebner.[9] Some remarks are then made regarding the reasons for the differences in the results found in Ref. 9 and those obtained here for the dense system. Finally, the basic limitations of the Sung-Arnold averaging technique are discussed and an alternative theory is suggested.

II. THEORETICAL BACKGROUND

A. Model

As was first shown by Nakamura,[14] the orientationally dependent part of the intermolecular potential between o-H_2 molecules in solid H_2 is dominated by the electric quadrupole-quadrupole (EQQ) interaction. The EQQ Hamiltonian may be written[9]

$$H_Q = \tfrac{1}{12}\sqrt{70\pi}\,\Gamma\mu_J \sum_{i\neq j} (a/|\vec{r}_{ij}|)^5 \times \sum_{mn} C_{mn} A_{2m}(\vec{r}_i)[Y_4^{m+n}(\Omega_{ij})]^* A_{2n}(\vec{r}_j)\ , \qquad (1)$$

where Γ is the EQQ coupling constant, a is the lattice spacing,

$$\mu_J = \tfrac{2}{15} J(J+1)(2J-1)(2J+3),$$

C_{mn} is the Clebsch-Gordan coefficient $C(224, mn)$, $\vec{r}_i$ and $\vec{r}_j$ are the locations of molecules i and j in the hcp lattice, $\Omega_{ij} = (\theta_{ij}, \phi_{ij})$ expresses the orientation of $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ with respect to the c axis, and Y_4^m is a spherical harmonic. The quantity $A_{lm}(\vec{r}_i)$ is the irreducible angular momentum operator at site $\vec{r}_i$ and has been discussed and defined in Refs. 14–18. In what follows, only the particular case of $J = 1$ will be considered. As a consequence, A_{2m} and A_{1m}, which are, respectively, quadratic and linear in the components of the angular momentum operator $\vec{J}$, are the only A_{lm} that will enter the calculation. The form of the Hamiltonian shown in Eq. (1) can be obtained from the standard version given by Eq. (2.1) of Ref. 2 by replacing the spherical harmonics $Y_2^m(\Omega_i)$ which occur in that equation by their operator equivalents[1,2] and then rewriting those operators in terms of the irreducible tensor operators $A_{lm}(\vec{r}_i)$.[9] Here Ω_i specifies the orientation of molecules i with respect to the c axis of the crystal. Since it has been shown[1] that other pairwise interactions and crystal-field effects are only small perturbations on H_Q, at least for moderately large o-H_2 concentrations, and since it has also been shown[1] that the only effect of three-body interactions, dielectric screening, and phonon interactions is to renormalize the interaction energy Γ the only intermolecular interaction that will be considered in this paper is H_Q with Γ taken as 0.712 K.[19]

The nuclear-spin–rotational angular momentum interactions which occur in solid H_2 are discussed in Refs. 2 and 6. Although these interactions have a negligible effect on the rotational angular momentum correlation functions to be discussed below,[2,6] they are of primary importance in the calculation of the nuclear-spin–lattice relaxation time to be discussed later. The interaction of the angular momentum $\vec{J}$ of a given molecule with its own nuclear spin $\vec{I}$ takes the form[6]

$$H_n = d[3(\vec{I}\cdot\vec{J})^2 - (\vec{I})^2(\vec{J})^2] + (\tfrac{3}{2}d - c')(\vec{I}\cdot\vec{J}), \tag{2}$$

where $d = 57.67$ kHz and $c' = 113.9$ kHz.[2] The terms proportional to d originate from the internuclear dipolar interaction of the two nuclei *within* the H_2 molecule and the term proportional to c' represents the interaction of the nuclear spin $\vec{I}$ with the magnetic field produced by the molecular rotation currents.[2] Harris[2] has written that part of H_n which is proportional to d in terms of the dipolar interaction between the two nuclear spins in the molecule. The above form can be obtained from his expression by taking matrix elements of it within a manifold of constant J and I and then by using the Wigner-Eckart theorem.[20] Strictly speaking, Eq. (2) should also include effects of the interactions of $\vec{J}$ and $\vec{I}$ with the external magnetic field.[2,6] This interaction will, however, have a negligible effect on the calculation of the angular momentum correlation functions except at extremely small concentrations.[2,6] Also, the effects of the external magnetic field on the nuclei and on T_1 can be transformed away by assuming that all calculations are performed in the rotating frame.[2,6] The effects of such an interaction will therefore be neglected in what follows.

B. Generalization of the Blume-Hubbard formalism

For convenience, the notation that will be used to describe the infinite-temperature correlation functions to be discussed below will be a generalization of that of Blume and Hubbard[13] combined with the tensor-operator notation.[14–18] The correlation functions considered here are therefore defined as[13]

$$G_{\alpha\beta}(\vec{r}_i, \vec{r}_j, t) = \langle \delta A_{\alpha\beta}(\vec{r}_i, \vec{r}_j, t)\rangle / \langle \delta A_{\alpha\beta}(\vec{r}_i, \vec{r}_j, 0)\rangle, \tag{3a}$$

where the angular brackets denote a thermal average, $\delta A_{\alpha\beta}$ is the response to a unit external magnetic field,

$$\delta A_{\alpha\beta}(\vec{r}_i, \vec{r}_j, t) = \lim_{\epsilon\to 0}\left(i\int_{-\infty}^{0} dt' [A_\alpha(\vec{r}_i, t), A_\beta(\vec{r}_j, t')]\, e^{\epsilon t'}\right), \tag{3b}$$

where the square brackets denote the commutator and the shorthand notation $A_\alpha = A_{lm}$ has been used. Although the notation is somewhat different, the correlation function defined in Eq. (3a) is precisely the same as the one defined in Eq. (2a) of Ref. 9. This fact will be shown explicitly in Appendix A.

In order to derive the equations of motion for the various correlation functions, it is necessary to begin with the equation of motion for the operator $A_\alpha(\vec{r}_i, t)$. The Hamiltonian in Eq. (1) and the commutation relations of the tensor operators lead to an equation of the form

$$\dot{A}_\alpha(\vec{r}_i, t) = \sum_\beta h_{\alpha\beta}(\vec{r}_i, t) A_\beta(\vec{r}_i, t), \tag{4a}$$

where

$$h_{\alpha\beta}(\vec{r}_i, t) = -i\sum_\gamma \sum_j \Omega_{\alpha\beta\gamma}(\vec{r}_i, \vec{r}_j) A_\gamma(\vec{r}_j, t). \tag{4b}$$

The $\Omega_{\alpha\beta\gamma}$'s in Eq. (4b) depend upon the Clebsch-Gordan coefficients C_{nm} and upon the spherical harmonics Y_4^m, which appear in Eq. (1). These $\Omega_{\alpha\beta\gamma}$'s are tabulated in Tables I–V and discussed in Appendix B. Equation (4a) is a matrix equation in the indices α and β and can thus be generalized to the form

$$\dot{A}(\vec{r}_i, t) = h(\vec{r}_i, t) A(\vec{r}_i, t), \tag{5}$$

where the A's without indices represent a column vector in the space of α and β and the h without indices represents a matrix in that space. Similarly, Eqs. (3a) and (3b) can be considered as matrix equations in the same space.

If the operation defined by the matrix version of Eq. (3b) is applied to Eq. (5) the result is

$$\delta\dot{A}(\vec{r}_i, \vec{r}_j, t) = h(\vec{r}_i, t)\,\delta A(\vec{r}_i, \vec{r}_j, t) + \delta h(\vec{r}_i, \vec{r}_j, t) A(\vec{r}_i, t). \tag{6}$$

As in Refs. 8, 12, and 13, the second term in Eq. (6) will be neglected here. This is equivalent to Blume and Hubbard's[13] "Approximation (A)," and is expected to be good at short times. It should also be pointed out that this approximation is necessary for the application of the Sung-Arnold[12] method of impurity averaging.

Neglect of the second term in Eq. (6) allows that equation to be directly integrated, giving

$$\delta A(\vec{r}_i, \vec{r}_j, t) = \exp_+\left\{i\int_0^t dt'\, h(\vec{r}_i, t')\right\}\delta A(\vec{r}_i, \vec{r}_j, 0), \tag{7}$$

where $\exp_+\{\ \}$ means that the quantity within the curly brackets is to be time ordered. The matrix version of Eq. (3a) then gives

$$G(\vec{r}_i, \vec{r}_j, t) = \left\langle \exp_+\left\{i\int_0^t h(\vec{r}_i, t')\,dt'\right\}\delta A(\vec{r}_i, \vec{r}_j, 0)\right\rangle \Big/ \langle \delta A(\vec{r}_i, \vec{r}_j, 0)\rangle \tag{8a}$$

or in Blume and Hubbard's[13] notation

$$G(\vec{r}_i, \vec{r}_j, t) = \left\langle\!\!\left\langle \exp_+\left\{i\int_0^t h(\vec{r}_i, t')\,dt'\right\}\right\rangle\!\!\right\rangle, \tag{8b}$$

where comparison of Eqs. (8a) and (8b) defines the double brackets. When both the cumulant expansion theory of Kubo,[21] and Blume and Hubbard's[13] "Approximation (B)" and its various corollaries[22] are applied to Eq. (8b) the result is (taking $\vec{r}_j = 0$)

$$G(\vec{r}_i, t) = \exp_+\left\{-\int_0^t dt' \int_0^{t'} dt'' \langle\langle h(\vec{r}_i, t')h(\vec{r}_i, t'')\rangle\rangle\right\} . \tag{8c}$$

After the definition of the double brackets in Eq. (8c) is taken into account and Blume and Hubbard's "Approximation (B)"[13] is again used,[22] the correlation function matrix takes the final form

$$G(\vec{r}_i, t) = \exp_+\left\{-\int_0^t dt' \int_0^{t'} dt'' \langle h(\vec{r}_i, t')h(\vec{r}_i, t'')\rangle\right\} , \tag{8d}$$

where it should now be emphasized that the argument of the exponential here contains a *single*-bracket average.

III. APPLICATION OF THE FORMALISM TO THE EQQ INTERACTION

A. Correlation function equations of motion for the dense system

In this paper, only the diagonal elements $G_{\alpha\alpha}$, of Eq. (8d) will be considered. Furthermore, only the cases $\alpha = (1, m)$ and $\alpha = (2, m)$ are important here since they are the only ones that are nonzero at high temperatures within the $J = 1$ manifold. These correlation functions will be denoted simply as G_α. In addition, in keeping with the spirit of Blume and Hubbard's "Approximation (A)" and its corollaries only the autocorrelation function will be considered.[13] Specialization to the autocorrelation function is also necessary in order to impurity average by the Sung-Arnold method.[12] The correlation functions will therefore be written with their position dependences suppressed. Under these conditions, Eq. (8d) becomes

$$G_\alpha(t) = \exp_+\left\{-\int_0^t dt' \int_0^{t'} dt'' \times \sum_\beta \langle h_{\alpha\beta}(\vec{r}_i, t')h_{\beta\alpha}(\vec{r}_i, t'')\rangle\right\} , \tag{9}$$

where the elements of the matrix h have been explicitly shown.

In order to obtain a closed set of equations for the functions $G_\alpha(t)$ it is necessary to substitute the $h_{\alpha\beta}$, given by Eq. (4b), into Eq. (9), to make use of the definition of the correlation function, given in Eq. (3a) and discussed further in Appendix A, and to again use the corollary to Blume and Hubbard's[13] "Approximation (A)" which neglects all correlation functions but the autocorrelation function. When these steps are taken, the equations for the correlation functions are

$$G_\alpha(t) = \exp_+\left\{-\int_0^t dt' \, (t-t') \sum_{\beta\gamma} \sum_j \Omega_{\alpha\beta\gamma}(\vec{r}_i, \vec{r}_j)\Omega_{\beta\alpha\tilde{\gamma}}(\vec{r}_i, \vec{r}_j)(-1)^{m_\gamma} G_\gamma(t')\right\} , \tag{10}$$

where one of the time integrations in Eq. (9) has been performed by a slight rearrangement, and $\tilde{\gamma} = (l_\gamma, -m_\gamma)$ when $\gamma = (l_\gamma, m_\gamma)$.

The equations which describe all of the $G_\alpha(t)$ can now be found from Eq. (10) and the $\Omega_{\alpha\beta\gamma}$'s listed in Tables I–V. Before this is done, however, a further simplification can be made by noting that with the neglect of magnetic field effects $G_{lm} = G_{l,-m}$. This simplification reduces the number of independent G_α's from eight to five. The equations of motion for these five functions are

$$G_{2m}(\tau) = \exp\left[-2\sum_{\vec{r}} \left(\frac{a}{|\vec{r}|}\right)^{10} \sum_{m'=0}^{2} F_m^{m'}(\theta, \phi) \int_0^\tau d\tau' (\tau - \tau')G_{2m'}(\tau')\right] , \tag{11a}$$

where $m = 0, 1, 2$ and

$$G_{1m}(\tau) = \exp\left[-2\sum_{\vec{r}} \left(\frac{a}{|\vec{r}|}\right)^{10} \sum_{m'=0}^{2} H_m^{m'}(\theta, \phi) \int_0^\tau d\tau' (\tau - \tau')G_{2m'}(\tau')\right] , \tag{11b}$$

where $m = 0, 1$.

These are the Blume-Hubbard equations of motion [within "Approximations (A) and (B)"] for the dense quadrupolar lattice. They are written in terms of the dimensionless time $\tau = (\frac{140}{27}\pi)^{1/2}\Gamma t$ which is useful for obtaining the numerical solutions which may be found in Sec. V. The functions $F_m^{m'}(\theta, \phi)$ and $H_m^{m'}(\theta, \phi)$ are given in Appendix C where it is also noted that $F_m^1(\theta, \phi) \equiv H_m^1(\theta, \phi)$, so that $G_{21}(\tau) \equiv G_{11}(\tau)$ within the approximations of this paper. Note that this is not true in general and that in particular it is not true in the calculations presented in Ref. 9.

Equations (11a) form a closed set which can be solved for the $G_{2m}(\tau)$; substitution of these into Eqs. (11b) then yields the $G_{1m}(\tau)$. This again is a consequence of the approximations used here and is in marked contrast to the equations of motion obtained for these functions in Ref. 9 by the spin self-energy method. In that paper, the solutions for the five independent G_α's had to be obtained by solving all five equations of motion simultaneously.

The fact that drastically different situations occur in the two cases with regard to the equations of motion for the G_α's is probably not as surprising as it might first appear. The differences are undoubtedly due to the different approximations made in the derivation of the equations here and in Ref. 9. In particular, the equations in Ref. 9 were obtained as the lowest-order approximation in a well-defined self-energy expansion and are valid to lowest order in $1/z$, where z is the number of nearest neighbors. On the other hand, the equations obtained in the present paper were derived by the use of Blume and Hubbard's[13] "Approximations (A) and (B)." Although it is not clear at the present time exactly what the physical differences are between the approximations made in the two cases, it is clear that the self-energy approximation does not restrict one to keeping only the autocorrelation function while "Approximation (A)" and its corollaries obviously do. In addition, it is clear how to generalize the "bubble" approximation used in Ref. 9 to higher orders in a Brillouin-Wigner type of perturbation theory, while it is not obvious how to generalize the Blume-Hubbard theory to higher orders in the interaction. As Blume and Hubbard themselves have shown, it is possible to use their theory without invoking "Approximation (A)." In fact, when this is done, their theory and the "bubble approximation" for the self-energy appear to be equivalent, at least for the Heisenberg paramagnet case.[15] This aspect of Blume-Hubbard theory applied to the EQQ interaction will not be considered here.

B. Sung-Arnold average: The correlation-function equations of motion for the impurity-averaged system and solutions

In order to obtain solutions for the correlation functions $G_\alpha(t)$ which are valid for other than a dense quadrupolar system, it is first necessary to impurity average Eqs. (11). When this is done, solutions to the averaged equations will be applicable to solid mixtures of o-H_2 and p-H_2. The averaging method that will be used was developed by Sung and Arnold[12] for their study of nuclear-spin-lattice relaxation via impurities in metals. This formalism is briefly reviewed below.

It is first convenient to rewrite Eqs. (11) in a more compact form:

$$G_\alpha(\tau)=\exp\left[-\sum_{\vec{r}} M_\alpha(\vec{r},\tau)\right], \qquad (12)$$

where direct comparison of Eqs. (11) with Eq. (12) defines the $M_\alpha(\vec{r},\tau)$. In the case of a dense quadrupolar system ($c=1$), the sum in Eq. (12) goes over all lattice sites. For $c<1$ however, the sum goes only over sites which are occupied by a $J=1$ molecule. If one assumes that $\vec{r}$ is a random variable for $c<1$, the quantity of interest here is $\langle G_\alpha(\tau)\rangle_{av}$, where $\langle\ \rangle_{av}$ denotes the average over the random variable $\vec{r}$. For convenience, this averaged correlation function will again be denoted as $G_\alpha(\tau)$. Assuming that for a specified α, the M_α at different lattice sites are statistically independent and that there is a uniform probability that a given $J=1$ molecule can be found at a given site $\vec{r}$, Sung and Arnold show that the averaged form of Eq. (12) can be written

$$G_\alpha(\tau)=\exp\left[-c\sum_{\vec{r}}\left(1-e^{-M_\alpha(\vec{r},\tau)}\right)\right], \qquad (13)$$

where c is the concentration of $J=1$ molecules; it is understood that the G's contained in $M_\alpha(\vec{r},\tau)$ in Eq. (13) are to be replaced by their average values, and the sum over $\vec{r}$ is now over all sites. Equation (13) with M_α obtained from Eqs. (12) and (11) are the equations of motion for the impurity averaged correlation functions.

These equations have been solved numerically for various values of the o-H_2 concentration in the interval $0.001\leq c\leq 1.0$. The procedure used to solve them was similar to that used in Refs. 8 and 12. One significant difference between the present treatment and that of Refs. 8 and 12 is that here the sum on $\vec{r}$ was done explicitly over 300 shells of the hcp lattice rather than being approximated by an integral. The results for the various $G_\alpha(\tau)$ are shown in Figs. 1 for $c=0.01$, 0.1, and 1.0; for small $c\leq 0.1$, the G_α are approximately Gaussian at short times ($G\sim e^{-A\tau^2}$), simple exponential at intermediate times ($G\sim e^{-B\tau}$), and exponential $\tau^{3/5}$ at long times ($G\sim e^{-C\tau^{3/5}}$). In this region of concentration, it is the long time behavior that is important in determining T_1.

It should be noted in passing that it is possible to obtain the incoherent quasielastic differential neutron scattering cross section in solid H_2 by using the $G_\alpha(\tau)$ for each c in a formula, derived in Ref. 9, which expresses the scattering cross section in terms of the frequency-dependent spectral functions. Since this paper is concerned primarily with studying nuclear-spin-lattice relaxation, such a calculation will not be done here but will be deferred to another paper.[23]

IV. DERIVATION OF RELAXATION TIMES: EXPERIMENTAL COMPARISON

An expression for $1/T_1$ can be obtained by applying the matrix generalization of the Blume-Hubbard[13] formalism that was discussed in Sec. II directly to the Hamiltonian, Eq. (2), which describes the nuclear-spin-rotational-angular-momentum interaction. In addition, this same calculation yields an expression for the transverse nuclear-spin relaxation time T_2 due to EQQ interactions, as well as relaxation times for the other three nuclear-spin correlation functions, which will be defined

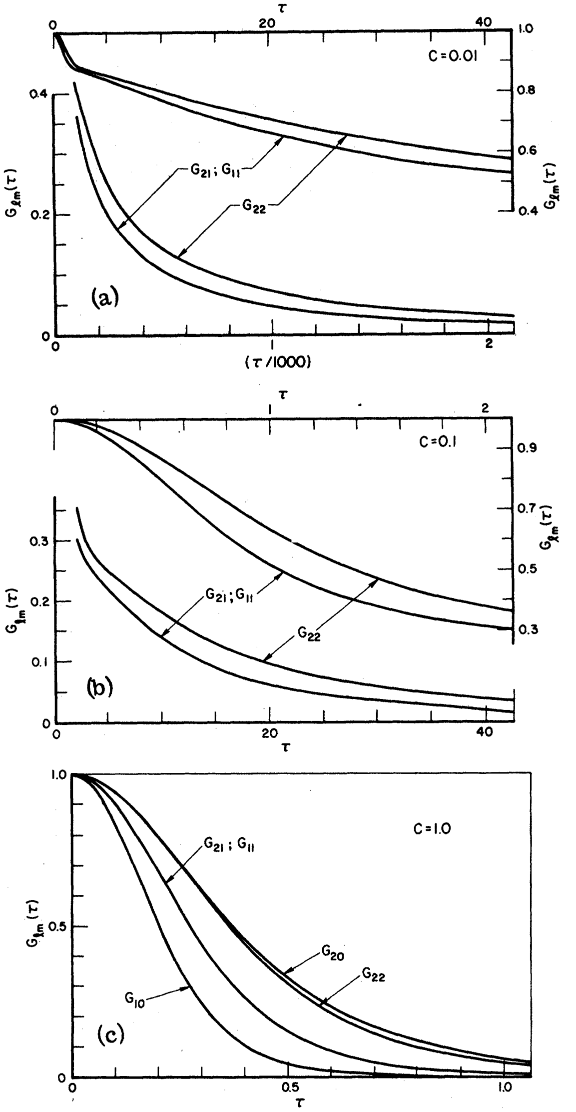

FIG. 1. Correlation functions $G_{lm}(\tau)$ vs dimensionless time τ at concentrations (a) $c=0.01$, (b) $c=0.1$, and (c) $c=1.0$; in Figs. 1(a) and 1(b), the upper pair of curves are referred to the upper and right scales while the lower pair of curves are referred to the lower and left scales.

below.

In analogy with Eq. (3a), one can define a *nuclear-spin correlation function* as

$$G^I_{\alpha\beta}(\vec{r}_i, \vec{r}_j, t) = \langle \delta A^I_{\alpha\beta}(\vec{r}_i, \vec{r}_j, t)\rangle / \langle \delta A^I_{\alpha\beta}(\vec{r}_i, \vec{r}_j, 0)\rangle , \quad (14)$$

where the superscript I means the nuclear spin and $\delta A^I_{\alpha\beta}$ is defined by Eq. (3b) with the A_α's replaced by A^I_α's. Here A^I_α means the nuclear-spin irreducible tensor operator. In order to obtain the equation of motion for these nuclear-spin correlation functions one must carry out the steps of Sec. II B, with the functions defined in Eq. (14) replacing the angular momentum correlation functions where appropriate and with the interaction given by Eq. (2) replacing the EQQ interaction. As before, only the autocorrelation functions and only G^I's diagonal in the indices α and β will be kept. Similarly, the only indices α in G^I_α that need be considered here are $\alpha=(1, m)$ and $\alpha=(2, m)$. If magnetic field effects are again neglected, the equations of motion for the nuclear-spin correlation functions take the general form

$$G^I_\alpha(t) = \exp\left[-\int_0^t dt'\,(t-t') \times \sum_{\beta\gamma} (-1)^{m_\gamma} \Omega^I_{\alpha\beta\gamma}\Omega^I_{\beta\alpha\bar{\gamma}} G_\gamma(t')\right] , \quad (15)$$

where $\Omega^I_{\alpha\beta\gamma}$ is analogous to $\Omega_{\alpha\beta\gamma}$ in Eq. (4b) and $G_\gamma(t)$ is the rotational angular momentum correlation function already discussed. The $\Omega^I_{\alpha\beta\gamma}$ are tabulated in Tables VI–X and are discussed in Appendix D.

Although Eq. (15) can certainly be evaluated for all t using the above results for $G_\gamma(t)$, it is the long time behavior that is usually experimentally observed. The expected large time exponential decay of the nuclear correlation functions can be obtained by the following reasoning. The quantities $\Omega^I_{\alpha\beta\gamma}$, as shown in Tables VI–X, vary on the scale of the nuclear-spin–rotational-angular-momentum interaction energies c' and d. On the other hand, the integrals of the form

$$\int_0^t dt'\,(t-t')G_\gamma(t')$$

vary inversely as the square of the EQQ interaction energy Γ. This can easily be seen by rewriting them in terms of the dimensionless time τ. The exponent in Eq. (15) is therefore proportional to the quantities $(c'/\Gamma)^2$ or $(d/\Gamma)^2$, which have a magnitude of the order of 10^{-12}. Since the number multiplying the integral in the exponent is so small, the nuclear correlation function $G^I_\alpha(t)$ itself will only differ from

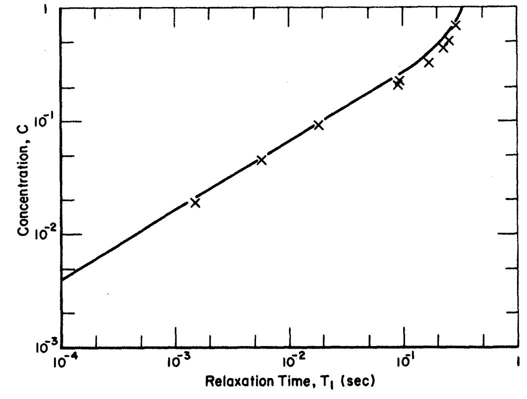

FIG. 2. Relaxation time T_1 (sec) as a function of o-H_2 concentration. The experimental points are from Ref. 4.

unity for very long times, at which Eq. (15) can be written

$$G_\alpha^I(t) = \exp\left(-t\int_0^\infty dt'\,\Gamma_\alpha(t')\right) \equiv e^{-t/T_\alpha}\,, \tag{16}$$

where $\Gamma_\alpha(t')$ and thus T_α^{-1} will be shown explicitly below for each α.

The only two of these relaxation times usually measured in solid H_2 are the longitudinal relaxation time T_{10}, commonly denoted T_1, and the transverse relaxation time T_{11}, commonly denoted T_2. From Eqs. (15) and (16) it can be shown after changing to dimensionless times that these quantities take the form (for $J = I = 1$)

$$\frac{1}{T_1} = \frac{2}{\hbar E}\int_0^\infty d\tau\left(\frac{2c'^2}{3}G_{11}(\tau) + \frac{3d^2}{2}[G_{21}(\tau) + 4G_{22}(\tau)]\right) \tag{17a}$$

and

$$\frac{1}{T_2} = \frac{2}{\hbar E}\int_0^\infty d\tau\left(\frac{c'^2}{3}[G_{11}(\tau) + G_{10}(\tau)] + \tfrac{3}{4}d^2[2G_{22}(\tau) + 5G_{21}(\tau) + 3G_{20}(\tau)]\right)\,, \tag{17b}$$

where $E = (\frac{140}{27}\pi)^{1/2}\Gamma$. These equations will give T_1 and T_2 in seconds if c', d, and E are all first expressed in ergs. Equation (17a) reduces to the expression for $1/T_1$ used in the Erratum to Ref. 9. Also, it is the same formula for $1/T_1$ obtained by others[2,5,6] using different methods. By the employment of the $G_\alpha(\tau)$ found in Sec. III B, T_1 has been evaluated for $0.001 \le c \le 1.0$; the result is plotted as a function of c in Fig. 2. For consistency and easy comparison with the relaxation times calculated in Ref. 9, we have used $\Gamma = 0.712$ K although the best fit to the data is obtained if $\Gamma = 0.754$ K. The data from Ref. 4, taken at a temperature of $T = 10$ K are also shown in Fig. 2. Here the experimental results have not been extrapolated to $T = \infty$ before comparison with the theory, as was done in Ref. 9 for the large-c data of Ref. 3. The reason for this is that, although one would naively expect T_1 to vary with temperature at all concentrations, even in the nondiffusive region, the data of Ref. 4 indicate that this is not the case for the low concentrations discussed there. In fact for $0.019 \le c \le 0.510$ the data indicate that, except for diffusive effects, T_1 is relatively constant in temperature over the range $6 \le T \le 10$ K. Thus, neglecting diffusion, $T_1(10\text{ K}) = T_1(\infty)$ and no extrapolation is necessary. This behavior is in marked contrast to the high-c data of Ref. 3 which show that T_1 varies markedly with T for $c > 0.5$ so that, in order to obtain a theoretical-experimental comparison in Ref. 9 it was necessary to extrapolate that data to $T = \infty$.

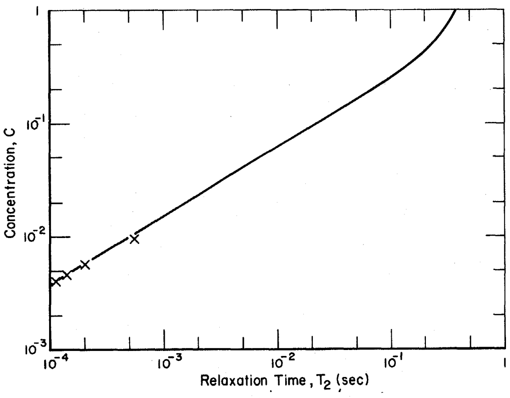

FIG. 3. Relaxation time T_2 (sec) as a function of o-H_2 concentration. See Ref. 24 for an explanation of where the experimental data were obtained.

Figure 2 shows that the slope of the theoretical curve for T_1 approaches $\frac{5}{3}$ for c very small and increases monotonically as c increases. Both the $c^{5/3}$ dependence at low c and the departures from this behavior at larger c are in general agreement with the experimental data. The theory is expected to be most accurate for $c \ll 1$ but large enough that crystal-field effects are not important. From Fig. 2 one sees that this expectation is realized; the experimental and theoretical values of T_1 are most nearly equal for o-H_2 concentrations between 2 and 10%. It is interesting to note that even though the Sung-Arnold method of averaging is not expected to be valid at large concentrations, the T_1 obtained from the solutions to the impurity-averaged equations at large c follows the general trend of the high-c experimental data[3,4] and the value for T_1 obtained at $c = 1$ by this method is $T_1 = 338$ msec (for $\Gamma = 0.712$ K), which is within 12% of the experimental value[3] at that concentration, $T_1^{\text{expt}} = 382$ msec, which was obtained in Ref. 9 by extrapolation to $T = \infty$. It should be noted that there are uncertainties in the EQQ parameter Γ. For example, Table IX of Ref. 1 shows that different experiments obtain values for this parameter differing by as much as 10%. Therefore, the theoretical values of T_1 obtained here have a built in uncertainty of at least 10%.

Experimental results on T_2 due to pure EQQ interactions in solid H_2 are somewhat sparse. In addition, the data available are for a restricted range of concentrations.[6,24] Nevertheless, T_2 given by Eq. (17b) has been evaluated for c in the range $0.001 \le c \le 1.0$ and the results are plotted in Fig. 3 along with the experimental data[24] taken from Ref. 6. The theoretical results for T_2 shown in that figure show the same $c^{5/3}$ dependence at low c and the same general increase with increasing c as was found for T_1. As can be seen from the figure, where the data are available, the theory and experiment are in general agreement.

Although, at the present time the nuclear-spin

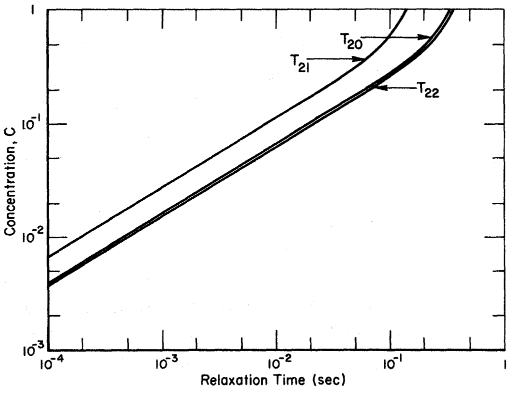

FIG. 4. Relaxation times T_{20}, T_{21}, and T_{22} as functions of o-H_2 concentration.

relaxation times T_{22}, T_{21}, and T_{20}, do not appear to have been measured, it is nevertheless interesting to show their forms as given by Eqs. (15) and (16) and to evaluate them as functions of concentration. These relaxation times are (for $J = I = 1$)

$$\frac{1}{T_{22}} = \frac{2}{\hbar E}\int_0^\infty d\tau \left(\frac{2c'^2}{3}[G_{11}(\tau) + 2G_{10}(\tau)] + \frac{3d^2}{2}[2G_{22}(\tau) + G_{21}(\tau)]\right), \tag{18a}$$

$$\frac{1}{T_{21}} = \frac{2}{\hbar E}\int_0^\infty d\tau \left(\frac{c'^2}{3}[5G_{11}(\tau) + G_{10}(\tau)] + \frac{3d^2}{4}[2G_{22}(\tau) + 25G_{21}(\tau) + 3G_{20}(\tau)]\right), \tag{18b}$$

and

$$\frac{1}{T_{20}} = \frac{2}{\hbar E}\int_0^\infty d\tau \left(2c'^2 G_{11}(\tau) + \frac{9d^2}{2}G_{21}(\tau)\right). \tag{18c}$$

Again, the formulas will give T_α in seconds if all energies are expressed in ergs. These relaxation times are plotted as functions of c in Fig. 4. As can be seen from that figure, their low-c behavior is again $c^{5/3}$ with the same general trend at high c as is displayed by T_1 and T_2. Since nuclear acoustic resonance (NAR) measures the higher-order nuclear-spin correlation functions G^I_{22}, G^I_{21}, G^I_{20}[16,25] in other systems, perhaps it could be used as a method of probing these functions in solid H_2 and thus of measuring T_{22}, T_{21}, and T_{20} in that system.

TABLE I. $-\Omega_{11,2m,2n}/(\frac{70}{27}\pi)^{1/2}\Gamma(a/r)^5$.

	m				
n	2	1	0	−1	−2
2	$2C_{21}Y_4^{3*}$	$\sqrt{6}\,C_{20}Y_4^{2*}$	$\sqrt{6}\,C_{2,-1}Y_4^{1*}$	$2C_{2,-2}Y_4^{0*}$	0
1	$2C_{11}Y_4^{2*}$	$\sqrt{6}\,C_{10}Y_4^{1*}$	$\sqrt{6}\,C_{1,-1}Y_4^{0*}$	$2C_{2,-1}Y_4^{-1*}$	0
0	$2C_{10}Y_4^{1*}$	$\sqrt{6}\,C_{00}Y_4^{0*}$	$\sqrt{6}\,C_{10}Y_4^{-1*}$	$2C_{20}Y_4^{-2*}$	0
−1	$2C_{1,-1}Y_4^{0*}$	$\sqrt{6}\,C_{10}Y_4^{-1*}$	$\sqrt{6}\,C_{11}Y_4^{-2*}$	$2C_{21}Y_4^{-3*}$	0
−2	$2C_{2,-1}Y_4^{0*}$	$\sqrt{6}\,C_{20}Y_4^{-2*}$	$\sqrt{6}\,C_{21}Y_4^{-3*}$	$2C_{22}Y_4^{-4*}$	0

TABLE II. $\Omega_{10,2m,2n}/(\frac{140}{27}\pi)^{1/2}\Gamma\,(a/r)^5$.

	m				
n	2	1	0	−1	−2
2	$2C_{22}Y_4^{4*}$	$C_{21}Y_4^{3*}$	0	$-C_{2,-1}Y_4^{1*}$	$-2C_{2,-2}Y_4^{0*}$
1	$2C_{21}Y_4^{3*}$	$C_{11}Y_4^{2*}$	0	$-C_{1,-1}Y_4^{0*}$	$-2C_{2,-1}Y_4^{-1*}$
0	$2C_{20}Y_4^{2*}$	$C_{10}Y_4^{1*}$	0	$-C_{10}Y_4^{-1*}$	$-2C_{20}Y_4^{-2*}$
−1	$2C_{2,-1}Y_4^{1*}$	$C_{1,-1}Y_4^{0*}$	0	$-C_{11}Y_4^{-2*}$	$-2C_{21}Y_4^{-3*}$
−2	$2C_{2,-2}Y_4^{0*}$	$C_{2,-1}Y_4^{-1*}$	0	$-C_{21}Y_4^{-3*}$	$-2C_{22}Y_4^{-4*}$

V. SOLUTIONS TO THE DENSE SYSTEM EQUATIONS: LIMITATIONS OF THE BLUME-HUBBARD-SUNG-ARNOLD METHOD

It is of some interest to solve the dense Blume-Hubbard equations, for the quadrupolar solid. It is worthwhile to obtain such solutions for two reasons. First, experimental data for T_1 exist[3] near $c = 1$ and the T_1 obtained theoretically could be compared to these data. Secondly, Myles and Ebner[9] have used the spin-self-energy method to obtain these correlation functions at large c and it would be interesting to compare their solutions with the solutions to Eqs. (11).

Equations (11a) and (11b) have been solved numerically by the same method used in Sec. IV. The resulting $G_\alpha(\tau)$ are very nearly identical with those shown in Fig. 1(c); they are basically Gaussian in character for short times and display an essentially exponential behavior at long times. The main difference that should be noted in the solutions found here and those found in Ref. 9 (see Fig. 4 of that reference) is that the functions G_{10} and G_{21} as found in Ref. 9 show marked oscillations in time, whereas the corresponding functions found here do not. Theoretical values of T_1 at $c = 1$ have been obtained by using these dense system solutions in Eq. (17a). The results of this calculation are (for $\Gamma = 0.712$ K)

$$T_1 = 355 \text{ msec}. \tag{19}$$

These results may be compared with the $T = \infty$, $c = 1$ experimental value of 382 msec, obtained from the $T = \infty$ extrapolation of the data of Amstutz *et al.*[3]

TABLE III. $\Omega_{22,1m,2n}/(\frac{280}{27}\pi)^{1/2}\Gamma\,(a/r)^5$.

	m		
n	1	0	−1
2	$C_{2,-1}Y_4^{1*}$	$\sqrt{2}\,C_{2,-2}Y_4^{0*}$	0
1	$C_{1,-1}Y_4^{0*}$	$\sqrt{2}C_{2,-1}Y_4^{-1*}$	0
0	$C_{10}Y_4^{-1*}$	$\sqrt{2}\,C_{20}Y_4^{-2*}$	0
−1	$C_{11}Y_4^{-2*}$	$\sqrt{2}\,C_{21}Y_4^{-3*}$	0
−2	$C_{21}Y_4^{-3*}$	$\sqrt{2}\,C_{22}Y_4^{-4*}$	0

TABLE IV. $-\Omega_{21,1m,2n}/(\frac{35}{27}\pi)^{1/2}\Gamma\ (a/r)^5$.

		m	
n	1	0	-1
2	$2\sqrt{3}\,C_{20}Y_4^{2*}$	$10C_{2,-1}Y_4^{1*}$	$2\sqrt{2}\,C_{2,-2}Y_4^{0*}$
1	$2\sqrt{3}\,C_{10}Y_4^{1*}$	$10C_{1,-1}Y_4^{0*}$	$2\sqrt{2}\,C_{2,-1}Y_4^{-1*}$
0	$2\sqrt{3}\,C_{00}Y_4^{0*}$	$10C_{10}Y_4^{-1*}$	$2\sqrt{2}C_{20}Y_4^{-2*}$
-1	$2\sqrt{3}\,C_{10}Y_4^{-1*}$	$10C_{11}Y_4^{-2*}$	$2\sqrt{2}\,C_{21}Y_4^{-3*}$
-2	$2\sqrt{3}\,C_{20}Y_4^{-2*}$	$10C_{21}Y_4^{-3*}$	$2\sqrt{2}\,C_{22}Y_4^{-4*}$

which was discussed in Ref. 9. The result given by Eq. (19) is within 7% of this experimental value. The experimental number is obtained here if Γ is taken to be 0.765 K.

The differences in the results for the dense-system correlation functions obtained here and in Ref. 9 as well as the difference for the theoretical T_1 values obtained in the two calculations are certainly almost wholly due to the different approximations that are made in Blume-Hubbard[13] theory with "Approximations (A) and (B)" and in the "bubble" approximation for the spin self-energy.[9] This point has already been discussed in Sec. III of the present paper. In light of the discussion there, it is really difficult to say which theory is "more correct," but it is clear that invoking "Approximation (A)" and its corollaries throws away terms which are kept in the self-energy expansion.

At this point is should be emphasized that the results obtained here for the correlation functions and for the relaxation times were obtained by the neglect of both crystal-field and magnetic field effects. As the concentration c becomes very small, these effects certainly become important.[1,26] Using the formalism described in Sec. II to take them into account is straightforward but algebraically complicated; such a calculation will be left for a future publication. It should also be mentioned in passing that although the calculations presented above were, for simplicity, performed in the $T=\infty$ limit, it is possible to treat the Blume-Hubbard theory at finite temperatures[27] and also to incorporate finite-temperature effects into the Sung-Arnold formalism.[8]

TABLE V. $\Omega_{20,1m,2n}/(\frac{140}{9}\pi)^{1/2}\Gamma\ (a/r)^5$.

		m	
n	1	0	-1
2	$C_{21}Y_4^{3*}$	0	$-C_{2,-1}Y_4^{1*}$
1	$C_{11}Y_4^{2*}$	0	$-C_{1,-1}Y_4^{0*}$
0	$C_{10}Y_4^{1*}$	0	$-C_{10}Y_4^{-1*}$
-1	$C_{1,-1}Y_4^{0*}$	0	$-C_{11}Y_4^{-2*}$
-2	$C_{2,-1}Y_4^{-1*}$	0	$-C_{21}Y_4^{-3*}$

TABLE VI. $\Omega^I_{11,\beta,\gamma}$.

			β			
γ	11	10	22	21	20	2, -1
11	0	$-c'u$	0	0	0	0
10	$c'u$	0	0	0	0	0
22	0	0	0	0	0	$-\frac{3}{4}\sqrt{2}\,dv$
21	0	0	0	0	$\frac{3}{4}\sqrt{3}\,dv$	0
20	0	0	0	$-\frac{3}{4}\sqrt{3}\,dv$	0	0
2, -1	0	0	$\frac{3}{4}\sqrt{2}\,dv$	0	0	0

One of the basic limitations of the Sung-Arnold[12] method of impurity averaging is that it is limited to the form of the Blume-Hubbard[13] correlation function theory in which "Approximations (A) and (B)" are used. The disadvantages of these two approximations are discussed in Sec. III and briefly in this section. Although in the general form of Blume-Hubbard theory[13] these approximations are not necessary,[13] it is not clear at the present time how to generalize the Sung-Arnold[12] method to treat this kind of correlation function theory. Since the general Blume-Hubbard theory is equivalent to the "bubble" approximation to the spin self-energy,[15] neither is it clear how to apply a Sung-Arnold impurity average to the equations resulting from the latter theory.

An additional disadvantage of the Sung-Arnold method is that it accurately treats only low concentrations of impurities but gives the wrong concentration dependence for T_1 at high c. On the other hand, the spin-self-energy method combined with an *ad hoc* method of averaging proposed in Ref. 9 gives the correct c dependence of T_1 only at high concentrations. It is therefore desirable to develop a theory which is capable of treating the entire concentration range $0 \leqslant c \leqslant 1$, and which is at the same time not restricted to "Approximations (A) and (B)" and their disadvantages. Such a theory, based upon the spin–self-energy method combined with a coherent-potential-like effective-medium approximation, has recently been proposed[28] and calculations which apply this theory to solid H_2 and other materials are now in progress.

APPENDIX A: RELATIONSHIP BETWEEN CORRELATION FUNCTION DEFINITIONS

The correlation function defined in Eq. (3a) and that defined in Ref. 9 are identical if only times

TABLE VII. $\Omega^I_{10,\beta,\gamma}$.

			β			
γ	11	1, -1	22	21	2, -1	2, -2
11	0	$-c'u$	0	0	0	0
1, -1	$c'u$	0	0	0	0	0
22	0	0	0	0	0	$-\frac{3}{2}dv$
21	0	0	0	0	$\frac{3}{4}dv$	0
2, -1	0	0	0	$-\frac{3}{4}dv$	0	0
2, -2	0	0	$\frac{3}{2}dv$	0	0	0

TABLE VIII. $\Omega^I_{22,\beta,\gamma}$.

γ	β 11	10	22	21
11	0	0	0	$-\sqrt{2}\,c'u$
10	0	0	$2c'u$	0
22	0	$3dw$	0	0
21	$-\frac{3}{2}\sqrt{2}\,dw$	0	0	0

$t \geq 0$ are considered. This can be shown rather easily in the following way. Equation (3a) gives

$$G_{\alpha\beta}(\vec{r}_i - \vec{r}_j, t) = \langle \delta A_{\alpha\beta}(\vec{r}_i, \vec{r}_j, t)\rangle / \langle \delta A_{\alpha\beta}(\vec{r}_i, \vec{r}_j, 0)\rangle , \tag{A1}$$

while Eq. (2a) of Ref. 9 gives

$$G_{\alpha\beta}(\vec{r}_i - \vec{r}_j, t) = \langle A_\alpha(\vec{r}_i, t) A^\dagger_\beta(\vec{r}_j, 0)\rangle \tag{A2}$$

for times $t > 0$. Blume and Hubbard[13] show that

$$\langle \delta A_{\alpha\beta}(\vec{r}_i, \vec{r}_j, t)\rangle = \beta \langle A_\alpha(\vec{r}_i, t) A^\dagger_\beta(\vec{r}_j, 0)\rangle , \tag{A3}$$

where $\beta = 1/kT$. Using Eq. (A3) in Eq. (A1) gives the result

$$G_{\alpha\beta}(\vec{r}_i - \vec{r}_j, t) = \langle A_\alpha(\vec{r}_i, t) A^\dagger_\alpha(\vec{r}_j, 0)\rangle / \langle A_\alpha(\vec{r}_i, 0) A^\dagger_\beta(\vec{r}_j, 0)\rangle . \tag{A4}$$

Now, according to Ref. 9, the A_α's are normalized so that the function in the denominator of Eq. (A4) is unity. Therefore, $G_{\alpha\beta}$ defined by Eqs. (A1) and (A2) are equivalent.

APPENDIX B: $\Omega_{\alpha\beta\gamma}(\vec{r}_i, \vec{r}_j)$

The $\Omega_{\alpha\beta\gamma}(\vec{r}_i, \vec{r}_j)$' s defined in Eq. (4b) are easiest to present in tabular form. In Tables I–V the C_{nm} represent the Clebsch-Gordan coefficients $C(224, nm)$, the property $C_{nm} = C_{mn} = C_{-n,-m}$ has been used, and Y_4^{m*} means $[Y_4^m(\theta, \phi)]^*$.

$\Omega_{1,-1;2m;2n}$, $\Omega_{2,-1;1m;2n}$, and $\Omega_{2,-2;1m;2n}$ can be obtained from the tables by the use of the properties

$$\Omega_{1,-l;2,-m;2,-n} = (-1)^{m+n+1}(\Omega_{1l;2m;2n})^* \tag{B1}$$

and

$$\Omega_{2,-l;1,-m;2,-n} = (-1)^{m+n+1}(\Omega_{2l;1m;2n})^* . \tag{B2}$$

Also, it should be noted that the following condition holds:

$$\Omega_{1l,1m,1n} = \Omega_{1l,1m,2n} = \Omega_{1l,2m,1n} = \Omega_{2l,2m,1n} = \Omega_{1l,2m,2n} = 0 . \tag{B3}$$

TABLE IX. $\Omega^I_{21,\beta,\gamma}$.

γ	11	10	β 1, −1	22	21	20
11	0	0	0	0	0	$-\sqrt{3}\,c'u$
10	0	0	0	0	$c'u$	0
1, −1	0	0	0	$\sqrt{2}\,c'u$	0	0
22	0	0	$\frac{3}{2}\sqrt{2}\,dw$	0	0	0
21	0	$\frac{15}{2}dw$	0	0	0	0
20	$-\frac{3}{2}\sqrt{3}\,dw$	0	0	0	0	0

TABLE X. $\Omega^I_{20,\beta,\gamma}$.

γ	11	β 1, −1	21	2, −1
11	0	0	0	$-\sqrt{3}\,c'u$
1, −1	0	0	$\sqrt{3}\,c'u$	0
21	0	$-\frac{3}{2}\sqrt{3}\,dw$	0	0
2, −1	$\frac{3}{2}\sqrt{3}\,dw$	0	0	0

APPENDIX C: FUNCTIONS $F^m_{m'}(\theta,\phi)$ and $H^m_{m'}(\theta,\phi)$

The functions $F^m_{m'}(\theta, \phi)$ and $H^m_{m'}(\theta, \phi)$ defined in Eqs. (11a) and (11b) are listed below. The symbol C_{nm} means the Clebsch-Gordan coefficient $C(224, mn)$, $|Y_4^m|^2$ means $|Y_4^m(\theta, \phi)|^2$, and the (θ, ϕ) dependence of the F's and H's has been suppressed:

$$F^2_2 = 2C^2_{22}|Y^4_4|^2 + C^2_{21}|Y^3_4|^2 + C^2_{2,-1}|Y^1_4|^2 + 2C^2_{2,-2}|Y^0_4|^2 ,$$

$$F^2_1 = 2C^2_{21}|Y^3_4|^2 + C^2_{11}|Y^2_4|^2 + 2C^2_{2,-1}|Y^1_4|^2 + C^2_{1,-1}|Y^0_4|^2 ,$$

$$F^2_0 = 2C^2_{20}|Y^2_4|^2 + C^2_{10}|Y^1_4|^2 ,$$

$$F^1_2 = H^1_2 = \tfrac{1}{2}(2C^2_{22}|Y^4_4|^2 + 5C^2_{21}|Y^3_4|^2 + 6C^2_{20}|Y^2_4|^2 + 5C^2_{2,-1}|Y^1_4|^2 + 2C^2_{2,-2}|Y^0_4|^2) ,$$

$$F^1_1 = H^1_1 = \tfrac{1}{2}(2C^2_{21}|Y^3_4|^2 + 5C^2_{11}|Y^2_4|^2 + 6C^2_{10}|Y^1_4|^2 + 5C^2_{1,-1}|Y^0_4|^2 + 2C^2_{2,-1}|Y^1_4|^2) ,$$

$$F^1_0 = H^1_0 = \tfrac{1}{2}(2C^2_{20}|Y^2_4|^2 + 5C^2_{10}|Y^1_4|^2 + 3C^2_{00}|Y^0_4|^2) ,$$

$$F^0_2 = 3(C^2_{21}|Y^3_4|^2 + C^2_{2,-1}|Y^1_4|^2)$$

$$F^0_1 = 3(C^2_{11}|Y^2_4|^2 + C^2_{1,-1}|Y^0_4|^2) ,$$

$$F^0_0 = 3C^2_{10}|Y^1_4|^2 ,$$

$$H^0_2 = 4C^2_{22}|Y^4_4|^2 + 5C^2_{21}|Y^3_4|^2 + 5C^2_{2,-1}|Y^1_4|^2 + 4C^2_{2,-2}|Y^0_4|^2 ,$$

$$H^0_1 = 4C^2_{21}|Y^3_4|^2 + 5C^2_{11}|Y^2_4|^2 + 5C^2_{1,-1}|Y^0_4|^2 + 4C^2_{2,-1}|Y^1_4|^2 ,$$

$$H^0_0 = 4C^2_{20}|Y^2_4|^2 + 5C^2_{10}|Y^1_4|^2 .$$

APPENDIX D: $\Omega^I_{\alpha\beta\gamma}$

The $\Omega^I_{\alpha\beta\gamma}$'s defined in Eq. (16) are tabulated in Tables VI–X. Columns in the tables which would have all zero entries have been left out. The quantities c' and d are the nuclear-spin–rotational angular momentum interaction energies defined in Eq. (2) and the abbreviations $u = \sqrt{\gamma_J}$, $v = (\mu_I \mu_J / \gamma_I)^{1/2}$, and $w = (\gamma_I \mu_J / \mu_I)^{1/2}$ have been used. Here $\gamma_J = \frac{1}{3}J(J+1)$, $\gamma_I = \frac{1}{3}I(I+1)$, $\mu_J = \frac{2}{15}J(J+1)(2J-1)(2J+3)$ and $\mu_I = \frac{2}{15}I(I+1)(2I-1)(2I+3)$. For $o-\mathrm{H}_2(J = I = 1)$ these last four quantities have values $\gamma_J = \gamma_I = \frac{1}{2}\mu_J = \frac{1}{2}\mu_I = \frac{2}{3}$. Nonzero $\Omega^I_{\alpha\beta\gamma}$ which are not shown can be obtained from those in the tables by use of the relation

$$\Omega^I_{\alpha\beta\gamma} = -\Omega^I_{\tilde{\alpha}\tilde{\beta}\tilde{\gamma}} , \tag{D1}$$

where $\tilde{\alpha} = (l, -m_l)$ when $\alpha = (l, m_l)$.

[*] Address after September 1, 1975: Laboratoire de Physique Éxperimentale, Departmente de Physique, École Polytechnique Fédérale de Lausanne, 33 av. de Cour, CH-1007 Lausanne, Switzerland.

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