

about 400 in the melt. The electrical conductivity of the solid¹⁴ at the melting point is $3 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ and the liquid¹⁸ is $8.4 \Omega^{-1} \text{ cm}^{-1}$, an increase of about 3000. Our observed increase in $T_1(\text{Li})$ is also large, but not as large as might be expected. We cannot say much else about molten LiF.

V. CONCLUSIONS

We have obtained jump frequencies of lithium and fluorine ions in a LiF single crystal over a wide temperature range with an accuracy comparable to conductivity and diffusion methods. As an added advantage, both quantities could be obtained for the same crystal by the

same set of measurements. It should be possible to extend this work to doped LiF crystals, or to other crystals containing nuclei with small quadrupolar interactions and reasonable magnetic moments.

ACKNOWLEDGMENTS

Several illuminating discussions were held with R. L. Garwin and C. P. Slichter. R. J. Blume and W. V. Kiselewsky developed most of the electronics for the experiment. Finally, we wish to thank A. G. Redfield for numerous suggestions on both the theoretical and experimental aspects of this work, and for his hospitality during the author's stay in his laboratory.

Nuclear Spin Relaxation by Translational Diffusion in Solids

M. EISENSTADT* AND A. G. REDFIELD

IBM Watson Laboratory, Columbia University, New York, New York

(Received 11 June 1963)

Expressions for T_1 and T_2 have been derived for dipolar relaxation via atomic diffusion using the general theory of nuclear spin relaxation. General methods of evaluating the autocorrelation functions of various terms in the dipole-dipole Hamiltonian are discussed, and cubic symmetry requirements are given. A random walk model is used for the calculation, but rough estimates are made of the effects of correlation in direction and time of successive jumps of atoms for the vacancy mechanism of diffusion; if account were taken of these correlations, the derived relaxation times might change by a factor of nearly 2. Detailed computations are made only in the limits of high and low field. The random walk model yields an expression for T_1 in the high-field limit identical to that given by Torrey. Zero-frequency spectral densities needed for computation of T_2 , and also T_1 at low field, are expressed as lattice sums involving only the dipolar interaction and the sum of the probabilities of n -step random walks between lattice points (an extension of the Polya problem). Detailed computations of T_1 and T_2 have been made for two or more species of spins diffusing on an NaCl or fcc lattice. The angular dependence of T_1 and T_2 may be large for the NaCl lattice in the high-field limit. The agreement with Torrey's theory for T_1 in the fcc lattice is good.

I. INTRODUCTION

THE possibility that nuclear magnetic resonance would be a useful technique for the study of atomic diffusion was suggested in the early paper of Bloembergen, Purcell, and Pound¹ and such studies have been made on a number of solids. The simplest theory of relaxation due to diffusion can be expressed by the formulas²

$$T_1^{-1} \approx \langle \omega_i^2 \rangle \tau_c (1 + \omega_0^2 \tau_c^2)^{-1}, \quad (1)$$

$$T_2^{-1} \approx \langle \omega_i^2 \rangle \tau_c \times \frac{1}{2} [1 + (1 + \omega_0^2 \tau_c^2)^{-1}]. \quad (2)$$

Here ω_0 is the resonance angular frequency, τ_c is of the order of the jump time for diffusion, and ω_i is the strength of the interaction of the nucleus with the per-

turbation responsible for relaxation, in frequency units. These expressions are based on the assumption of an autocorrelation function for the interaction of the simple form $\langle \omega_i^2 \rangle \exp(-t/\tau_c)$, as discussed in Sec. 5.7 of Ref. 2. They are applicable only to the "motionally narrowed" region of temperature; that is, where $\tau_c \ll \omega_i^{-1}$. This is the only region we will consider in this paper. For nuclei having spin $\frac{1}{2}$ or a small electric quadrupole moment, relaxation occurs via the magnetic dipolar interaction between spins, and ω_i is of the order of the rigid lattice linewidth, typically a few kc/sec. If relaxation occurs because of electric quadrupolar interactions, ω_i may be many Mc/sec. For systems in which ω_i is reasonably well known, Eqs. (1) and (2) can predict τ_c from T_1 and T_2 measurements to within an order of magnitude. For more precise results, it is necessary to use a more complicated correlation function based on a detailed model of the microscopic diffusion process. We will develop such a formulation in this paper. We restrict ourselves to the case of relaxation via magnetic dipolar interactions, because the form and

* Present address: Columbia University, Hudson Laboratories, Dobbs Ferry, New York.

¹ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

² C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, Inc., New York, 1963).

magnitude of these interactions are well known, at least for light nuclei, where electron-coupled spin interactions are negligible. In principle, this formulation could readily be extended to the case of quadrupolar relaxation due to vacancy motion, but this refinement of the simple theory did not seem warranted for that case, in view of the relatively poor knowledge of the quadrupolar interaction strength.

Torrey³ has developed a detailed theory of dipolar relaxation via translational diffusion, based on the BPP theory of relaxation¹ and applicable to a single spin species in a bcc or fcc lattice. Since then, the theories of BPP and Wangness and Bloch⁴ have been generalized and applied to complex systems. We will use the generalized theory,^{5,6} applied to two or more spin species diffusing in a NaCl lattice and also in a fcc lattice. Our starting point is similar to that of Torrey, but our method of calculation is different, being restricted to solids and designed to predict the large angular variations of T_1 and T_2 which have been observed.⁷

II. GENERAL METHOD

A. Model for Diffusion

A solid typically contains a fraction of vacant sites which is so small that the number of vacancies close to each other is negligible. Thus, the probability that a vacancy will jump in a given direction is independent of its previous history. This is not true for the atoms which diffuse as a result of vacancy motion; for example, an atom which has just jumped from one site to a neighboring vacant site has a probability C^{-1} , where C is the like-neighbor coordination number of jumping immediately back to where it came from. This correlation between successive jumps reduces the diffusion coefficient relative to that expected for a purely random walk process by a factor of the order of $1-C^{-1}$. The effect of correlations on the diffusion coefficient has been calculated precisely by a method due to Bardeen and Herring⁸ and Lidiard.⁹

The calculation of these correlation effects on spin relaxation is a more difficult problem because we are concerned with the relative motion of pairs of nuclei. To make a precise theory, explicit account must be taken of the vacancy mechanism. A relative displacement of two nearby spins occurs when a passing vacancy interchanges with one of them. The vacancy jumps on very rapidly, but there is a significant probability that

it will return once or more to the same spin (or to the other spin if they are both on the same sublattice) before wandering away to infinity. The time for these interchanges is small compared to the time the two spins must wait before another vacancy comes by, and all that matters is their *relative* positions after the vacancy has wandered away; the precise trajectory of the vacancy is irrelevant. Probabilities for various relative displacements of two spins resulting from the visit of a passing vacancy might be calculated by considering all possible trajectories of the vacancy, but to use these probabilities to compute a relaxation time would be a formidable task.

Instead, we use a simplified model of the solid in which nuclei are assumed to diffuse about independently on their appropriate lattice, with a jump probability or jump frequency ν which is constant in time and independent of their previous history.¹⁰ Estimates of the effect of correlations will be given in Sec. IV. Torrey's theory also neglects correlations, and his diffusion model is similar to ours.

B. Theory of Relaxation

Abragam⁵ has given a concise treatment of the general theory of relaxation via the dipolar interaction and we will use his results as our starting point. We will restrict our treatment to cubic crystals and assume there is no static quadrupolar interaction or quadrupolar relaxation. We suppose that there are two nuclear species present on the NaCl lattice which we label I and S , each on its own fcc sublattice. The case of a single species on a fcc lattice can be immediately obtained from the NaCl results. We neglect the possibility that measurements of T_1 for one species will produce transient nuclear polarization of the other species. A calculation by us of these cross relaxation effects indicate that for typical static magnetic fields used in relaxation experiments they are likely to be negligible.

The Hamiltonian of the spin system consists of the usual Zeeman interaction plus the sum over pairs of spins of the classical dipolar interaction. The dipolar interaction between two spins i and j can be most conveniently written as the sum

$$\hbar\mathcal{H}_{ij} = \sum_q F_{ij}^{(q)} A_{ij}^{(q)}. \quad (3)$$

The sum over q is from -2 to $+2$, and $A^{(q)}$ is a spin operator given in Abragam,¹¹ which connects spin states of the spins i and j differing by $\hbar q$ in total angular momentum ($m_i + m_j$). The $F^{(q)}$ are given by

$$F_{ij}^{(0)} = r_{ij}^{-3} (1 - 3\cos^2\theta_{ij}), \quad (4)$$

$$F_{ij}^{(1)} = r_{ij}^{-3} \sin\theta_{ij} \cos\theta_{ij} \exp(-i\varphi_{ij}), \quad (5)$$

¹⁰ In this paper ν denotes a jump frequency in sec^{-1} , and ω denotes a resonance frequency in $\text{rad}\cdot\text{sec}^{-1}$.

¹¹ See Ref. 5, p. 289.

³ H. C. Torrey, Phys. Rev. **92**, 962 (1953); **96**, 690 (1954); henceforth referred to as Torrey.

⁴ R. K. Wangness and F. Bloch, Phys. Rev. **89**, 728 (1953).

⁵ A. Abragam, *The Principles of Nuclear Magnetism* (The Clarendon Press, Oxford, England, 1961).

⁶ A. G. Redfield, I.B.M. J. Res. Develop. **1**, 19 (1957).

⁷ M. Eisenstadt, preceding paper, Phys. Rev. **132**, 630 (1963).

⁸ J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals* (John Wiley & Sons, Inc., New York, 1952).

⁹ A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 327.

$$F_{ij}^{(2)} = r_{ij}^{-3} \sin^2 \theta_{ij} \exp(-2i\varphi_{ij}), \quad (6)$$

$$F_{ij}^{(-q)} \equiv F_{ij}^{(q)*}. \quad (7)$$

Here r_{ij} , θ_{ij} , and φ_{ij} are polar coordinates of the vector \mathbf{r}_{ij} connecting positions of spins i and j ; the polar axis is the magnetic field direction and the azimuthal plane is arbitrary. Strictly speaking, $F^{(q)}$ is a lattice operator and we should solve the lattice Hamiltonian to determine its properties. Since this is impossible in practice, we treat $F^{(q)}$ as a classical quantity which varies randomly as the spins i and j move about the lattice.

The relaxation times are obtained in terms of correlation function of the $F^{(q)}$, defined by the equation

$$G_{ij}^{(q)}(\tau) = \langle F_{ij}^{(q)}(t) F_{ij}^{(q)*}(t+\tau) \rangle. \quad (8)$$

Here $F_{ij}^{(q)}(t)$ is the value of $F_{ij}^{(q)}$ at time t , and the average is carried over all time t , or equivalently over an ensemble. The nuclear spin relaxation times are given by certain sums of the Fourier transforms (spectral densities) of the $G^{(q)}$, defined by

$$J_{ij}^{(q)}(\omega) = \int_{-\infty}^{\infty} G_{ij}^{(q)}(\tau) e^{-i\omega\tau} d\tau. \quad (9)$$

Before writing expressions for the relaxation times, it is convenient to use the fact that identical spins will move in an identical way in a statistical sense. This means that $G_{ij}^{(q)}$ and $J_{ij}^{(q)}$ will be the same for all equivalent pairs of spins i and j . Thus, to calculate relaxation times for the I species we need know only the spectral density functions

$$g^{(q)} = NJ_{ij}^{(q)}, \quad (10)$$

$$\mathcal{K}^{(q)} = NJ_{ik}^{(q)}, \quad (11)$$

where spins i and j are any two I -species spins, k is an S -species spin, and for convenience we multiply by N , where N is the total number of I sites (or S sites). Then the relaxation times of the I species are given by

$$T_1^{-1} = \frac{3}{2}\gamma_I^4 \hbar^2 I(I+1) f_I \{ g^{(1)}(\omega_I) + g^{(2)}(2\omega_I) \} \\ + \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) f_S \left\{ \frac{1}{12} \mathcal{K}^{(0)}(\omega_I - \omega_S) \right. \\ \left. + \frac{3}{2} \mathcal{K}^{(1)}(\omega_I) + \frac{3}{4} \mathcal{K}^{(2)}(\omega_I + \omega_S) \right\}, \quad (12)$$

$$T_2^{-1} = \gamma_I^4 \hbar^2 I(I+1) f_I \\ \times \left\{ \frac{3}{8} g^{(0)}(0) + \frac{1}{4} g^{(1)}(\omega_I) + \frac{3}{8} g^{(2)}(2\omega_I) \right\} \\ + \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) f_S \left\{ \frac{1}{6} \mathcal{K}^{(0)}(0) + \frac{1}{24} \mathcal{K}^{(0)}(\omega_I - \omega_S) \right. \\ \left. + \frac{3}{4} \mathcal{K}^{(1)}(\omega_I) + \frac{3}{2} \mathcal{K}^{(1)}(\omega_S) + \frac{3}{8} \mathcal{K}^{(2)}(\omega_I + \omega_S) \right\}. \quad (13)$$

Here I , γ_I , ω_I , and f_I are the spin, gyromagnetic ratio, resonance frequency, and fractional isotopic abundance of the I species; similarly for the S species. In computing sum and difference frequencies $\omega_I \pm \omega_S$ it is important to assign opposite signs to ω_I and ω_S if γ_I and γ_S are of opposite sign. Expressions for the relaxation times of

the S species are obtained by reversing I and S . Equations (12) and (13) are obvious generalizations of Eqs. (77), (88a), (79), and (89) in Abragam.¹² The formidable appearance of (12) and (13) is somewhat misleading; to the approximation we shall use, the calculations of the various terms are all quite similar, and many can be neglected.

The central objective of this work is to calculate the correlation functions $G(\tau)$ or, more precisely, their Fourier transforms. We note first that lattice vibrations can be ignored. It is well known that lattice vibrations produce negligible relaxation in themselves; thus the dipolar interaction between jumps can be replaced by its value averaged over many lattice vibrations, since the jump frequency is always slow compared to the lattice frequency. This average interaction is equal to the interaction the spins would have if they were sitting stationary on their equilibrium lattice points.¹³ Thus, we assume that the spins are stationary between jumps.

We will work in a coordinate system in which spin i of the I species is fixed at the origin (we will call this the *reference spin*) and the other spin j or k moves about, one lattice spacing at a time. If we wish to calculate $g^{(q)}(\omega)$, we consider the other spin (which we will call the *moving spin*) to be jumping about on the I lattice, one of whose points is the origin. In this relative coordinate system the probability μ that the moving spin will jump is $\mu = 2\nu_I$, where ν_I is the jump probability or jump frequency for a single I spin in the usual fixed coordinate system.

To calculate $\mathcal{K}^{(q)}(\omega)$, the moving spin k is confined to the S lattice, which is displaced from the origin or reference spin. The jump probability in the relative coordinate system is $\mu = \nu_I + \nu_S$. In what follows, we will not explicitly discuss calculations of the $\mathcal{K}^{(q)}$ since they are similar to those of the $g^{(q)}$.

If we denote points on the I lattice by l and m we can express the correlation functions as

$$G^{(q)}(\tau) = \sum_{lm} P_l(t) F_l^{(q)} P(l, t; m, t+\tau) F_m^{(q)*}. \quad (14)$$

Here $F_l^{(q)}$ is equal to $F_{ij}^{(q)}(\mathbf{r}_{ij})$ for $\mathbf{r}_{ij} = \mathbf{r}_l$, $P_l(t)$ is the probability that the moving spin occupies the point l at time t , and $P(l, t; m, t+\tau)$ is the conditional probability of finding it on m at $t+\tau$ if it was on l at time t .

The general expression (14) simplifies considerably in our model which ignores correlations. The probability of occupancy of all points is the same, so

$$P_l(t) = N^{-1}. \quad (15)$$

Since the direction of successive jumps is random, and

¹² See Ref. 5, Chap. VIII.

¹³ This true to second order in the rms lattice vibration amplitude only for cubic crystals, provided correlations in the motion of neighboring atoms are ignored. This follows quite generally from the fact that the dipolar interaction $\mathcal{K}_{ij}(r_{ij})$ obeys the equation $\nabla^2 \mathcal{K}_{ij}(r_{ij}) = 0$.

the jump probability is time-independent, we can rewrite the conditional probability as the sum

$$P(l, t; m, t + \tau) = \sum_n p_n(\tau) P_n(r_{lm}). \quad (16)$$

Here $p_n(\tau)$ is the probability that the moving spin will make exactly n jumps in a time τ , and $P_n(r_{lm})$ is the probability that a random walk of exactly n steps will end on m if it started on l . $P_n(r_{lm})$ is a function only of the distance r_{lm} between l and m , and is equal to the number of n -step paths connecting l and m , divided by C^n , the total number of n -step paths starting from l . In calculating $P_n(r_{lm})$ for the like-neighbor case, we do not exclude paths through the origin, even though these are physically impossible. This greatly simplifies the calculation, and probably does not affect the final results significantly. Of course, the sum over l and m in Eq. (14) excludes the origin. The probability p_n can be shown to be the n th term of the Poisson distribution¹⁴

$$p_n(\tau) = (\tau\mu)^n \exp(-\mu\tau) / n! \quad (17)$$

The Fourier cosine transform of p_n is¹⁵

$$\begin{aligned} \mathfrak{F}_n(\omega, \mu) \equiv 2 \int_0^\infty p_n(\tau) \cos \omega \tau d\tau = & \frac{2}{\mu} \left(\frac{1}{1 + \omega^2/\mu^2} \right)^{n+1} \\ & \times \sum_{0 \leq 2r \leq n+1} (-1)^r \binom{n+1}{2r} \left(\frac{\omega}{\mu} \right)^{2r}, \end{aligned} \quad (18)$$

where the usual binomial coefficient notation is used. The \mathfrak{F}_n can be reduced¹⁶ to the analytic expression

$$\mathfrak{F}_n = 2\mu^{-1} \cos[(n+1)\psi] \cos^{n+1}\psi, \quad (18a)$$

where $\psi = \tan^{-1}(\omega/\mu)$.

Combining (9) and (10) with (14)–(18) and assuming $G^{(q)}(\tau)$ is an even function of τ as required by the principle of microscopic reversibility, we obtain

$$\mathcal{G}^{(q)}(\omega) = \sum_n \mathfrak{F}_n(\omega, \mu) \sum_{lm} P_n(r_{lm}) F_{lm}^{(q)}, \quad (19)$$

where $F_{lm}^{(q)}$ is an abbreviation for the real part of $F_l^{(q)} F_m^{(q)*}$. Only the real part of $F_l^{(q)} F_m^{(q)*}$ enters into the sum (14) since its complex conjugate $F_m^{(q)} F_l^{(q)*}$ occurs with the same coefficient. This latter term corresponds to the inverse (or time reversed) path and both paths will have equal probabilities at equilibrium. The $F_{lm}^{(q)}$ are given by

$$F_{lm}^{(0)} = (1 - 3\cos^2\theta_l)(1 - 3\cos^2\theta_m) / r_l^3 r_m^3, \quad (20)$$

$$F_{lm}^{(1)} = \sin\theta_l \cos\theta_l \sin\theta_m \cos\theta_m \cos(\varphi_l - \varphi_m) / r_l^3 r_m^3, \quad (21)$$

$$F_{lm}^{(2)} = \sin^2\theta_l \sin^2\theta_m \cos(2\varphi_l - 2\varphi_m) / r_l^3 r_m^3. \quad (22)$$

¹⁴ W. Feller, *An Introduction to Probability Theory and its Applications* (John Wiley & Sons, Inc., New York, 1958).

¹⁵ A. Erdelyi, *Tables of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 1, p. 14.

¹⁶ Equation (18a) can be obtained if the sum is replaced by $\frac{1}{2}[(1+i\omega/\mu)^{n+1} + (1-i\omega/\mu)^{n+1}]$.

Here r_l, θ_l, φ_l are polar coordinates of the vector \mathbf{r}_l connecting the reference spin with the point l ; the polar axis is the field direction. The method of evaluating (19) is discussed in Sec. III.

C. Symmetry

It is useful to state cubic symmetry requirements on T_1 and T_2 before proceeding. Any relaxation rate will have the form

$$T_1^{-1}, T_2^{-1} = C_1 + C_2 \sum_{i=1}^3 \cos^4 \xi_i, \quad (23)$$

where $\cos \xi_i$ is the i th direction cosine of the magnetic field with respect to the crystal axes. This form follows from the fact that the angular part of the $F_{lm}^{(q)}$ can be represented as a vector function of $\mathbf{r}_l, \mathbf{r}_m$ and \mathbf{H}_0 . For example,

$$F_{lm}^{(1)} = (\mathbf{r}_l \cdot \mathbf{H}_0)(\mathbf{r}_m \cdot \mathbf{H}_0)(\mathbf{r}_l \times \mathbf{H}_0) \cdot (\mathbf{r}_m \times \mathbf{H}_0) / r_l^5 r_m^5 H_0^4. \quad (24)$$

If we rewrite (24) in Cartesian coordinates coinciding with the cubic axes, only direction cosines of \mathbf{H}_0 appear, and only up to the fourth power. Any cubically symmetric sum of the $F_{lm}^{(q)}$ such as $\mathcal{G}^{(q)}$ can contain only even powers of the direction cosines of \mathbf{H}_0 because of reflection symmetry, and all such sets of direction cosines reduce to the form (23).

Turning to the limit of high temperature, it is well known that in this limit $T_1 = T_2$. It does not seem to have been stated in the literature that in this case T_1 and T_2 are independent of angle if there is cubic symmetry. (For noncubic symmetry neither statement is true.) The relaxation times approach constant values independent of \mathbf{H}_0 when the resonance frequency is small compared to the jump frequency. Thus we first study how the magnetization behaves in zero external field, and then carry the result for zero field over to finite field. Suppose that at $t=0$ the field is turned off. Then the magnetization is expected to obey a linear equation:

$$d\mathbf{M}/dt = -W\mathbf{M}. \quad (25)$$

Here W is, in general, a tensor; it is a scalar T_1^{-1} for a cubic crystal. Thus, in zero field T_1 is isotropic. In finite field the usual terms $\gamma\mathbf{M} \times \mathbf{H}_0 + W\mathbf{M}_0$ are added, but T_1 will not change (and thus will remain isotropic) as long as $\gamma\mathbf{H}_0$ is much less than the inverse of the correlation or jump time. In the same limit this argument shows $T_1 = T_2$.

III. METHOD OF CALCULATION

We now come to the heart of the problem, which is the calculation of the spectral densities \mathcal{G} and \mathcal{K} . We achieve relative ease of calculation by restricting our calculation to solids, and by avoiding the domain where $\omega/\mu \approx 1$. We use two different methods of calculation, one for the *high-frequency* region ($\omega/\mu \gg 1$) and another

for the *low-frequency* region ($\omega/\mu \ll 1$). The ω occurring in the previous sentence refers to those frequencies which appear as arguments of the spectral densities in Eqs. (12) and (13), and may be multiples, sums, or differences of ω_I and ω_S , or zero.

In the *low-temperature* limit, where $\omega_I \pm \omega_S/\mu \gg 1$, the high-frequency approximation is used to calculate T_1 while the low-frequency approximation is used to calculate T_2 . The latter statement follows because $g^{(q)}(0) \gg g^{(q)}(\omega)$ if $\omega \gg \mu$. Of course, the present theory is only valid for T_2 in the "motionally narrowed" limit, in which T_2 is considerably greater than its rigid lattice value. At *high temperature*, defined by the condition $\omega_I \pm \omega_S/\mu \ll 1$, the low-frequency approximation is used for both T_1 and T_2 . At intermediate temperatures the spectral densities might be interpolated with some function similar to (1). We will not discuss the interpolation procedure further, but we remind the reader that any interpolation must be consistent with sum rules such as Eqs. (71) and (73) of Torrey. The intermediate temperature region can also be treated systematically using (18a), but the labor involved seems unjustified in view of the uncertainties introduced by correlation effects, as discussed in Sec. IV.

A. High-Frequency Approximation

It will be seen from (18a) that in the limit $\omega/\mu \gg 1$, $\mathfrak{F}_0(\omega)$ and $\mathfrak{F}_1(\omega)$ are much greater (by a factor ω^2/μ^2 or more) than $\mathfrak{F}_n(\omega)$ for $n > 1$. The sum of $P_n(r_{lm})F_{lm}^{(q)}$ can be shown to decrease with increasing n , thus, only the terms with $n=0, 1$ in (19) need be retained. Since $P_0(r_{lm}) = \delta_{lm}$, and $P_1(r_{lm}) = C^{-1}$, if and only if l and m are nearest neighbors, we have

$$g^{(q)}(\omega) = \frac{2\mu}{\omega^2} \left\{ \sum F_{ll}^{(q)} - C^{-1} \sum_{lm} {}^{(1)}F_{lm}^{(q)} \right\}. \quad (26)$$

To get (26) we used the fact that for $\omega \gg \mu$, $\mathfrak{F}_1(\omega) = -\mathfrak{F}_2(\omega) = 2\mu/\omega^2$. The superscript on the second sum is to indicate that the sum is only over points l and m which are nearest neighbors to each other. Equation (26) is identical to Torrey's Eq. (76).

The sum in (26) has been evaluated for two field orientations and the results are given in Table I. The first summation was carried over points l which are first through third neighbors of the origin, while the

TABLE I. Lattice sums needed to evaluate spectral densities in the limit of high frequency. The numbers given in this table correspond to a_0^6 times the sums in the curly bracket of Eq. (16). Here a_0 is the nearest neighbor (Na to Cl) distance.

Sum given	Orientation	$q=0$	1	2
$a_0^6(\omega^2/2\mu)g^{(q)}(\omega)$	[100]	0.98	0.248	0.86
(like neighbor)	[110]	1.36	0.206	0.86
$a_0^6(\omega^2/2\mu)\mathfrak{K}^{(q)}(\omega)$	[100]	13.7	0.087	4.75
(unlike neighbor)	[110]	3.82	1.19	3.64

double sum was carried over all pairs l and m for which either l or m is a nearest neighbor to the origin. The values in Table I are probably a few percent larger than the sum over all lattice points. The value of the sum for any orientation can be found using (23) if its values for two orientations are known.

B. Zero-Frequency Approximation

In the limit of zero frequency all the $\mathfrak{F}_n(\omega, \mu)$ approach the same value $2/\mu$. Then (19) can be rewritten as

$$g^{(q)}(0) = \frac{2}{\mu} \sum_{lm} F_{lm}^{(q)} Z(r_{lm}), \quad (27)$$

where

$$Z(r_{lm}) = \sum_n P(r_{lm}). \quad (28)$$

It is interesting to discuss the physical meaning of the quantity $Z(r_{lm})$. With the aid of (16) and (18a) we find

$$Z(r_{lm}) = \mu \int_0^\infty P(l, 0; m, \tau) d\tau. \quad (29)$$

Thus, $Z(r_{lm})$ is the jump frequency multiplied by the average time a randomly walking particle spends on point m after initially being placed on point l . In other words, $Z(r_{lm})$ is the average number of times a particle will visit m , if it randomly walks from l .

$Z(r)$ has been evaluated¹⁷ directly (see Appendix A) for $r=0, \sqrt{2}a_0$, and $2a_0$ (where a_0 is the Na to nearest Cl distance) and it is found that $Z(0) = 1.347$; $Z(\sqrt{2}a_0) = 0.347$; and $Z(2a_0) = 0.231$. For $r > 2a_0$ we used the asymptotic form $Z(r) = 3a_0/2\pi r$ which is obtained from the fact that for large r_{lm} , $P(l, 0; m, \tau)$ must be a solution of the diffusion equation:

$$P(l, 0; m, \tau) \cong 2a_0^3(4\pi D\tau)^{-3/2} \exp(-r^2/4D\tau). \quad (30)$$

Setting the diffusion coefficient equal to $D = \frac{1}{3}a_0^2\mu$, and using (29), we get the asymptotic result. This approximation differs from our directly calculated result by only 3% for $r = 2a_0$.

Using these values of $Z(r)$, the sum (27) was obtained for $q=0$ only and for two field orientations. The sum was evaluated point by point for the first three sets of like and unlike neighbors of the reference spin; the important (~30%) contribution of more distant points was obtained by averaging over field orientation and by converting lattice sums to volume integrals. Negligible error is probably introduced by these approximations;

¹⁷ Calculation of $Z(0)$ was discussed by G. Polya, *Math. Ann.* **84**, 149 (1921). Montroll has shown analytically that $Z(0)$ is given by an integral which has been evaluated by G. N. Watson and is equal to $9[\Gamma(\frac{3}{2})]^6(2^{14/3}\pi^4)^{-1} = 1.3446610732$. See E. W. Montroll, in *Applied Combinatorial Mathematics*, edited by E. F. Beckenbach [John Wiley & Sons, Inc., New York, (to be published)]. Montroll also gives $Z(0)$ for the bcc and sc lattices, and gives an analytic integral form for $Z(r)$. Evaluation of $Z(r)$ to the accuracy required here is probably more easily accomplished with the approximations described in present article than with these integral forms.

most of the orientation dependence comes from the contribution of points nearest the origin.

These approximations are detailed in Appendix A; the results of this calculation are $(a_0^6\mu/2)g^{(0)}(0)=2.71$ and 3.27 for \mathbf{H}_0 in the $[100]$ and $[110]$ directions, respectively, and $(a_0^6\mu/2)\mathcal{K}^{(0)}(0)=12.76$ and 4.44 in the $[100]$ and $[110]$ directions.

C. Low- and High-Temperature Approximations

The low-temperature limits for T_1 and T_2 are readily obtained by substituting the above results and Table I into Eqs. (12) and (13).

The high-temperature limit requires more discussion. Since T_1 and T_2 are isotropic, field angular averages of the $g^{(a)}$ and $\mathcal{K}^{(a)}$ can be used. In Appendix A we show that the values of $F_{lm}^{(a)}$, averaged over field orientation (but keeping \mathbf{r}_l and \mathbf{r}_m constant) are given by

$$\begin{aligned} \frac{5}{4}\langle F_{lm}^{(0)} \rangle &= \frac{15}{2}\langle F_{lm}^{(1)} \rangle = \frac{15}{8}\langle F_{lm}^{(2)} \rangle \\ &= \left(\frac{3}{2} \cos^2\alpha_{lm} - \frac{1}{2}\right)r_l^{-3}r_m^{-3}, \end{aligned} \quad (31)$$

where α_{lm} is the angle between r_l and \mathbf{r}_m . Since $\langle g^{(0)} \rangle$, $\langle g^{(1)} \rangle$, and $\langle g^{(2)} \rangle$ are in the ratio 6:1:4, we obtain from (12) and (13),

$$T_1^{-1} = T_2^{-1} = \frac{5}{4}A_I\langle g^{(0)}(0) \rangle + \frac{5}{6}A_S\langle \mathcal{K}^{(0)}(0) \rangle, \quad (32)$$

where

$$A_I = \gamma_I^4 \hbar^2 I(I+1) f_I, \quad (33a)$$

and

$$A_S = \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) f_S. \quad (33b)$$

The $g^{(a)}$ and $\mathcal{K}^{(a)}$ must have angular variations of the form (23), so that their angle average is 0.8 times their value for \mathbf{H}_0 in the $[110]$ direction plus 0.2 times their $[100]$ direction value. This fact with Eq. (31) can be used to check sums such as those of Table I.

IV. EFFECT OF CORRELATIONS

So far we have calculated T_1 and T_2 for a simple but slightly unrealistic model characterized by jump probabilities ν_I and ν_S . It has been implied that the theory developed would be reasonably accurate if the true jump probabilities were used for ν_I and ν_S . By true jump probability, we mean the average number of jumps per second which an atom makes. This is the quantity inferred directly from ionic conductivity measurements, and is equal to the vacancy jump probability multiplied by vacancy concentration. We now discuss qualitatively the validity of this assumption for vacancy-induced diffusion (similar remarks apply to interstitial diffusion), and estimate the corrections which must be made in order to take account of the correlations in the probabilities of successive atomic jumps.

Correlations in the *directions* of successive jumps are known⁹ to reduce the diffusion coefficient for the fcc lattice by a factor of 0.78 relative to the random walk

value. These correlations arise because once a vacancy has interchanged with an atom there is a significant probability it will interchange with the same atom again, and if so it is likely to return the atom toward the general direction from which it came.

These directional correlations are also important for nuclear relaxation, but there is another, possibly more important, correlation which is irrelevant for diffusion. Atomic jumps have a greater than random tendency to be bunched into groups of two or more, each group being produced by a single vacancy. In nuclear relaxation we are interested in the time scale for successive jumps since we deal with temporal correlation functions, and this bunching effect must be taken into account.

First, consider the motion of a single spin j caused by a single vacancy. Suppose the vacancy has walked randomly from some distance and has jumped to the site occupied by spin j displacing it. The probability per unit time of the initial displacement is very small, being of the order of ν_v/N , where ν_v is the vacancy jump rate; but subsequently there is a high probability (of the order of $\frac{1}{4}$) that the spin j will be displaced one or more times by the same vacancy before the vacancy diffuses away to infinity. We call the individual spin displacements "jumps," and a series of such displacements produced by a single vacancy an "encounter."

It is of interest to know the average number of jumps per encounter. Despite the differences between this situation and that considered above in connection with the zero-frequency approximation, it can be shown that the average number of jumps per encounter is just the quantity $Z(0)=1.347$ mentioned there and calculated in Appendix A. This means that a spin j , once displaced by a vacancy, will be displaced an average of 0.347 times again by the same vacancy.

These subsequent jumps are likely to occur close in time after the initial jump (the probability that the vacancy will return to spin j after the vacancy makes 100 jumps is only about 0.02). In most cases, only the total displacement per encounter will enter into the result; the position which a spin may occupy between jumps during a single encounter has negligible influence on $G_{ij}^{(a)}$ because the spin spends so little time (of order $10/\nu_v$) at such an intermediate position, compared to the time ($>10^4/\nu_v$) it spends between encounters.

During an encounter a spin may be displaced by one like-neighbor distance $\sqrt{2}a_0$; or it may be displaced more than this distance or jump back to its original position. Probabilities for these various displacements might be computed along the lines outlined by Bardeen and Herring,⁸ but instead we may guess that the probability of zero displacement is about 0.1, that of unit ($\sqrt{2}a_0$) displacement is about 0.8, and the probability of more than unit displacement is about 0.1. A spin having a jump frequency of ν_I experiences $\nu_I/1.347$ encounters per second; of these only about 0.9 $\nu_I/1.347$ result in a

net displacement of the spin, and most of these displacements are unit displacements.

Turning now to the effect that these correlations in jump probabilities have on the spectral densities $g^{(a)}$ and $\mathcal{K}^{(a)}$, we consider first the $\mathcal{K}^{(a)}$, which result from unlike neighbor interactions. Since the two spins under consideration diffuse on different sublattices, the jumps of one spin are completely uncorrelated with those of the other (at the usual low-vacancy concentrations), hence, the two spins can be considered separately.

Consider first the high-frequency limit. The quantity $\mu \equiv \nu_I + \nu_S$ multiplying the *first* sum in (26) is just the probability per unit time of a relative displacement (of *any* magnitude) of one spin relative to another. This probability is reduced by the factor $0.9/1.347 \approx 0.7$ deduced above. The second term in (26) should presumably be multiplied by about $0.8/1.347$, since spin j makes about $(0.8/1.347)\nu_I$ single displacements per second. Since displacements of more than $\sqrt{2}a_0$ are possible in a single encounter, there should be added to (26) double sums with l and m separated by more than $\sqrt{2}a_0$, multiplied by numbers less than $\frac{1}{10}$. The net result is to multiply (26) by about 0.7, since the first sum in (26) is at least ten times the second, and opposite in sign.

In the zero-frequency limit, the terms in (27) with $l=m$ are still the most important in the sum, but terms for which $l \neq m$ and l or m are far from the origin are also significant. Most of these latter were handled with the implicit use of the diffusion equation, of which (30) is the solution. The correlation correction to the diffusion coefficient is 0.78, so the net correction to (27) is presumably to multiply μ by between 0.7 and 0.78

Correlation effects are likely to be even more important for like-neighbor interactions (and also for chemically identical unlike isotopes). Here both spins i and j must be considered as taking part in a single encounter. If spin j is the first to be displaced by a given vacancy, it will make 1.347 jumps as before, and spin i will make $Z(r)$ jumps, where r is the initial distance between i and j . Thus, there are $Z(0)+Z(r)$ *relative* jumps per encounter. Since there are $2\nu_I$ (relative) jumps per second there must be $2\nu_I[Z(0)+Z(r)]^{-1}$ encounters per second of a single vacancy with the two spins i and j . This is in contrast with $2\nu_I$ relative displacements in the random walk model. The probabilities for various relative displacements resulting from a single encounter are likely to be roughly the same as for a single spin; the probability for zero displacement and for more than unit displacement may be somewhat greater in the present case. Taking the probability for zero displacement in an encounter to be 0.1 as before, we conclude that the high-frequency approximation result (26) should be multiplied by about $0.9/[Z(0)+Z(\sqrt{2}a_0)] \approx 0.55$. Here we use the value of $Z(r)$ appropriate to the nearest neighbor because terms for which l is nearest to the origin are by far the most important in (25). The zero-

frequency result (27) should be divided by a number which is between the high-frequency correction of 0.55 and the diffusion coefficient correction of 0.78.

We have tried to show that correlation effects may play an even greater role in nuclear relaxation than in tracer diffusion. It is to be hoped that relaxation measurements will be as useful as diffusion measurements for the elucidation of diffusion mechanisms in solids.¹⁸ Unfortunately in most cases dipolar relaxation is partially obscured by quadrupolar and electronic relaxation, making such studies difficult.

V. SUMMARY OF RESULTS

In the high-field, low-temperature limit the results of this calculation can be summarized by the formulas

$$T_1^{-1} = j_1 A_I a_0^{-6} \nu_I \omega_I^{-2} + A_S a_0^{-6} (\nu_I + \nu_S) \times [k_0 (\omega_I - \omega_S)^{-2} + k_1 \omega_I^{-2} + k_2 (\omega_I + \omega_S)^{-2}], \quad (34a)$$

$$T_2^{-1} = j_3 A_I a_0^{-6} \nu_I^{-1} + k_3 A_S a_0^{-6} (\nu_I + \nu_S)^{-1}. \quad (34b)$$

The numbers j and k are tabulated in Table II for the

TABLE II. Constants occurring in Eqs. (34) and (35) for three field orientations.

Lattice Orientation	j_1	k_0	k_1	k_2	j_3	k_3	j_4	k_4	
NaCl	[100]	2.78	2.28	0.26	7.12	1.03	4.25	3.96	10.2
	[110]	2.53	0.64	3.56	5.45	1.23	1.48	3.96	10.2
	[111]	2.45	0.09	4.66	4.90	1.30	0.56	3.96	10.2
fcc	[100]	2.78	0.163	0.744	1.29	1.03	0.92	3.96	5.27
	[110]	2.53	0.226	0.618	1.30	1.23	1.09	3.96	5.27
	[111]	2.45	0.247	0.576	1.30	1.30	1.15	3.96	5.27

NaCl lattice, and also for the fcc lattice of cube edge $2a_0$ containing two isotopes. The other terms have been previously defined. These relaxation times are those of the I species, assuming that the S species remains at thermal equilibrium. This assumption is likely to be valid unless the difference in resonance frequencies $|\omega_I| - |\omega_S|$ of the two species is small. The sum and difference frequencies $\omega_I \pm \omega_S$ are computed using opposite signs for ω_I and ω_S when γ_I and γ_S have opposite signs.

In the low-field, high-temperature limit the calculation predicts

$$T_1^{-1} = T_2^{-1} = j_4 A_I a_0^{-6} \nu_I^{-1} + k_4 A_S a_0^{-6} (\nu_I + \nu_S^{-1}). \quad (35)$$

These formulas by no means exhaust the applications of our calculations. They are applicable whenever ν_I and ν_S are not of the same order of magnitude as ω_I , ω_S , or $\omega_I \pm \omega_S$. Dynamic polarization of the S species through saturation of the I species could be easily treated, using Eq. (87) and (88).¹²

These results were obtained assuming that the I and S species walk randomly with jump probability ν_I and ν_S . If account were taken of the correlation in

¹⁸ P. G. Shewman, *Diffusion in Solids* (McGraw-Hill Book Company, Inc., New York, 1963).

direction of successive jumps of the nuclei, and of the tendency of jumps to occur close together, the results will be altered, as discussed in the previous section. For the NaCl lattice, j_1 will be multiplied by about 0.55 and k_0 , k_1 and k_2 by 0.75; j_3 and j_4 will be divided by roughly 0.65, and k_3 and k_4 by 0.75. For the fcc lattice j_1 , k_0 , k_1 , and k_2 will be multiplied by about 0.55 and j_3 , j_4 , k_3 , and k_4 divided by roughly 0.65

This calculation is in good agreement with Torrey's calculation of T_1 in the fcc lattice. In the high-field (low-temperature) limit our result for T_1^{-1} is 5% greater than that predicted from Torrey's Eq. (80). The discrepancy probably represents an error in our result due to omission of all but near neighbors in evaluating the second sum in (26); the error would be less for the $\mathcal{K}^{(a)}(\omega)$ and in either case it is small compared to the correlation correction discussed in Sec. IV. In the low-field (high-temperature) limit our calculation yields a value for T_1^{-1} which is 18% larger than that of Torrey. This is reasonable agreement considering the differences between our respective models. The low-temperature angular dependence of T_1 and T_2 is small for the fcc lattice, according to our theory, but it is easy to see from (26) that for the bcc lattice the angular variation should be large (of the order of 2:1). No indication of such angular dependence has been reported in measurements¹⁹ on bcc metals.

APPENDIX A: DETAILS OF THE ZERO-FREQUENCY APPROXIMATION

We first describe the method of calculation of $P_n(\mathbf{r})$, which is C^{-n} multiplied by the number of n -step paths from one point to another at a distance \mathbf{r} from the first. Choose $\mathbf{r} = a_0 \sum k_i \mathbf{x}_i$ where the \mathbf{x}_i are unit cube axis vectors and the k_i are integers. Each step in a path can be represented by a symbol such as (0+-) or (- -0); the symbol (0+-), for example, signifies no displacement in the x_1 direction and positive and negative displacements, respectively, in the x_2 and x_3 directions. A path of n steps can be represented by an array of n such symbols. Such an array has 3 columns and n rows. Each row must have one and only one zero, so there are n zeros. If there are $n-n_1$ zeros in the first column, $n-n_2$ in the second, and $n-n_3$ in the third, then there are $n!/(n-n_1)!(n-n_2)!(n-n_3)!$ distinct ways to distribute the n zeros under this requirement. The number n_i is the number of steps in the $\pm x_i$ direction, so such a path can connect the origin with \mathbf{r} only if for all i , n_i is odd or even as k_i is odd or even. In that case, there are

$$\prod_i n_i! / \left[\left(\frac{n_i - k_i}{2} \right)! \left(\frac{n_i + k_i}{2} \right)! \right] \quad (\text{A1})$$

ways to distribute pluses and minuses on the array to

have the path end on \mathbf{r} , because the number of \pm signs in the i th column must be $\frac{1}{2}(n_i \pm k_i)$. Summing over all allowed n_i we have

$$P_n = n! C^{-n} \sum_{n_1=k_1}^n \sum_{n_2=k_2}^n \prod_{i=1}^3 n_i! / \left[(n-n_i)! \left(\frac{n_i+k_i}{2} \right)! \left(\frac{n_i-k_i}{2} \right)! \right]. \quad (\text{A2})$$

Here $n_3 = 2n - n_1 - n_2$; terms in the summation for which any of the $\frac{1}{2}(n_i - k_i)$ is negative or nonintegral are to be taken as zero. To obtain the quoted values of $Z(\mathbf{r})$, P_n was computed for $n \leq 10$; for $n > 10$ an asymptotic expression was used which is based on the fact that for large n the overwhelming majority of paths will have all n_i approximately equal to $\frac{2}{3}n$. The probability of a net displacement of k_i steps during a one-dimensional random walk of $\frac{2}{3}n$ steps is $(3/\pi n) \exp(-3k_i^2/4n)$ for large n , so that in the three-dimensional case we have

$$P_n(\mathbf{r}) = \frac{1}{4} \left(\frac{3}{\pi n} \right)^{3/2} \exp\left(-\frac{3r^2}{4na_0^2} \right). \quad (\text{A3})$$

The factor $\frac{1}{4}$ is required because, for a randomly chosen set of n_i subject to the condition $\sum n_i = 2n$, there is a probability $\frac{1}{4}$ of fulfilling the condition that, for all i , n_i be odd or even as k_i is odd or even. The expression (A3) was integrated from $n = 10.5$ to infinity to estimate the terms in (28) for $n > 10$. The part of the summation for $n > 10$ is about 0.14 for $r \leq 2a_0$.

The evaluation of (27) was carried out point by point for $l = m$ in the first three shells, and also for $r_{lm} = \sqrt{2}a_0$ with either r_l or r_m in the first shell. By a "shell" we mean a set of points equidistant from the origin. In what follows we will use the abbreviation $(l) = 1$ to mean that point l is in the first shell.

All other terms in (27) were treated by an approximation in which a magnetic field orientation average was first taken; thus these other terms were assumed isotropic. However, in the case of the sum for unlike neighbors the $F_{lm}^{(0)}$ are identically zero if \mathbf{H}_0 is in the $[111]$ direction and either (l) or $(m) = 1$, or if \mathbf{H}_0 is in the $[100]$ direction and either (l) or $(m) = 2$. The exact angular variation of all terms of the sum involving these shells was inferred using the angular form (23).

In order to perform the field average, the value of $\langle F_{lm}^{(a)} \rangle$ given by (31) was used. To obtain (31), the $F_{lm}^{(a)}$ are written in vector form [e.g., Eq. (24)] and then rewritten in terms of components of \mathbf{r}_l , \mathbf{r}_m , and \mathbf{H}_0 in a Cartesian coordinate system for which \mathbf{r}_l is along the Z axis and \mathbf{r}_m is in the x - z plane. Taking the spherical average of the products of direction cosines of \mathbf{H}_0 occurring in this expression, we readily obtain (31). Equation (31) was used for those l, m for which either (l) or $(m) = 1$ and $r_{lm} > \sqrt{2}a_0$, and also for $l = m$, $(l) > 3$.

¹⁹ D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

Those terms $l \neq m$, for which $(l), (m) > 1$ and those for which either (l) or $(m) > 3$ were averaged over orientation of \mathbf{r}_l with respect to \mathbf{r}_m . This is a good approximation for most shells of neighbors which contain many points. The quantity $F_{lm}^{(0)}Z(r_{lm})$ for these points was replaced by

$$\begin{aligned} \langle \langle F_{lm}^{(0)} \rangle Z(r_{lm}) \rangle & \equiv \langle \frac{4}{5} (\frac{3}{2} \cos^2 \alpha_{lm} - \frac{1}{2}) r_l^{-3} r_m^{-3} (3a_0/2\pi r_{lm}) \rangle \\ & = \frac{6}{25\pi r_l^6 r_m} \quad \text{if } r_l > r_m. \quad (\text{A4}) \end{aligned}$$

Here the inner angular bracket on $F_{lm}^{(0)}$ is the field average previously introduced in connection with (31), and the outer bracket represents the angular average over the direction of \mathbf{r}_l , keeping \mathbf{r}_m fixed, and keeping the magnitudes r_l and r_m fixed. Note that the asymptotic expression for $Z(r)$ is used in (A4). This integration is straightforward. When $(l) = (m)$ the expression above was multiplied by $(1 - 5n_l^{-1/2})$, where n_l is the number of points at radius r_l ; the term $-5n_l^{-1/2}$ results from the exclusion, in the spherical average over \mathbf{r}_l

orientation, of a region near $\mathbf{r}_l = \mathbf{r}_m$ occupying $1/n_l$ of the total solid angle. This exclusion was made to avoid double counting of points for $l = m$ which were already summed above, and to avoid the region of integration $r_{lm} \approx 0$ where the asymptotic expression for $Z(r_{lm})$ was invalid.

Finally, the contribution of points for which either (l) or $(m) > 7$ was approximated by

$$\begin{aligned} \frac{6}{25\pi} \sum_m \frac{2\rho}{r_m} \int_{R_s}^{\infty} \frac{4\pi r^2 dr}{r^6} \\ + \frac{6}{25\pi} \int_{R_s}^{\infty} 4\pi r'^2 \left(\frac{2\rho^2}{r'} \int_{r'}^{\infty} \frac{4\pi r^2 dr}{r^6} \right) dr'. \quad (\text{A5}) \end{aligned}$$

The sum over m is taken over all $(m) \leq 7$ and R_s is the radius of a sphere whose volume equals that of the first seven shells. The quantity ρ is the density of points in the lattice, i.e., $1/2a_0^3$. The first term in (A5) approximates the sum over pairs l, m for which one member of the pair is within R_s and the other is outside; the factor 2 is included because each pair must be summed twice in (27). The second term approximates the sum for both l and m outside R_s .