which the Cd^{111} is contained. The vibrations might, in turn, cause reorientations of the spin in times shorter than τ_N. Such vibrations, on the other hand, should be very short lived and this, too, seems an unlikely mechanism.

It should be emphasized that for γ-γ cascades following almost instantaneously after K capture, the electronic configuration during the lifetime of the intermediate state of the nucleus is less clearly defined than it would be for a γ-γ cascade from a long-lived isomer, such as 48-min Cd^{111}. In such a case, the radiation from the isomer could be observed in a normal chemical environment. For all other correlations than pure γ-γ and γ-conversion electron, the surroundings of the nucleus in its intermediate state are not well known and it is difficult to draw quantitative conclusions from observed perturbations of the correlation.

IX. ACKNOWLEDGMENTS

Our interest in this subject was aroused through discussion of a related subject with Professor N. Bloembergen. We wish to thank him and also Professor H. Brooks, Professor M. Deutsch, Dr. M. Goldhaber, and Professor E. M. Purcell for helpful discussions. One of us (A.A.) wishes to thank the Shell Oil Company for support through a research grant.

PHYSICAL REVIEW VOLUME 92, NUMBER 4 NOVEMBER 15, 1953

Nuclear Spin Relaxation by Translational Diffusion*

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(Received July 21, 1953)

The general theory of Bloembergen, Purcell, and Pound of nuclear spin relaxation has been extended to a more quantitative study of relaxation by translational diffusion. It has been found necessary to treat the problem by the theory of random walk. In the case of isotropic diffusion two cases have been studied: one in which the flight distance has a probability distribution, and the other in which it is constant. The problem of random walk to nearest neighbor sites in a lattice is also treated and quantitative results are obtained for a face-centered cubic lattice.

I. INTRODUCTION

BLOEMBERGEN, Purcell, and Pound have given a general solution to the problem of nuclear spin relaxation.[1,2] An important and prevalent mechanism has been shown to be the coupling of spin orientation with nuclear thermal motion via the dipolar magnetic interaction of the nuclear moments. This influence and the corresponding relaxation are particularly strong whenever the nuclei perform random diffusive motions such as occur in liquids of appropriate viscosity. Such diffusive motions may occur also in the solid phase particularly in the case of solid solutions; for example, hydrogen in palladium, but also in the case of self-diffusion. Bloembergen[2] has applied his theory to diffusive motions. His treatment of translational diffusion is, however, admittedly crude and must be regarded as only semiquantitative. It is the purpose of this paper to present a more quantitative theory and in particular to emphasize the possibility of examining certain microscopic details of the diffusion process which cannot be ascertained from a study of gross diffusion phenomena alone. In Bloembergen's treatment only the diffusion constant D enters as a parameter. Thus his theory gives no basis for a closer study of the diffusion mechanism than can be obtained by conventional measurements of macroscopic diffusion. Nuclear spin relaxation is however essentially microscopic in character. The magnetic field of one nucleus at the position of another depends on the inverse cube of the distance and the influence of nearest neighbors is thus relatively strong. It is apparent from this that one needs to consider the individual motions of neighboring spins, that is to say, the process of random flights of which, as is well known, the phenomenon of diffusion is only the limiting macroscopic approximation. Thus it may be expected that certain details of random flights such as $\langle r^2\rangle$, the mean squared flight distance, and τ, the mean time between flights, will enter into the description of relaxation in other ways than merely in the familiar combination:

$$D=\langle r^2\rangle/6\tau. \qquad (1)$$

This is indeed the case and leads at least in principle to the possibility of independent measurement of these parameters in certain cases.

II. APPLICATION OF THE THEORY OF RANDOM FLIGHTS

We start from the general formula derived by Bloembergen[1,2] for the relaxation time T_1:

$$T_1^{-1}=\tfrac{3}{4}\gamma^4\hbar^2 I(I+1)[S_2(2\omega_0)+2S_1(\omega_0)]. \qquad (2)$$

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* Supported by the joint program of the U. S. Office of Naval Research and U. S. Atomic Energy Commission, by the Radio Corporation of America, and by the Rutgers Research Council.

[1] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[2] N. Bloembergen, thesis, Leiden, 1948 (Martinus Nijhoff, The Hague).

Here S_1 and S_2 are the spectral densities of the random time functions:

$$F_1=\sum_j F_{ij}^{(1)}(t), \tag{3a}$$

$$F_2=\sum_j F_{ij}^{(2)}(t), \tag{3b}$$

where

$$F_{ij}^{(1)}(t)=\sin\theta_{ij}\cos\theta_{ij}e^{i\varphi_{ij}}/r_{ij}^3, \tag{4a}$$

$$F_{ij}^{(2)}(t)=\sin^2\theta_{ij}e^{2i\varphi_{ij}}/r_{ij}^3, \tag{4b}$$

and $(r_{ij}, \theta_{ij}, \varphi_{ij})$ are the spherical coordinates of spin j relative to spin i and are to be regarded as random functions of the time.

The functions S_1 and S_2 may be more specifically defined as follows. Let $k_1(t)$ and $k_2(t)$ be correlation functions given by

$$k_1(t)=\sum_j\langle F_{ij}^{(1)}(t')F_{ij}^{(1)*}(t'+t)\rangle_{\text{Av}(t')}, \tag{5a}$$

$$k_2(t)=\sum_j\langle F_{ij}^{(2)}(t')F_{ij}^{(2)*}(t'+t)\rangle_{\text{Av}(t')}, \tag{5b}$$

where an asterisk denotes the complex conjugate.

Then

$$S_{1,2}(\omega)=\int_{-\infty}^{+\infty}e^{i\omega t}k_{1,2}(t)dt. \tag{6}$$

In evaluating the spectral density functions, we replace the time averages in (5) by ensemble averages. To do this we first introduce probability functions as follows:

(a) Let $P(\mathbf{r}, \mathbf{r}_0, t)d\mathbf{r}$ be the probability that, if spin j is located at zero time at $\mathbf{r}_0$ relative to spin i, at time t spin j will lie within the volume element $d\mathbf{r}$ located at $\mathbf{r}$ relative to the new position of spin i.

(b) Let $N^{-1}f(\mathbf{r}_0)d\mathbf{r}_0$ be the probability that at zero time, spin j is located in $d\mathbf{r}_0$ at $\mathbf{r}_0$ relative to spin i. N designates the number of spins in the system; thus $f(\mathbf{r}_0)$ is the initial spin density.

We may now write for the correlation functions the ensemble averages,

$$k_1(t)=\int\int P(\mathbf{r}, \mathbf{r}_0, t)F_{ij}^{(1)}(\mathbf{r}_0)F_{ij}^{(1)*}(\mathbf{r})f(\mathbf{r}_0)d\mathbf{r}_0d\mathbf{r}, \tag{7}$$

with a similar expression for $k_2(t)$. The sum over j in (5) has been replaced by multiplication by N.

The solution of the problem thus depends on the construction of the probability functions. Of these $f(\mathbf{r}_0)$ is an initial datum depending on the circumstances of the particular problem. Thus for a uniform spin density $f(\mathbf{r}_0)$ is a constant, while for lattice diffusion $f(\mathbf{r}_0)$ may be expressed as a sum over delta functions centered at the lattice points. The function $P(\mathbf{r}, \mathbf{r}_0, t)$ can be found from the theory of random flights as follows.

We shall assume that every position of a spin is statistically equivalent in the sense that at each position the same probability exists that after one flight from this position, the new spin position will be at $\mathbf{r}$ in $d\mathbf{r}$ relative to the previous position. We designate this probability by $P_1(\mathbf{r})d\mathbf{r}$ and the corresponding probability after n flights by $P_n(\mathbf{r})d\mathbf{r}$. The theory of random flights then gives[3]

$$P_n(\mathbf{r})=(1/8\pi^3)\int A^n(\boldsymbol{\varrho})\exp(-i\mathbf{r}\cdot\boldsymbol{\varrho})d\boldsymbol{\varrho}, \tag{8}$$

where the integration is over the whole of $\boldsymbol{\varrho}$ space.

The function $A(\boldsymbol{\varrho})$ occurring in (8) is defined by inverting the three-dimensional Fourier transform (8) in the case $n=1$:

$$A(\boldsymbol{\varrho})=\int P_1(\mathbf{r})\exp(i\boldsymbol{\varrho}\cdot\mathbf{r})d\mathbf{r}. \tag{9}$$

The probability $P(\mathbf{r}, t)d\mathbf{r}$ that a spin initially at the origin will at time t be located in $d\mathbf{r}$ at $\mathbf{r}$ is

$$P(\mathbf{r}, t)=\sum_n P_n(\mathbf{r})w_n(t), \tag{10}$$

where $w_n(t)$ is the probability that n flights take place in time t. For $w_n(t)$ we assume the Poisson distribution

$$w_n(t)=(1/n!)(t/\tau)^ne^{-t/\tau}, \tag{11}$$

where τ is the mean time between flights.

The sum in (10) includes of course $n=0$ where evidently

$$P_0(\mathbf{r})=\delta(\mathbf{r}), \tag{12}$$

$\delta(\mathbf{r})$ being the three-dimensional delta function.

Substituting (8) and (11) in (10) we get

$$P(\mathbf{r}, t)=(1/8\pi^3)\int\exp\{-i\mathbf{r}\cdot\boldsymbol{\varrho}-(t/\tau)[1-A(\boldsymbol{\varrho})]\}d\boldsymbol{\varrho}. \tag{13}$$

Finally $P(\mathbf{r}, \mathbf{r}_0, t)$ is found by

(a) forming the product

$$P(\mathbf{r}_i, t)P(\mathbf{r}_j-\mathbf{r}_0, t)d\mathbf{r}_id\mathbf{r}_j, \tag{14}$$

where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the position vectors of spins i and j relative to a common origin;

(b) transforming to relative-centroidal coordinates,

$$\mathbf{r}=\mathbf{r}_j-\mathbf{r}_i,\quad \mathbf{R}=\tfrac{1}{2}(\mathbf{r}_j+\mathbf{r}_i);$$

and (c) integrating (14) over all centroidal positions $\mathbf{R}$. If, as is usually the case, $A(\boldsymbol{\varrho})=A(-\boldsymbol{\varrho})$ the result is easily found to be

$$P(\mathbf{r}, \mathbf{r}_0, t)=(1/8\pi^3)\int\exp\{-i\boldsymbol{\varrho}\cdot(\mathbf{r}-\mathbf{r}_0)-(2t/\tau)\times[1-A(\boldsymbol{\varrho})]\}d\boldsymbol{\varrho}, \tag{15}$$

or

$$P(\mathbf{r}, \mathbf{r}_0, t)=P(\mathbf{r}-\mathbf{r}_0, 2t). \tag{16}$$

If the condition $A(\boldsymbol{\varrho})=A(-\boldsymbol{\varrho})$ does not hold, one must replace $A(\boldsymbol{\varrho})$ in (15) by $\tfrac{1}{2}[A(\boldsymbol{\varrho})+A(-\boldsymbol{\varrho})]$ and (16) no longer holds.

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[3] See, for example, S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

Substitution in Eq. (7) of $P(\mathbf{r}, \mathbf{r}_0, t)$ as given by (15), together with an appropriate $f(\mathbf{r}_0)$, completes the formal solution of the problem. In the following sections we shall investigate the results of particular assumptions as to the forms of $P_1(\mathbf{r})$ and $A(\boldsymbol{\varrho})$.

It might be thought that a useful approximation could be obtained by taking $P(\mathbf{r}, t)$ as that solution of the diffusion equation,

$$\partial P/\partial t = D\nabla^2 P, \tag{17}$$

with the initial form $P(\mathbf{r}, 0) = \delta(\mathbf{r})$. This solution is, as is well known,

$$P(\mathbf{r}, t) = (4\pi Dt)^{-\frac{3}{2}} \exp(-r^2/4Dt). \tag{18}$$

However, the conditions under which this approximation is justified are so stringent that it is unlikely to correspond, except under exceptional circumstances, to any physical reality. Equation (18) is of course the limiting case of the random flight theory in which the mean squared flight path $\langle r^2\rangle$ is small and the mean time τ between flights is short. It can in fact be obtained from the above theory under these assumptions, as will now be shown. In the case of isotropic diffusion we may expand (9) in powers of ρ:

$$A(\boldsymbol{\varrho}) = \sum_{n=0}^{\infty} \frac{(i\rho)^n}{n!} \int\int\int P_j(\mathbf{r}) r^{n+2} dr \cos^n\theta \sin\theta d\theta d\varphi,$$

or

$$A(\boldsymbol{\varrho}) = \sum_{n=0}^{\infty} (-1)^n \langle r^{2n}\rangle \rho^{2n}/(2n+1)! \tag{19}$$

$$= 1 - \tfrac{1}{6}\langle r^2\rangle\rho^2 + O(\rho^4), \tag{20}$$

where

$$\langle r^n\rangle = 4\pi \int_0^{\infty} P_1(\mathbf{r}) r^{n+2} dr \tag{21}$$

is the nth moment of the distribution $P_1(\mathbf{r})$.

If the series (19) is substituted in (13), it is clear that if $\langle r^2\rangle$ is sufficiently small and t/τ sufficiently large, the integral will be cut off by the term in ρ^2 in (19) before higher powers of ρ become effective. We then obtain precisely (18) with $D = \langle r^2\rangle/6\tau$. In the following section it will appear that the physical conditions thus imposed on $\langle r^2\rangle$ and τ are so severe that this approximation has little physical interest. Thus it is necessary to assume specific forms for $P_1(\mathbf{r})$ and examine their consequences. In Sec. III we treat the case of isotropic diffusion and in Sec. IV the case of random flights to nearest neighbor positions in a lattice.

III. ISOTROPIC DIFFUSION

The case of isotropic diffusion is defined by the conditions: (1) $A(\boldsymbol{\varrho})$ depends on the magnitude of $\boldsymbol{\varrho}$ only and (2) $f(\mathbf{r}_0) = n$ (uniform spin density). If these conditions hold, we may perform all integrations in the calculation of the correlation functions and their spectral densities save that over ρ which must await a specific choice for the form of $A(\boldsymbol{\varrho})$. As an illustration we shall carry out these calculations for $k_1(t)$ and $S_1(\omega)$. Substituting (4a) and (15) in (7) we obtain

$$k_1(t) = \frac{n}{4\pi} \int\int\int \frac{\sin\theta_0 \cos\theta_0 \cdot \sin\theta \cos\theta}{r_0{}^3 r^3} e^{i(\varphi_0 - \varphi)}$$
$$\times \exp\left\{ -i\boldsymbol{\varrho}\cdot(\mathbf{r} - \mathbf{r}_0) - \frac{2t}{\tau}[1 - A(\boldsymbol{\varrho})] \right\} d\mathbf{r} d\mathbf{r}_0 d\boldsymbol{\varrho}. \tag{22}$$

We now introduce expansions of $\exp(-i\boldsymbol{\varrho}\cdot\mathbf{r})$ and $\exp(i\boldsymbol{\varrho}\cdot\mathbf{r}_0)$ by means of the formula:

$$\exp(i\rho r \cos\Phi) = (\pi/2\rho r)^{\frac{1}{2}} \sum_{n=0}^{\infty} (2n+1) i^n J_{n+\frac{1}{2}}(\rho r) P_n(\cos\Phi), \tag{23}$$

where J_m and P_n are the usual Bessel and Legendre functions. For $P_n(\cos\Phi)$ in (23) we use the addition formula for the Legendre polynomials:

$$P_n(\cos\Phi) = P_n(\cos\theta)P_n(\cos\alpha) + \sum_{m=1}^{n} \frac{(n-m)!}{(n+m)!}$$
$$\times P_n{}^m(\cos\theta) P_n{}^m(\cos\alpha) \cos m(\varphi - \beta), \tag{24}$$

where (θ, φ) and (α, β) are the polar-azimuthal angular coordinates of two directions separated by the angle Φ. The integrals over r and r_0 have the limits a and ∞ where a may be physically interpreted as approximately the closest possible distance of approach of two nuclei. Making use of the orthonormal properties of the Legendre functions, we obtain after some reduction

$$k_1(t) = \frac{8\pi n}{15a^3} \int_0^{\infty} \exp\left\{ -\frac{2t}{\tau}[1 - A(\rho)] \right\} J_{\frac{3}{2}}{}^2(a\rho) \frac{d\rho}{\rho}. \tag{25}$$

A similar calculation for $k_2(t)$ gives

$$k_2(t) = 4k_1(t). \tag{26}$$

The spectral density function by Eq. (6) is, e.g.,

$$S_1(\omega) = 2\int_0^{\infty} \cos\omega t\, k_1(t) dt. \tag{27}$$

Substituting (25) in (27) and integrating first with respect to t, we get

$$S_1(\omega) = \frac{8\pi n\tau}{15a^3} \int_0^{\infty} J_{\frac{3}{2}}{}^2(a\rho) \frac{1 - A(\rho)}{[1 - A(\rho)]^2 + (\omega\tau/2)^2} \frac{d\rho}{\rho} \tag{28}$$

and

$$S_2(\omega) = 4S_1(\omega). \tag{29}$$

Before proceeding to discuss the consequences of possible assumptions as to the form of $A(\boldsymbol{\varrho})$, we first consider three limiting cases to which all possible choices of $A(\boldsymbol{\varrho})$ must conform.

We shall first consider the limiting cases (a) $\omega\tau \gg 1$ and (b) $\omega\tau \ll 1$. Since in practice we may assume that τ

varies with temperature according to

$$\tau=\tau_0 e^{E/kT}, \tag{30}$$

where E is an activation energy, these limiting cases give respectively the low-temperature and high-temperature asymptotes for T_1 in between which T_1 will have a minimum.

(*a*) ($\omega\tau\gg 1$). By Eq. (9)

$$|A(\boldsymbol{\rho})|\leq\int|\exp i\boldsymbol{\rho}\cdot\mathbf{r}|P_1(\mathbf{r})d\mathbf{r}=1.$$

Thus $1-A(\boldsymbol{\rho})$ never becomes larger than the order of unity, and we may neglect the factor $[1-A(\boldsymbol{\rho})]^2$ in the denominator of (28), obtaining

$$S_1(\omega)=\frac{32\pi n}{15a^3\omega^2\tau}\int_0^\infty J_{\frac{3}{2}}{}^2(a\rho)[1-A(\rho)]\frac{d\rho}{\rho}. \tag{31}$$

Thus,

$$T_1\propto\omega^2\tau=\omega^2\tau_0 e^{E/kT}. \tag{32}$$

(*b*) ($\omega\tau\ll 1$). Here we simply put $\omega\tau=0$ in the denominator of the integrand in (28) and obtain

$$S_1(\omega)=\frac{8\pi n\tau}{15a^3}\int_0^\infty\frac{J_{\frac{3}{2}}{}^2(a\rho)d\rho}{[1-A(\rho)]\rho}. \tag{33}$$

By Eq. (20) the integral in (33) always converges and so

$$T_1\propto 1/\tau=(1/\tau_0)e^{-E/kT}. \tag{34}$$

(*c*) We now consider the special case for which the mean flight path is long: $\langle r^2\rangle\gg a^2$. The function $1-A(\rho)$ which enters in the integrand of (28) in two places has the following general behavior. By Eq. (20) it vanishes at $\rho=0$; at large ρ it approaches unity by Eq. (9). It may increase monotonously or may oscillate about its asymptotic value. In any case, the rapidity with which it approaches unity is essentially determined by the magnitude of the mean squared flight path $\langle r^2\rangle$. Thus, if $\langle r^2\rangle\gg a^2$, the value of $P_1(\mathbf{r})$ is everywhere small and by Eq. (9) $1-A(\rho)$ approaches unity quickly for small values of $a\rho$. Thus it may be replaced by unity in the integrand of (28).

We then obtain

$$S_1(\omega)=\frac{8\pi n}{45a^3}\cdot\frac{\tau}{1+(\omega\tau/2)^2}, \tag{35}$$

and, for the relaxation time,

$$\frac{1}{T_1}=\frac{8\pi}{15}\gamma^4\hbar^2 I(I+1)\frac{n}{a^3}\left[\frac{\tau/2}{1+(\omega\tau/2)^2}+\frac{\tau}{1+\omega^2\tau^2}\right]. \tag{36}$$

It will be recognized that (35) and (36) have the well-known forms appropriate to an exponentially decaying correlation function with a "correlation time" $\tau_c=\tau/2$.

The minimum T_1 obtained from (36) when $\omega\tau=\sqrt{2}$ is given by

$$T_{1m}{}^{-1}=(16\sqrt{2}\pi/45)\gamma^4\hbar^2 I(I+1)n/a^3\omega. \tag{37}$$

It may be shown that the approximation made here by putting $A(\rho)=0$ is equivalent to the neglect of all but the first term in the series of Eq. (10).

(*d*) We now consider the consequences of assuming special forms for $P_1(\mathbf{r})$ and $A(\boldsymbol{\rho})$. We first take

$$P_1(\mathbf{r})=(4\pi D\tau r)^{-1}\exp[-r/(D\tau)^{\frac{1}{2}}], \tag{38}$$

which corresponds to

$$A(\boldsymbol{\rho})=[1+D\tau\rho^2]^{-1}. \tag{39}$$

Equation (39) is the mathematically simplest form for A which satisfies all the conditions that can be imposed for an acceptable form. It leads to a closed form solution for T_1 expressible in terms of elementary functions. We first show that the following physical conditions lead to (39). Let us suppose that a spin can exist in one of two states: (*a*) bound in a potential well, or (*b*) a thermally excited state in which the nucleus may move rapidly about in a random diffusive type of motion. We suppose that the motion in the excited state is so rapid that its details contribute only to very high frequencies in the Fourier spectrum $S(\omega)$ and have no effect on the relaxation. It is possible that this type of motion may approximate the motion of protons in highly rifted metallic lattices such as in hydrogenated palladium or other metallic hydrides. It will not be necessary to specify the excited state precisely, but we shall assume that the motion in this state can be described by the solution of the diffusion equation (17) given by Eq. (18). That is, we shall suppose that after a spin has vacated a trapping site and before capture by another, the probability after time t that it will be at $\mathbf{r}$ in $d\mathbf{r}$ relative to the site it has vacated is

$$(4\pi D't)^{-\frac{3}{2}}\exp(-r^2/4D't)d\mathbf{r}, \tag{40}$$

where D' is a diffusion coefficient appropriate to the excited state. We shall later see how D' is related to the overall diffusion constant D. We now multiply (40) by $e^{-t/\tau'}\cdot dt/\tau'$, which we take to be the probability that the nucleus will become trapped again after a time t in dt. Thus τ' is the mean life time in the excited state and will be small compared with $\tau-\tau'$, the mean life of the trapped state. Integrating the resulting expression over t we obtain the probability $P_1(\mathbf{r})d\mathbf{r}$ that a single jump (i.e., a single life in the excited state) will find the nucleus a distance $\mathbf{r}$ in $d\mathbf{r}$ from its starting place. Hence:

$$P_1(\mathbf{r})=\int_0^\infty(4\pi D't)^{-\frac{3}{2}}\exp(-r^2/4D't-t/\tau')dt/\tau'. \tag{41}$$

This integral is easily evaluated[4] and we get Eq. (38)

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[4] See, for example, W. Magnus and F. Oberhettinger, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949), p. 128.

TABLE I. Tables of the functions $f(\alpha, x)$ [Eq. (55)] and $\varphi(\alpha, x)$[Eq. (56)].

x	$f(1/12, x)$	$\varphi(1/12, x)$	$f(\frac{1}{2}, x)$	$\varphi(\frac{1}{2}, x)$
0.2			0.0130	0.0455
0.4	0.0266	0.0770	0.0688	0.1996
0.6	0.0552	0.1531	0.1451	0.3915
0.8	0.0890	0.2425	0.2286	0.5445
1.0	0.1265	0.3336	0.2920	0.6090
1.071				0.6128(max)
1.1			0.3112	0.6122
1.2	0.1685	0.4160	0.3215	0.5983
1.3			0.3231	0.5756
1.4	0.2046	0.4784	0.3182	0.5489
1.6	0.2353	0.5240	0.2942	0.4849
1.8	0.2596	0.5490	0.2582	0.4135
2.0	0.2753	0.5566	0.2290	0.3585
2.041		0.5568(max)		
2.2	0.2866	0.5534	0.1989	0.3075
2.4	0.2902	0.5392	0.1728	0.2649
2.6	0.2884	0.5185	0.1493	0.2281
2.8	0.2823	0.4931	0.1318	0.1998
3.0	0.2730	0.4655	0.1161	0.1757
3.6	0.2354	0.3813	0.0821	0.1269
4.2	0.1954	0.3070	0.0608	0.0936
4.8	0.1604	0.2475		
5.4	0.1323	0.2022		
6.0	0.1097	0.1667		
6.6	0.0918	0.1391		
7.2	0.0782	0.1180		
7.8	0.0669	0.0909		

with $D'\tau'$ in place of $D\tau$. Now clearly $D'\tau' = \langle r^2\rangle/6 = D\tau$, and so we get Eq. (39).

We shall now adopt Eq. (39) and examine its consequences. Substituting (39) in (28) we get

$$S_1(\omega) = (16\pi n/15a^3)\,\mathrm{Re}(J), \tag{42}$$

where

$$J = \int_0^\infty \frac{1+D\tau\rho^2}{2D\rho^2 - i\omega(1+D\tau\rho^2)} \cdot J_{\frac{3}{2}}^2(a\rho)\frac{d\rho}{\rho}. \tag{43}$$

If now we define

$$\beta^2 = i\omega/D(2-i\omega\tau), \tag{44}$$

we can put (43) in the form:

$$J = \frac{\tau}{2-i\omega\tau}\int_0^\infty \left[\left(1+\frac{1}{D\tau\beta^2}\right)\frac{\rho^2}{\rho^2-\beta^2} - \frac{1}{D\tau\beta^2}\right] J_{\frac{3}{2}}^2(a\rho)\frac{d\rho}{\rho}. \tag{45}$$

Making use of the integral formula,[5]

$$\int_0^\infty J_{\frac{3}{2}}^2(a\rho)(\rho^2-\beta^2)^{-1}\rho d\rho = (i\pi/2)J_{\frac{3}{2}}(a\beta)H_{\frac{3}{2}}^{(1)}(a\beta), \tag{46}$$

we obtain

$$J = i/3\omega + \{\pi/[\omega(2-i\omega\tau)]\}J_{\frac{3}{2}}(a\beta)H_{\frac{3}{2}}^{(1)}(a\beta), \tag{47}$$

where β is the root of (44) with positive imaginary part. Substituting (47) in (42), we get

$$S_1(\omega) = \frac{16\pi^2 n}{15a^3\omega}\,\mathrm{Re}\left\{\frac{J_{\frac{3}{2}}(a\beta)H_{\frac{3}{2}}^{(1)}(a\beta)}{2-i\omega\tau}\right\}. \tag{48}$$

If we put

$$a\beta = u + iv, \tag{49}$$

where u and v are real, we obtain from Eq. (44):

$$\begin{pmatrix} u \\ v \end{pmatrix} = \frac{(\omega a^2/2D)^{\frac{1}{2}}}{(4+\omega^2\tau^2)^{\frac{1}{4}}}\left\{1 \mp \frac{\omega\tau}{(4+\omega^2\tau^2)^{\frac{1}{2}}}\right\}^{\frac{1}{2}}. \tag{50}$$

If we define parameters x, q, and α by

$$\alpha = \langle r^2\rangle/12a^2, \quad x = (\omega a^2/D)^{\frac{1}{2}}, \tag{51}$$

$$q = \frac{\omega\tau/2}{[1+(\omega\tau/2)^2]^{\frac{1}{2}}} = \frac{\alpha x^2}{(1+\alpha^2 x^4)^{\frac{1}{2}}}, \tag{52}$$

we can write Eq. (50) as

$$\begin{pmatrix} u \\ v \end{pmatrix} = \frac{1}{2}\left[\frac{q(1\mp q)}{\alpha}\right]^{\frac{1}{2}}. \tag{53}$$

If now we substitute (49) in (48), and use the expressions of the half-integral Bessel and Hankel functions in terms of elementary functions,

$$J_{\frac{3}{2}}(z)H_{\frac{3}{2}}^{(1)}(z) = (1/\pi z)[1+1/z^2+(1+i/z)^2 e^{2iz}]$$

we get

$$S_1(\omega) = (8\pi n/15a^3\omega)f(\alpha, x), \tag{54}$$

where

$$\begin{aligned} f(\alpha, x) = (2/x^2)\{&v[1-1/(u^2+v^2)] \\ &+[v(1+1/(u^2+v^2))+2]e^{-2v}\cos 2u \\ &+u[1-1/(u^2+v^2)]e^{-2v}\sin 2u\}. \end{aligned} \tag{55}$$

The function $f(\alpha, x)$ is tabulated in Table I as a function of x for $\alpha = \frac{1}{12}$, $(\langle r^2\rangle = a^2)$ and $\alpha = \frac{1}{2}$, $(\langle r^2\rangle = 6a^2)$.

From (58), (29), and (2) we get for T_1:

$$T_1^{-1} = \tfrac{4}{5}\pi\gamma^4\hbar^2 I(I+1)(n/a^3\omega)\varphi(\alpha, x), \tag{56}$$

where $\varphi(\alpha, x) = f(\alpha, x) + f(\alpha, \sqrt{2}x)$.

The function $\varphi(\alpha, x)$ is tabulated as a function of x for $\alpha = \frac{1}{2}, \frac{1}{12}$ in Table I. In this table are also given the maximum values of $\varphi(\alpha, x)$ from which the minimum values of T_1 may be obtained.

The asymptotic forms of $\varphi(\alpha, x)$ for large and small x are of interest. First, if $\alpha x^2 = \omega\tau/2 \gg 1$ (limiting case of low temperature or high frequency), u and v reduce approximately to $u = 0$, $v = 1/(2\alpha)^{\frac{1}{2}}$, and

$$f(\alpha, x) = (4/3\omega\tau)F(v), \tag{57}$$

where

$$F(v) = (3/2v^3)[v^2 - 1 + (v+1)^2 e^{-2v}]. \tag{58}$$

For the relaxation time, we obtain in this case:

$$(\omega\tau \gg 1): \quad T_1^{-1} = (8\pi/5)\gamma^4\hbar^2 I(I+1)(n/a^3\omega^2\tau) \times F[(6a^2/\langle r^2\rangle)^{\frac{1}{2}}]. \tag{59}$$

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[5] G. N. Watson, *Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1944), second edition, p. 428, Eq. (4).

$F(v)$ as given by (58) descends monotonously from unity at $v=0$. For small v,

$$F(v)\simeq 1-\tfrac{2}{5}v^2+\tfrac{1}{3}v^3-(6/35)v^4+\cdots. \tag{60}$$

In order to obtain the limiting case for $\omega\tau\ll 1$, one may expand the Bessel and Hankel functions in (48) in powers of $a\beta$ and then proceed to the limit $\omega\tau\to 0$. In this way it is found that

$$(\omega\tau\ll 1):\quad T_1^{-1}=(4\pi/5)\gamma^4\hbar^2 I(I+1) \times(n\tau/a^3)(1+12a^2/5\langle r^2\rangle). \tag{61}$$

If in Eq. (50) one neglects $\omega\tau$ in comparison with unity, one obtains $u=v=x/2$ and, substituting these values in (55), one gets

$$f(\alpha,x)\simeq\frac{1}{x}-\frac{2}{x^3}+\frac{e^{-x}}{x}\left[\left(1-\frac{2}{x^2}\right)\sin x +\left[1+\frac{4}{x}+\frac{2}{x^2}\right]\cos x\right], \tag{62}$$

which no longer depends explicitly on α. If (62) is substituted in (56) one obtains precisely the same result that follows on taking for $P(\mathbf{r},t)$ the expression (18). A detailed analysis shows that (62) is valid only if in addition to $\omega\tau\ll 1$ one assumes $\langle r^2\rangle\ll 6a^2$. Thus (62) and inferentially (18) have only a very limited range of validity. Equation (62) has a maximum giving a minimum T_1, but of course does not behave correctly at the low temperature limit.

(*e*) As a final example we mention the case in which a nucleus walks randomly in direction, but makes jumps of equal magnitude l in distance. In this case we may take for $P_1(\mathbf{r})$:

$$P_1(\mathbf{r})=\delta(r-l)/4\pi l^2. \tag{63}$$

The corresponding $A(\boldsymbol{\rho})$ is given by

$$A(\boldsymbol{\rho})=(\sin l\rho)/l\rho, \tag{64}$$

and by Eq. (28)

$$S_1(\omega)=(8\pi n\tau/15k^3l^3)G(k,\tfrac{1}{2}\omega\tau), \tag{65}$$

where $k=a/l$ and

$$G(k,y)=\int_0^\infty J_{\frac{3}{2}}{}^2(kx)\frac{1-\sin x/x}{(1-\sin x/x)^2+y^2}\cdot\frac{dx}{x}. \tag{66}$$

We shall defer a detailed study of this case to the following section, in which it will be shown it has particular relevance in the case of lattice diffusion.

IV. LATTICE DIFFUSION

We now attempt to apply Eq. (7) with $P(\mathbf{r},\mathbf{r}_0,t)$ given by (15) to the case of random walk in a space lattice. We consider specifically the case in which a spin-bearing nucleus jumps between nearest-neighbor lattice sites. For $f(\mathbf{r}_0)$ we may take

$$f(\mathbf{r}_0)=c\sum\nolimits_k\delta(\mathbf{r}_0-\mathbf{r}_k), \tag{67}$$

where c is the ratio of the number of nuclei to the number of lattice sites. The sum is over all lattice sites. Also,

$$P_1(\mathbf{r})=(1/z)\sum_{i=1}^{z}\delta(\mathbf{r}-\mathbf{r}_i), \tag{68}$$

where the sum is over the z nearest neighbors of a lattice site. From (9) we find

$$A(\boldsymbol{\rho})=(1/z)\sum_{i=1}^{z}\exp(i\boldsymbol{\rho}\cdot\mathbf{r}_i). \tag{69}$$

It is not possible to carry out explicitly all the integrations to find $k(t)$ or $S(\omega)$ in the general case. We can, however, find $k(0)$ which normalizes the spectral density function according to the transform of (6):

$$k(t)=(1/2\pi)\int_{-\infty}^{+\infty}e^{-i\omega t}S(\omega)d\omega, \tag{70}$$

so that

$$k(0)=(1/2\pi)\int_{-\infty}^{+\infty}S(\omega)d\omega. \tag{71}$$

Putting $t=0$ in (15) and substituting in (7), we get

$$\begin{aligned}k(0)&=(c/8\pi^3)\int\int\int F(\mathbf{r}_0)F^*(\mathbf{r})\sum\nolimits_k\delta(\mathbf{r}_0-\mathbf{r}_k)\\&\qquad\times\exp[-i\boldsymbol{\rho}\cdot(\mathbf{r}-\mathbf{r}_0)]d\mathbf{r}d\mathbf{r}_0d\boldsymbol{\rho},\\&=(c/8\pi^3)\sum\nolimits_k\int\int F(\mathbf{r}_k)F^*(\mathbf{r})\\&\qquad\times\exp[-i\boldsymbol{\rho}\cdot(\mathbf{r}-\mathbf{r}_k)]d\mathbf{r}d\boldsymbol{\rho},\\&=c\sum\nolimits_k|F(\mathbf{r}_k)|^2.\end{aligned} \tag{72}$$

Making use of (4a) and (4b) we find, after averaging over all crystal orientations,

$$k_1(0)=(2c/15)\sum\nolimits_k r_k^{-6};\quad k_2(0)=4k_1(0). \tag{73}$$

There is one extreme case in which an explicit result for $S(\omega)$ may be obtained, namely the case $\omega\tau\gg 1$, i.e., the low-temperature asymptote.

For $S(\omega)$ we have, in general,

$$S(\omega)=c\tau\sum_k\frac{1}{8\pi^3}\int\int F(\mathbf{r}_k)F^*(\mathbf{r})\exp[+i\boldsymbol{\rho}\cdot(\mathbf{r}_k-\mathbf{r})] \times\frac{1-A(\boldsymbol{\rho})}{[1-A(\boldsymbol{\rho})]^2+(\omega\tau/2)^2}\cdot d\mathbf{r}d\boldsymbol{\rho}. \tag{74}$$

If $[1-A(\boldsymbol{\rho})]^2$ in the denominator is negligible compared with $(\omega\tau/2)^2$, we get

$$S(\omega)=\frac{4c}{\omega^2\tau}\sum_k\frac{1}{8\pi^3}\int\int F(\mathbf{r}_k)F^*(\mathbf{r})\exp[+i\boldsymbol{\varrho}\cdot(\mathbf{r}_k-\mathbf{r})]$$

$$\times\left[1-\frac{1}{z}\sum_{i=1}^{z}\exp i\boldsymbol{\varrho}\cdot\mathbf{r}_i\right]d\mathbf{r}d\boldsymbol{\varrho}$$

$$=\frac{4c}{\omega^2\tau}\sum_k\left[|F(\mathbf{r}_k)|^2-\frac{1}{z}F(\mathbf{r}_k)\sum_{i=1}^{z}F^*(\mathbf{r}_k+\mathbf{r}_i)\right].\tag{75}$$

As an example we compute $S_1(\omega)$. Substituting from Eq. (4a) we get

$$S_1(\omega)=\frac{4c}{\omega^2\tau}\sum_k\left\{\frac{\sin^2\theta_k\cos^2\theta_k}{r_k^6}-\frac{1}{z}\sum_j\frac{\sin\theta_k\cdot\cos\theta_k}{r_k^3}\right.$$

$$\left.\cdot\frac{\sin\theta_j\cos\theta_j}{r_j^3}e^{i(\varphi_k-\varphi_j)}\right\}.\tag{76}$$

In this expression $\mathbf{r}_j=\mathbf{r}_k+\mathbf{r}_i$; θ_j, φ_j are the polar and azimuthal angles of $\mathbf{r}_j$, and the sum over j is over all nearest neighbors of the lattice site at $\mathbf{r}_k$. In this sum all terms for which $\mathbf{r}_j=0$ have to be excluded of course. This expression must now be averaged over all lattice orientations. We average each term in the sum over k, independently. For each term we transform to Eulerian angular coordinates θ, β, ψ where $\theta=\theta_k$, $\beta=\varphi_k+\pi/2$ and ψ is the azimuthal angle of $\mathbf{r}_j$ about $\mathbf{r}_k$. Averaging over the angle ψ we find

$$\langle\sin\theta_j\cos\theta_j e^{-i\varphi_j}\rangle_{\text{Av}}$$

$$=[1-\tfrac{3}{2}(l^2/r_j^2)\sin^2\alpha_j]\sin\theta_k\cos\theta_k e^{-i\varphi_k},\tag{77}$$

where α_j is the angle between $\mathbf{r}_j$ and $\mathbf{r}_k$.

Thus we obtain, after the average over ψ,

$$S_1(\omega)=\frac{4c}{\omega^2\tau}\sum_k\frac{\sin^2\theta_k\cos^2\theta_k}{r_k^6}\left\{1-\frac{1}{z}\sum_j\left(\frac{r_k}{r_j}\right)^3\right.$$

$$\left.\times\left(1-\frac{3l^2}{2r_j^2}\sin^2\alpha_j\right)\right\}.\tag{78}$$

Finally averaging over θ_k, since $\langle\sin^2\theta_k\cos^2\theta_k\rangle_{\text{Av}}=2/15$, we get

$$S_1(\omega)=\frac{8c}{15\omega^2\tau}\sum_k\frac{1}{r_k^6}\left\{1-\frac{1}{z}\sum_j\left(\frac{r_k}{r_j}\right)^3\right.$$

$$\left.\times\left(1-\frac{3l^2}{2r_j^2}\sin^2\alpha_j\right)\right\}.\tag{79}$$

This sum which converges fairly rapidly can be applied to find $S_1(\omega)$ for various lattice structures. For a face-centered cubic lattice we obtain

$$S_1(\omega)=98.245b^{-6}(8c/15\omega^2\tau),\tag{80}$$

where b is the edge of a unit cell. A similar calculation gives $S_2(\omega)=4S_1(\omega)$.

Since it is not possible to integrate (74) in the general case, we have sought to obtain an approximate formula which will give $S(\omega)$ with sufficient accuracy over the whole range of $\omega\tau$.

To this end we turn to the case, considered in Sec. III(e), of isotropic diffusion for which the single jump distance has always the value l. There are good reasons for believing that Eq. (65) properly normalized will meet these requirements. For the case of random walk in a lattice the jumps are to nearest neighbors which in many cases (e.g., f. c.c. lattice) are symmetrically disposed on a sphere. The use of Sec. III(e) approximates this situation by allowing a jump to any point on the sphere. Furthermore, the fact that in the lattice case we eventually would average the result over all lattice orientations, lends support to the isotropic approximation in which this averaging may be considered to have already been performed in a different, if less precise, way.

Normalization of (65) involves a proper choice of the parameter k, which amounts to a proper choice of the lower limits of integration for r and r_0 in Eq. (22). Fortunately, the proper normalization to apply to the lattice case can be obtained from Eqs. (71) and (73). From Eqs. (65) and (66) we obtain

$$(2\pi)^{-1}\int_{-\infty}^{+\infty}S_1(\omega)d\omega=8\pi n/45k^3l^3.\tag{81}$$

Substituting for n, $n=cn_0b^{-3}$, where n_0 is the number of lattice sites in a unit cell, and by Eq. (71) equating the right member of (81) to $k_1(0)$ as given by (73a), we obtain

$$k^3=(4/3)\pi n_0 b^{-3}l^{-3}/\textstyle\sum_k r_k^{-6}.\tag{82}$$

For a face-centered cubic lattice $\sum_k r_k^{-6}=115.375b^{-6}$, $n_0=4$, and $b=\sqrt{2}l$, and inserting these values in (82) we find

$$k=0.74335.\tag{83}$$

The assumption that Eq. (65) gives a good approximation to the lattice diffusion problem may be tested by comparing its low temperature ($\omega\tau\gg1$) asymptote with the exact result of Eq. (80) for a f. c.c. lattice. For large y we may neglect the term in $1-\sin x/x$ in the denominator of the integrand of Eq. (66), and find

$$G(k,y)=(4/\omega^2\tau^2)\int_0^\infty J_{\frac{3}{2}}^2(kx)(1-\sin x/x)dx/x.$$

This integration can be performed exactly, with the result

$$G(k,y)=(1/\omega^2\tau^2)(1-1/12k^2)\quad(k>\tfrac{1}{2}).\tag{84}$$

Substituting (84) in (65), using k as given by (83), and putting $n=4cb^{-3}$, $l=b/\sqrt{2}$, we obtain from (65)

$$S_1(\omega)=98.85b^{-6}(8c/15\omega^2\tau), \qquad (85)$$

which agrees with (80) to 0.6 percent. We may therefore have some confidence in the use of (65) as an adequate approximation to the lattice diffusion problem. The function $G(k, y)$ as given by Eq. (66) has been calculated by numerical methods with k as given by (83) and is tabulated as a function of y in Table II.

Substituting (65) and $S_2(\omega)=4S_1(\omega)$ in Eq. (2), we get (with $y=\frac{1}{2}\omega\tau$)

$$T_1^{-1}=(8\pi/5)\gamma^4\hbar^2 I(I+1)(n/k^3l^3\omega)\psi(k, y), \qquad (86)$$

where

$$\psi(k, y)=yG(k, y)+2yG(k, 2y). \qquad (87)$$

In Table II we have also tabulated $\psi(k, y)$ as a function of y for k given by (83).

Finally we state the limiting form of (86) for $\omega\tau\ll 1$ (high temperature asymptote). For small y, $\psi(k, y)\simeq 3yG(k, 0)$. By numerical integration $G(k, 0)=0.6151$ (f. c.c. lattice) so that Eq. (86) reduces to

$$(\omega\tau\ll 1):\ T_1^{-1}=11.292\gamma^4\hbar^2 I(I+1)n\tau/l^3. \qquad (88)$$

V. APPLICATION

In applying the results obtained above to nuclear spin relaxation times as determined from nuclear resonance data, one must be sure that the relaxation is entirely the result of the diffusion process. It is rarely possible to be perfectly sure of this, but one can be more confident about it in the neighborhood of the minimum in $T_1(T_{1m})$ than well up on the asymptotes of the T_1-temperature curve. One needs therefore a way of analyzing data in terms of the above theory in the neighborhood of the minimum T_1. It is convenient for this purpose to express the above results in terms of universal curves. One way of doing this is to express T_{1m}/T_1 as a function of τ/τ_m, where τ_m is the value of τ at $T_1=T_{1m}$. From experimental values of T_{1m}/T_1 one can then obtain from these curves the corresponding values of τ/τ_m. Plots of $\log(\tau/\tau_m)$ thus obtained against the reciprocal of the absolute temperature should result in straight lines whose slopes give the activation energy, provided a relationship of the type of Eq. (30) holds. Graphs of T_{1m}/T_1 *versus* τ/τ_m can easily be constructed with the aid of the above tables.

TABLE II. Tables of the functions $G(k, y)$ [Eq. (66)] and $\psi(k, y)$ [Eq. (87)] ($k=0.74335$).

y	$G(k, y)$	$\psi(k, y)$
0	0.61505	0
0.025	0.53804	0.03887
0.05	0.50844	0.07181
0.10	0.46388	0.12632
0.15	0.42913	0.16936
0.20	0.39965	0.20325
0.25	0.37357	0.22959
0.30	0.34997	0.24966
0.35	0.32832	0.26458
0.40	0.30831	0.27535
0.45	0.28971	0.28262
0.50	0.27239	0.28732
0.55	0.25621	0.28981
0.60	0.24111	0.29060
0.6024		0.29060(max)
0.65	0.22700	0.29003
0.70	0.21381	0.28840
0.80	0.19004	0.28287
0.90	0.16916	0.27528
1.00	0.15113	0.26662
1.20	0.12161	0.24802
1.40	0.09909	0.22958
1.60	0.08178	0.21242
1.80	0.06835	0.19687
2.00	0.05775	0.18282
2.25	0.04749	0.16742
2.5	0.03963	0.15406
3.0	0.02867	0.13236
3.5	0.02161	0.11570
4.0	0.01683	0.10249
5.0	0.01100	0.08327
6.0	0.00772	0.06999
7.0	0.00571	0.06030
10.0	0.00283	0.04253
20.0	0.000712	0.02138
30.0	0.000317	0.01427
40.0	0.000178	0.01070

VI. CONCLUSION

It is hoped that the results derived here will be of some aid in analyzing data on nuclear spin relaxation when the dominant mechanism is of the translational diffusion type. We have not attempted to treat certain special diffusive processes such as ring-type diffusion involving the correlated motion of several nuclei. For rotational diffusion, the Bloembergen treatment is satisfactory.

The author wishes to acknowledge the help of Mr. J. Olds, Mr. S. Hussieni, and Mr. E. Apgar in computational work.