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Spin Diffusion in Inhomogeneously Broadened Systems*

A. KIEL
Radiation Laboratory, The Johns Hopkins University, Baltimore, Maryland

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The theory of cross-relaxation within inhomogeneous spin systems (spin diffusion) is discussed. The qualitative theory of Bloembergen, Shapiro, Pershan, and Artman is generalized. For the special case where the exchange- and concentration-independent contribution to the cross-relaxation linewidth are zero, the diffusion time is given by $\tau = T_{12}\langle\nu_c^2\rangle^{-\frac{3}{2}}(T_2^*)^{-3}$. An exact theory of cross-relaxation in the limit $T_2 \gg T_2^*$ is also developed and spin-diffusion is shown to be governed by an integro-differential equation. The conditions under which an ordinary diffusion equation describes spin diffusion is examined and the diffusion constant derived. The expression for τ given above is verified by this theory.

I. INTRODUCTION

THE theory of cross-relaxation developed by Bloembergen *et al.*[1] has proven capable of explaining, at least qualitatively, a number of interesting effects observed in paramagnetic resonance experiments in solids. A number of these effects are discussed.[1-3] In this paper we shall consider in detail the application of this theory to cross-relaxation in inhomogeneously broadened systems.[4] We will first discuss briefly cross-relaxation. In Sec. II, we will consider the qualitative theory of spin diffusion presented in reference 1 and some possible generalizations. In Sec. III we develop an exact theory of spin diffusion.

The theory of cross-relaxation has shown that the dipolar coupling terms in the Hamiltonian are capable of maintaining spin temperature equilibrium in paramagnetic systems.

More recent work[5-7] has demonstrated that the effective linewidth for cross-relaxation,[8] $\langle\omega_c^2\rangle^{\frac{1}{2}}$, can be much greater than the paramagnetic resonance linewidth in *dilute* systems. This latter fact explains how cross-relaxation can occur between pairs of energy levels with resonance frequencies differing by hundreds of megacycles per second whereas the linewidths may be only tens of megacycles per second.

The second moment for cross-relaxation in a pure dipolar system with two species of ions, α and γ (see reference 5 for notation) is given by

$$\begin{aligned}\hbar^2\langle\omega_c^2\rangle &= \tfrac{1}{5}[S(S+1)+I(I+1)-\tfrac{3}{2}]g_\alpha^2 g_\gamma^2\beta^4 \\ &\quad\times\sum_\xi \frac{(1-3\cos^2\theta_{p\xi})^4}{r_{p\xi}^{12}} \Big/ \sum_\xi \frac{(1-3\cos^2\theta_{p\xi})^2}{r_{p\xi}^{6}} \\ &\quad+\frac{S(S+1)}{3}\left(\frac{11}{4}g_\alpha^4\beta^4 f_\alpha + g_\alpha^2 g_\gamma^2 \beta^4 f_\gamma\right) \\ &\quad\times\sum_\xi (1-3\cos^2\theta_{p\xi})^2 r_{p\xi}^{-6} \\ &\quad\times\frac{I(I+1)}{3}\left(\frac{11}{4}g_\gamma^4\beta^4 f_\gamma + g_\alpha^2 g_\gamma^2 \beta^4 f_\alpha\right) \\ &\quad\times\sum_\xi (1-3\cos^2\theta_{p\xi})^2 r_{p\xi}^{-6} + \text{exchange terms.} \end{aligned} \tag{1}$$

In Eq. (1), S is the spin of the α-type ions, I that of the γ-type ions, g is the spectroscopic splitting factor, and f the concentration.

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[1] N. Bloembergen, S. Shapiro, P. Pershan, and J. Artman, Phys. Rev. **114**, 445 (1959).

[2] C. H. Townes, *Quantum Electronics* (Columbia University Press, New York, 1960), several papers from pp. 293–369.

[3] J. Singer, *Quantum Electronics* (Columbia University Press, New York, 1961), Vol. II, paper delivered by N. Bloembergen.

[4] Hereafter we shall usually use the term spin diffusion to describe cross-relaxation within an inhomogeneously broadened system. Spin diffusion was first discussed by A. M. Portis, Phys. Rev. **104**, 584 (1956), in a slightly different context. The theory of inhomogeneous broadening was discussed by A. M. Portis, *ibid.* **91**, 107 (1953).

[5] A. Kiel, Phys. Rev. **120**, 137 (1960). A number of errors occur in this paper. The correct form of the cross-relaxation linewidth is given in Phys. Rev. **123**, 2202 (1961).

[6] M. Hironi, J. Phys. Soc. Japan **16**, 66 (1961).

[7] V. Kopvillem, Soviet Phys.—Solid State **2**, 1653 (1961).

[8] We will often use the abbreviation C-R for cross-relaxation in the following.

It is the first term on the right in Eq. (1) which results in the large cross-relaxation line width in dilute salts since it is concentration independent. The fact that the exchange terms (including isotropic exchange) contribute directly to the $\langle\omega_c^2\rangle$ was first pointed out in reference 5.

It is immediately evident that when $S=I=\frac{1}{2}$ the concentration independent term in Eq. (1) is zero. Hence the C-R linewidth may be quite narrow in such salts if the concentration is small enough so that the exchange terms are not significant. Kopvillem[7] has investigated the case of cross-relaxation in the presence of crystal fields. He shows that in some special cases the concentration independent term will disappear in this case as well.

A number of experimental studies[9–11] have reported effects which may be interpreted as spin diffusion within an inhomogeneously broadened resonance line.

For such effects to be experimentally observable we will show that it is necessary for the concentration independent term in $\langle\omega_c^2\rangle$ to vanish (see below). If the exchange terms are negligible, $n_\alpha=n_\gamma$, $g_\alpha=g_\gamma$, $S=I=\frac{1}{2}$.

$$\langle\nu_c^2\rangle=(15/8)g^4(\beta^4/h^2)f_\alpha\times 13.3d^{-6}\simeq 1.7\times 10^{-25}g^4d^{-6}f_\alpha,$$

where d is the lattice spacing (a simple cubic has been assumed). For a concentration f equal to 0.1%, $d=7\times 10^{-8}$ cm, $g\simeq 2$ we have $\langle\nu_c^2\rangle^{\frac{1}{2}}\simeq 0.23\times 10^8$ cps ($\simeq 8$ gauss). In noncubic crystals of the same d, the C-R linewidth would probably be smaller.

The cross-relaxation rates have been computed in references 1 and 5 and are given by

$$W_{12}{}^\alpha=(n_\gamma/N)w,\quad W_{12}{}^\gamma=(n_\alpha/N)w,$$

$$\begin{aligned}w=(\pi/8)&g_\alpha{}^2g_\gamma{}^2\beta^4/h^2\\ &\times(S+M_S)(S-M_S+1)(I+M_I+1)(I-M_I)\\ &\times\left[\textstyle\sum_\xi{}'\,(1-3\cos^2\theta_{p\xi})^2r_{p\xi}{}^{-6}\right]g_{12}(\omega).\end{aligned}\tag{2}$$

It is seen from Eq. (2) that if $\langle\omega_c^2\rangle^{\frac{1}{2}}$ is comparable to or greater than the inhomogeneous line width $(T_2{}^*)^{-1}$, the system comes to spin equilibrium in a fraction of a microsecond. This explains the difficulty in "burning holes" in lines[12] and observing spin diffusion, in general. (This explanation was first given by Bloembergen *et al.*[1])

In reference 1 a simple qualitative theory of spin diffusion is presented. It seems worth while to discuss this theory and indicate some generalization of it before deriving our exact theory.

II. QUALITATIVE THEORY OF SPIN DIFFUSION

The theory of Bloembergen *et al.*[1] can be summarized as follows: Consider an inhomogeneous resonance line to be made up of many "homogeneous" resonances, that is, adjacent spins are assumed to have quite different resonant frequencies. The overall linewidth of the inhomogeneous line is designated $(T_2{}^*)^{-1}$; the linewidth of the homogeneous components is $T_2{}^{-1}$, $T_2\gg T_2{}^*$. T_2 is a function of the concentration of the ions while $T_2{}^*$ is presumably independent of concentration. (There is evidence that $T_2{}^*$ sometimes depends on concentration but this does not alter what follows.) Bloembergen *et al.* assume that the probability per unit time (as a function of frequency) of a cross-transition between two adjacent ions of resonant frequencies ω_α and ω_γ, respectively, will be large ($\approx T_2{}^{-1}$) if $|\omega_\alpha-\omega_\gamma|<T_2{}^{-1}$ and essentially zero otherwise. The problem hence reduces to a random walk problem with steps of length $T_2{}^{-1}$ and reflecting boundaries separated by $(T_2{}^*)^{-1}$. After weighting the step lengths of the probability that adjacent spins fall within the frequency interval $T_2{}^{-1}$ [that is, multiply $T_2{}^{-1}$ by $(T_2{}^*/T_2)$] one obtains for the diffusion time in an inhomogeneous line

$$\tau\simeq T_2{}^4/T_2{}^{*3}.$$

This expression should be altered to take into account the more accurate expressions (1) and (2). The formula for the spin diffusion time τ is then given by

$$\tau=(\langle\nu_c^2\rangle^{\frac{1}{2}}T_2{}^*)^{-3}T_{12},\tag{3}$$

where $\langle\nu_c^2\rangle$ is the mean square cross-relaxation line width and T_{12} is the inverse of the maximum cross-relaxation rate given in Eq. (2).

In the present case a single inhomogeneously broadened spin species, Eqs. (1) and (2) become (a cubic lattice is assumed and terms on the extreme right assume $S=\frac{1}{2}$)

$$\begin{aligned}\langle\nu_c^2\rangle=(5/4)&S(S+1)(g^4\beta^4/h^2)\\ &\times(13.3/d^6)f=3.55\times 10^{-26}fd^{-6},\end{aligned}\tag{1a}$$

$$\begin{aligned}T_{12}{}^{-1}&=\pi(g^4\beta^4/8h^2)f(S+M)(S-M+1)(S+M'+1)\\ &\qquad\times(S-M')(13.3/d^6)g_{12}(\Delta\omega)\\ &=5.3\times 10^{-25}fd^{-6}g_{12}(\Delta\omega).\end{aligned}\tag{1b}$$

Taking $g(\omega)=(2\pi\langle\omega_c^2\rangle)^{-\frac{1}{2}}\exp[(\omega-\omega_0)^2/2\langle\omega_c^2\rangle]$, we obtain

$$\tau=8.65\times 10^{50}f^{-2}d^{12}(T_2{}^*)^{-3}.\tag{4}$$

For $d=10$ A, $T_2{}^*=10^{-8}$ sec, $f=10^{-3}$, we get $\tau=0.86$ msec.

If the exchange term is not completely negligible, the spin-diffusion time will be shorter than that predicted above.

For concentrations of the order of one-half percent or greater, the exchange terms will probably make the cross-relaxation linewidth greater than the inhomogeneous linewidth. This condition is the usual case for paramagnetic systems.

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[9] K. D. Bowers and W. B. Mims, Phys. Rev. **115**, 285 (1959).

[10] W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. **123**, 2059 (1961). The results of Mims *et al.*, have been discussed by J. R. Klauder, Bull. Am. Phys. Soc. **6**, 103 (1961), and J. R. Klauder and P. W. Anderson, Phys. Rev. **125**, 912 (1962).

[11] T. M. Bray, G. C. Brown, and A. Kiel (to be published).

[12] J. A. Giordmaine, L. E. Alsop, F. R. Nash, and C. H. Townes, Phys. Rev. **109**, 302 (1958).

III. RIGOROUS DESCRIPTION OF SPIN-DIFFUSION IN INHOMOGENEOUS RESONANCE LINES

The previous description of spin diffusion is quite crude in some respects. It would be worth while to develop a more exact theory of spin diffusion. The results given below are, except in a few special cases, too complicated to be of much value in analyzing the data presented in references 9–11. However, the method is of some interest and so is presented here.

To consider spin diffusion in an inhomogeneous resonance line, it is convenient to use as a model a finite system of resonances coupled through the cross-relaxation term. The resonance may be overlapping in the frequency domain. We will finally go the limit of an infinite number of resonances to obtain an integro-differential equation describing the spin diffusion. We shall restrict ourselves to a spin $\frac{1}{2}$ system.

The set of spins at a given resonance frequency ω_i will be referred to as the "spin packet" in what follows. The rate equation for the spin packet i may be written as (we use i, j, k instead of the α, γ used above)

$$\begin{aligned}(d/dt)(n_{i-}-n_{i+})=(2w_{ij}/N)(n_{i+}n_{j-}-n_{i-}n_{j+})\\ +2B_{ik}(n_{i+}-n_{i-})-2(n_{i-}u_{-+}-n_{i+}u_{+-}),\end{aligned}\quad(5)$$

where w_{ij} is the C-R rate w defined in (2); n_{i+}, n_{i-} are, respectively, the number of spins up or down with resonant frequency $\omega_i=2\pi\nu_i$; n_{i+}^0, n_{i-}^0 are the populations at equilibrium; n_i is the total number of spins in packet i; n is the total number of spins, $n_i+n_j+\cdots$; B_{ik} is the relative transition rate of spin packet i due to an input frequency ω_k; u_{+-}, u_{-+} are the spin-lattice relaxation rates "down" and "up," assumed constant through the inhomogeneous line; $T_1=1/(u_{+-}+u_{-+})$; and N is the total number of lattice sites available to the paramagnetic ions.

Let $-\Delta_i=n_{i+}^0-n_{i+}=n_{i-}-n_{i-}^0$, $A_{ik}=(n_{i-}^0-n_{i+}^0)B_{ik}$. Since we shall restrict ourselves to fairly narrow inhomogeneous lines, $(\omega_{0i}-\omega_{0j})/\omega_{0i}\ll 1$ and we can take $(n_{i+}^0n_{j-}^0-n_{i-}^0n_{j+}^0)=0$. Furthermore, $n_{i+}n_{j-}-n_{i-}n_{j+}=n_j\Delta_i-n_i\Delta_j$ and $n_{i-}u_{-+}-n_{i+}u_{+-}=-\Delta_i/T_1$. Substituting these relations into Eq. (5), we get as the rate equation for spin packet i

$$\begin{aligned}d\Delta_i/dt=A_{ik}-\textstyle\sum_j (w_{ij}n_j/N+2B_{ik}+T_1^{-1})\Delta_i\\ +(1/N)\textstyle\sum_j w_{ij}n_j\Delta_j.\end{aligned}\quad(6)$$

Naturally we obtain similar equations for all spin packets. Subtracting the rate equation of the ith spin packet from the equation for $i+1$, we get

$$\begin{aligned}(d/dt)(\Delta_{i+1}-\Delta_i)\\ =(A_{i+1,k}-A_{ik})-(1/N)\textstyle\sum_j (w_{i+1,j}\Delta_{i+1}-w_{i,j}\Delta_i)n_j\\ -\textstyle\sum_j 2(B_{i+1,k}\Delta_{i+1}-B_i\Delta_i)+T_1^{-1}(\Delta_{i+1}-\Delta_i)\\ +(1/N)\textstyle\sum_j (w_{i+1,j}n_{i+1}-w_{ij}n_j)\Delta_j.\end{aligned}$$

We now assume $w_{i+1}-w_i$ is infinitesimal. By taking limits and noting that we can drop the derivative with respect to x, we get the following integro-differential equation (x now becomes the frequency)

$$\begin{aligned}(d/dt)\Delta(x,t)=A(x-x_0)-[2B(x-x_0)+T_1^{-1}]\Delta(x,t)\\ -\frac{\Delta(x,t)}{N}\int_{-\infty}^{\infty} w(x,y)n(y)dy\\ +\frac{n(x)}{N}\int_{-\infty}^{\infty} w(x,y)\Delta(y,t)dy.\end{aligned}\quad(7)$$

The infinite limits of integration are of no importance since both $w(y)$ and $n(y)$ fall off to zero. Equation (7) is a general expression for spin diffusion in an inhomogeneous line.

We assume $B(x)=0$, $t>0$. We assume that $n(x)$ is uniform over the inhomogeneous line

$$\begin{aligned}n(x)&=\tfrac{1}{2}nT_2^*, & |x-x_0|&<T_2^{*-1}\\ &=0, & |x-x_0|&>T_2^{*-1}.\end{aligned}\quad(8a)$$

Also

$$\frac{1}{N}\int_{-\infty}^{\infty} n(y)w(x-y)dy=\frac{T_2^*W'}{2},\quad[\langle\Delta\nu_c^2\rangle^{\frac{1}{2}}\ll(T_2^*)^{-1}],\quad(8b)$$

where

$$W'=f\int_{\infty}^{\infty} w(x-y)dy,\quad(f=n/N)$$

and

$$\frac{1}{N}\int_{-\infty}^{\infty} n(y)w(x-y)dy=fw(0)=W(0),\quad(\langle\Delta\nu_c^2\rangle^{\frac{1}{2}}\gg(T_2^*)^{-1}).\quad(8c)$$

An important property of Eq. (8c) can be derived by integrating the equation with respect to x. It can be easily proved that the integrals of the last two terms on the right (the C-R terms) cancel. Therefore

$$\frac{d}{dt}\int\Delta(x,t)dx=\int A(x-x_0)dx-\int[2B(x-x_0)+T_1^{-1}]\Delta(x,t)dx.\quad(9)$$

In many practical cases $2B(0)T_1(T_2^*/T_2)\ll 1$. Then for $t>T_{12}$, where $\Delta(y)$ is spread over a large part of the inhomogeneous line, we get ($t\gg T_{12}$)

$$\int\Delta(x,t)dx\simeq e^{-t/T_1}\int\Delta(y,0)dy+(1-e^{-t/T_1})T_1\int A(y)dy.\quad(10)$$

For $B=0$, $t\geq 0$ the above is an exact expression for $t>0$ (with of course the second term on the right zero)

Also, if $B(x) \ll W(0)$ and t is less than the spin diffusion time τ, (the time required for the $\Delta(x,t)$ to become uniform over the inhomogeneous line),

$$\Delta(x,t)dx = t\int A(x-x_0)dx \cong \frac{nT_2{}^*}{2}\left(\frac{h\nu}{2kT}\right)t\int B(x)dx. \quad (11)$$

Equations (10) and (11) will prove valuable in the following:

Another important characteristic of Eq. (7) is the tendency toward cancellation of the last two terms on the right when $\Delta(y,t)$ becomes broader than $W(x,y)$. If $\Delta(x)$ is uniform, the two terms cancel exactly if $n(x)$ is uniform. Also, for very sharp $W(x,y)$ (for example, a Dirac delta function), the two terms cancel exactly.

All these properties follow from the simple notions of cross-relaxation but it seemed worthwhile to derive these here as an indication of internal consistency.

$\langle \boldsymbol{\nu}_c{}^2\rangle^{-\frac{1}{2}} \ll \boldsymbol{T}_2{}^*$

Let us now consider the usual (but not very interesting) case of spin diffusion in an inhomogeneous line, that is, $\langle \nu_c{}^2\rangle^{-\frac{1}{2}} \ll T_2{}^*$. Equation (7) reduces [using Eq. (8c)] to

$$(d/dt)\Delta(x,t) \cong A(x,x_0) - [2B(x-x_0)+T_1{}^{-1}]\Delta(x,t) - W(0)\Delta(x,t) + \frac{n(x)}{N}w(0)\int \Delta(y,t)dy. \quad (12)$$

If we assume the microwave signal is off, $B=0$, the solution of

$$\Delta(x,t) = \Delta(x,0)\exp\{-[W(0)+T_1{}^{-1}]t\} + \frac{n(x)}{n}\left(e^{-t/T_1} - e^{-[W(0)+1/T_1]t}\right)\int \Delta(y,0)dy. \quad (13)$$

The first term on the right of Eq. (13) describes the decay of the initial population distribution while the second term gives the diffusion of the initial excitation through the inhomogeneous line. It is easily seen that after a time of the order of $W(0)^{-1}$ ($\leq 10^{-8}$ sec) the whole line comes to spin equilibrium. But as noted above, when $\Delta(x,t)$ becomes uniform over the line, the cross-relaxation terms cancel and the system then will behave exactly like a homogeneous line, but of width $(T_2{}^*)^{-1}$ and population n. Since for realizable powers $B(0) \ll W(0)$, these statements remain true when $B \neq 0$. These statements may be proved by solving Eq. (12) when $B \neq 0$. This presents no difficulty if Eq. (10) can be used. Using Eqs. (10), (8a), and (8c), we obtain in the limit $t \gg T_{12}$, and $W(0) \gg B(0)$, $T_1{}^{-1}$

$$\Delta(x,t) \simeq \tfrac{1}{2}T_2{}^* e^{-t/T_1}\int \Delta(y,0)dy + \frac{(1-e^{-t/T_1})T_1}{W(0)}\int A(y)dy + \frac{A(x)}{W(0)}. \quad (14)$$

The power absorbed by the lattice is just $(h/T_1)\int x\Delta(x,t)dx$. At equilibrium $t > T_1$, the second term on the right dominates and the power absorbed is approximately $h\bar{\nu}(h\bar{\nu}/2kT)nB'(0)$, where $B'(0)$ is the same as $B(0)$ except that T_{12} replaces T_2.

For $B(0) \neq 0$ and for $W(0)t < 1$, Eq. (7) becomes [making use of (8c) and (11)]

$$(d/dt)\Delta(x,t) + [2B(x-x_0)+W(0)+T_1{}^{-1}]\Delta = A(x-x_0) + \frac{n(x)n(x_0)bw(0)}{N}\left(\frac{h\nu}{2kT}\right)t,$$

where

$$b = \int B(x-x_0)dx,$$

$$\Delta(x,t) = \Delta(x,0)e^{-D(x)t} + \frac{nT_2{}^*B(x-x_0)}{2D(x)}\left(\frac{h\nu}{2kT}\right)(1-e^{-D(x)t}) + nbW(0)(T_2{}^*)^2\left(\frac{D(x)t-(1-e^{-D(x)t})}{D^2(x)}\right)\Big/4, \quad (15)$$

$$D(x) = 2B(x-x_0)+W(0)+T_1{}^{-1}.$$

Equation (15) describes the diffusion of spins for time $\tau < W(0)^{-1}$ when the C-R linewidth is much greater than the inhomogeneous linewidth which in turn is much greater than $1/T_2$.

$\langle \boldsymbol{\nu}_c{}^2\rangle^{-\frac{1}{2}} \gg \boldsymbol{T}_2{}^*$

Let us consider now the more interesting case where $\langle \omega_c{}^2\rangle^{-\frac{1}{2}} \gg T_2{}^*$. If $W(0)t > 1$, the width of $\Delta(x,t)$ becomes larger than $\langle \omega_c{}^2\rangle^{\frac{1}{2}}$. We write

$$\Delta(y) = \Delta(x) + \Delta'(x)(y-x) + \tfrac{1}{2}\Delta''(x)(y-x)^2.$$

Substituting this into Eq. (7), and assuming $n(x)$ is uniform and $W(x,y)=W(x-y)$ is symmetric, we obtain the expression

$$d\Delta(x,t)/dt + [2B(x-x_0)+T_1{}^{-1}]\Delta(x,t) = (nh\nu/4kT)T_2{}^*B(x-x_0) + \kappa d^2\Delta(x,t)/dx^2, \quad (16)$$

where

$$\kappa = \tfrac{1}{4}T_2{}^*\int_{-\infty}^{\infty} W(x,y)(y-x)^2dy.$$

If $|x-x_0| > T_2{}^{-1}$ so that $B(x-x_0)$ may be neglected, this becomes

$$d\Delta(x,t)/dt+T_1^{-1}\Delta(x,t)=\kappa d^2\Delta(x,t)/dx^2. \qquad (17)$$

Equation (17) is very similar to the diffusion equation and has the solution

$$\Delta(x,t)=\frac{e^{-t/T_1}}{(4\pi\kappa t)^{\frac{1}{2}}}\int\Delta(y,0)\exp[-(x-y)^2/4\kappa t]dy. \qquad (18)$$

Note the concentration dependence enters only through the parameter κ. The spin diffusion time τ is roughly given by

$$\tau=(4\kappa)^{-1}(x-x_0)^2{}_{\text{max}}\simeq[4\kappa(T_2{}^*)^2]^{-1}.$$

For a Gaussian C-R linewidth,

$$\tau=2\pi[W'\langle\Delta\nu_c{}^2\rangle(T_2{}^*)^3]^{-1}. \qquad (19)$$

Equation (19) is easily shown to be precisely equal to Eq. (4). [W' is defined in (8).] Equation (18), however, also describes the spin-lattice relaxation. The properties of (18) are too well known to dwell on the properties of this equation further.

This is the expression which describes the decay of the susceptibility in pulse saturation experiments when spin diffusion occurs.

The general solution of Eq. (16) is naturally very difficult but satisfactory solutions for cases of interest should present no great obstacle.

When $W(0)t<1$, Eq. (15) may be applied except that in the definition of the function $D(x)$, $W(0)$ must be replaced by $(T_2{}^*/2)\int W(x)dx$.

In a later publication, the application of these results will be discussed in relation to relaxation effects in $K_3(Co,Fe)(CN)_6$.

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Fermion Ensembles of Maximum Entropy

Martin C. Gutzwiller
International Business Machines, Research Laboratory, Adliswil-Zurich, Switzerland

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Ensembles of particles obeying Fermi-Dirac statistics are considered from a point of view which is analogous to some recent work of Mayer on classical particle statistics. The density functions ρ_n are defined for n much smaller than the average number of particles in the ensemble. Since the knowledge of only a few ρ_n is sufficient for the computation of most averages of physical interest, it is important to compare different ensembles with the same density functions, say ρ_1 and ρ_2. The ensemble with the largest entropy is constructed as being the most significant. A number of simple examples are briefly considered.

INTRODUCTION

THE purpose of the present article is to give a quantum-mechanical analog for a theorem which was recently stated and proved by Mayer[1] for classical statistical mechanics. The theorem for Fermi statistics has the same intuitive content, but its statement and proof is more involved. As for the general idea behind the problem, the following may be said: Instead of starting from an assumed kinetic energy, external field, and interaction energy for the particles in order to find their correlation, it is shown how their assumed probabilities of occurrence in certain states and their correlations can be used to find, at least in principle, the simplest Hamiltonian responsible for these probabilities and correlations.

STATEMENT OF THE PROBLEM

An ensemble of Fermi-Dirac particles is more conveniently described if the total number of particles is not assumed to be exactly known. The state vectors Φ of the dynamical system will therefore not necessarily belong to an exact total number of particles. It is then also appropriate to use the formalism of second quantization, in particular the operators $\Psi(x)$ and $\Psi^*(x)$ of particle annihilation and creation, where the coordinate x refers to the position and spin of one particle. The Hilbert space H in which $\Psi(x)$ and $\Psi^*(x)$ operate can be described using an orthonormalized set of one-particle wave functions $\varphi_\kappa(x)$ whose label κ refers, e.g., to wave vector and spin direction, or to a lattice site and rotational state, and so forth. Every state vector of the whole system can be written as a linear combination of Slater determinants which are constructed from an arbitrary subset of the set $\{\varphi_\kappa(x)\}$. The creation and annihilation operators, $\Psi^*(x)$ and $\Psi(x)$, are then defined in terms of the creation and annihilation operators $a_\kappa{}^*$ and a_κ in the customary manner

$$\Psi(x)=\textstyle\sum_\kappa a_\kappa\varphi_\kappa(x),\quad \Psi^*(x)=\textstyle\sum_\kappa a_\kappa{}^*\varphi_\kappa{}^*(x). \qquad (1)$$

The operators $a_\kappa{}^*$ and a_κ satisfy the anticommutation relations

$$\begin{aligned}&a_\kappa{}^*a_\lambda+a_\lambda a_\kappa{}^*=\delta_{\kappa\lambda},\\&a_\kappa a_\lambda+a_\lambda a_\kappa=a_\kappa{}^*a_\lambda{}^*+a_\lambda{}^*a_\kappa{}^*=0.\end{aligned} \qquad (2)$$

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[1] Joseph E. Mayer, J. Chem. Phys. 33, 1484 (1960).